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FOREWORD

The National Center for Electron Microscopy at the Lawrence Berkeley Laboratory, with recently installed state-of-the-art high voltage microscopes for both ultra high resolution studies and a wide range of in-situ experiments and other applications, is an appropriate location for the second conference on high voltage electron microscopy to be held in the United States. HVEM eighty-three is now the 7th in the series of International Conferences on High Voltage Electron Microscopy that began in Monroeville, Pennsylvania in 1969. Comprehensive summaries of the first two conferences (Monroeville, 1969 and Stockholm, 1971) were published in several journals. Beginning with the Oxford meeting (1973), separate conference proceedings were published to provide a more complete record of the papers presented. As in the case for this Berkeley conference, the proceedings were preprinted for distribution at the meeting in Toulouse (1975) and Kyoto (1977).

Perusal of past and present programs reaffirms that major advances have occurred in instrumentation, specimen preparation, in-situ experimentation and image interpretation. Many of the early papers dwell on the special features of imaging and diffraction with high voltage electrons and the advantages they offer for characterizing the fine structure of matter. The improvement in resolution that is inherent in the shorter electron wavelength at high voltage has now been achieved as a result of painstaking attention to lens design and electrical and mechanical stability. Other characteristics of high voltage microscopy have been explored theoretically and experimentally and are now being applied to a wide range of applications in the material and biological sciences.

At the Antwerp meeting (1981), it was agreed that the primary emphasis at HVEM eighty-three should be placed on the fundamental aspects of high-resolution imaging, dynamic in-situ observations and those applications that utilize the increased penetration and atom displacement that occur at high voltage. As anticipated, many of the papers fall into the announced categories while others describe important innovations in techniques or applications that exemplify the continuing growth in the field.

Despite the many advances in our knowledge that have derived from the HVEM, its value for research is still not widely recognized. This seems to be particularly true for industrial and biological applications even though valuable information can usually be obtained from specimens of very difficult to prepare materials that would not be usable at 100kV. It is hoped that HVEM eighty-three and the distribution of these proceedings will serve to enhance general awareness of the scientific and technological importance of high voltage microscopy.

Berkeley, June 1983

R. M. Fisher

International Conferences on High Voltage Electron Microscopy

1969	Monroeville	U.S.A.
1971	Stockholm	Sweden
1973	Oxford	U. K.
1975	Toulouse	France
1977	Kyoto	Japan
1980	Antwerp	Belgium
1983	Berkeley	U.S.A.

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HIGH VOLTAGE ELECTRON MICROSCOPY -

PRESENT ACHIEVEMENTS AND FUTURE PROSPECTS

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ABSTRACT

The value of high voltage electron microscopy in work of industrial importance is often overlooked. This paper highlights three such areas of achievement: cement, semiconductors and catalysts. The important development of high resolution high voltage microscopes is then discussed with particular reference to the prospect, in the near future, of resolving rows of single atoms in semiconductors for the first time.

INTRODUCTION

The objects of this paper are to review briefly results of some current work which can only be performed using the high voltage electron microscope (HVEM) and to discuss future prospects. In particular, the exciting possibilities opened up by new high voltage, high resolution microscopes will be discussed. It may be of interest to note that LMV microscopes have existed for over 20 years and have been regarded by many as being a different category of microscope from conventional 100kV instruments. The last few years have seen the start of a trend to increase the accelerating voltage of conventional microscopes, first to 200kV and more recently to 300 and 400kV. The advantage of these latter instruments is that they have better resolution and penetration than 100kV microscopes, yet they still fit into a reasonably standard size of room. Thus the 'gap' between conventional and high voltage microscopes is beginning to close.

The advantages of HVEM have been summarized by Thomas, Mishra and Westmacott [1], and HVEM and STEM have been compared by Loretto and Jones [2]. In this paper, out of the vast range of topics that could be reviewed, I have selected some which are of particular technological relevance, in which the HVEM is providing invaluable underpinning materials research.

CEMENT.

The HVEM is an essential tool for the study of cement, both for determining hydration mechanisms and for understanding the microstructure. Environmental cells have been used to observe hydration in-situ and to study hydrates in a moist environment. The in-situ observations were a key element in establishing a radically new model for the hydration mechanism, and the morphology of hydrate growth predicted by the model could be directly observed developing (see Double and Alford [3]).

Recently a new, stronger, 'macro-defect-free' cement has been developed and the HVEM has again played a major role. The tensile strength and toughness of the new cements are increased by a factor of at least 10, and technological exploitation is expected to be worth many millions of pounds. Cement paste sections are of very irregular thickness and the HVEM is essential for their examination over large areas. The HVEM has shown that the fine-scale microstructure of the new, stronger, 'macro-defect-free' cement pastes is not essentially different to that of conventional pastes of low water content, confirming the theory that the greatly increased strength of the new pastes is due solely to the absence of large irregular pores in the structure, i.e. features on a much larger scale than the fine-scale microstructure [4].

SEMICONDUCTORS

Much HVEM work on the characterisation of semiconductor materials is in progress in many countries. The HVEM is essential because of its increased penetration, particularly for thick compound semiconductor devices. The improvement of the quality of semiconductor epitaxial layers, for example, is of great importance to the semiconductor industry. For the production of efficient, high yield, reliable devices it is necessary to characterise and control crystal defects. Materials characterisation performed by HVEM (often in conjunction with other techniques) is being used to enable industry to optimise fabrication routes.

As a specific example, silicon MOSFETS, suitable for Very Large Scale Integration (VLSI) are being studied by HVEM to determine accurately device geometries and to assess defects present [5]. Accurate measurements of gate oxide thickness, junction depths and lateral spread of the junction beneath the polysilicon gate are being made. The HVEM can make these 'geometrical' measurements more accurately than any other method. Precise knowledge of these parameters is needed to predict the device behaviour. The HVEM is therefore providing a detailed scientific assessment of state-of-the-art devices.

CATALYSIS

The HVEM gas reaction cell is a unique facility for studying changes in catalyst microstructure under reacting conditions. For example, the HVEM is being used to study in-situ metal particle catalyst sintering and migration at reaction temperatures as a function of gas environments at realistic pressures. Also heterogeneous catalysts (e.g. metal oxides and sulphides) are being studied in-situ under reacting conditions in the HVEM. Progress is being made in understanding catalyst activity and selectivity, mechanisms of the nucleation and growth of defects and their role in catalysis [6].

THE FUTURE - HIGH RESOLUTION

An important future area of HVEM is undoubtedly HREM. It is highly appropriate that this Seventh International Conference on HVEM is being held at Berkeley where, at the time of writing, a 1MV HREM is being installed which should have the highest resolution in the world.

The motivation in going to higher voltages to achieve higher resolution is, of course, that the point resolution of an electron microscope is proportional to $C_s^{1/4} \lambda^{3/4}$. Hence for a given C_s the resolution is better the smaller the value of λ , i.e. the higher the incident electron energy. This has been well demonstrated experimentally on some high resolution, high voltage instruments (e.g. [7, 8, 9]). When considering the ultimate in HREM, an easy-to-remember set of numbers is that a point resolution of 1Å would be achieved with a 1MV microscope having $C_s = 1.0\text{mm}$ (assuming good electrical and mechanical stability) [10]. Provided sufficient money is available it seems clear that the best way to achieve very high resolution is to operate at around 1MV.

If less money is available, an HREM operating at, say, 400kV with a C_s of 0.9mm has a point resolution of 1.7Å. This is insufficient to resolve at Scherzer defocus individual atom rows in semiconductors (e.g. Si) in the 110 projection (separation 1.36Å). However, provided the electrical stability of the microscope is sufficiently good, the information resolution limit (at 14% contrast) of the microscope should approach 1Å. It would then be possible to resolve individual atom rows in semiconductors using 'passband' defoci (see for example, Humphreys and Spence [11]).

The ability to resolve individual atom rows in semiconductors, metals and many other materials will be a major breakthrough. For example, electron microscopy has already provided us with an enormous amount of information on the structure of interfaces (for a review see Gronsky [12]). In some cases it is essential to know the interface structure at the atomic level, for example it is believed that Schottky barrier heights in silicon/silicide interfaces are controlled by the atomic structure of the interface [13]. Similarly the new multi-layer of semiconductor 'quantum well structures' have electrical properties which are believed to depend upon interfacial steps of atomic height, and other

atomic level features of the interface. The new high resolution high voltage microscopes will be unique instruments for determining local atomic structure. The existence of many problems, both scientific and technological, which require atomic resolution for their solution, should ensure the success of this latest development in high voltage electron microscopy.

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HIGH RESOLUTION



ATOMIC RESOLUTION ELECTRON MICROSCOPE AT ACCELERATING VOLTAGES FROM 400 TO 1000 kV FOR THE NCEM, BERKELEY CALIFORNIA

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ABSTRACT

An atomic resolution electron microscope at accelerating voltages from 400 to 1000 kV was constructed. The microscope has an optical property of $C_s\lambda = 0.02 \text{ mm}\text{\AA}$ (C_s : spherical aberration coefficient, λ : wave length) by using the high resolution objective lens and specimen height control goniometer. Clean high vacuum with hydrocarbon partial pressures less than 3×10^{-10} Torr was obtained. Structure image of $\alpha\text{-Si}_3\text{N}_4$ taken at 1000 kV was compared with computed images and the resolution of the microscope was determined to 1.6 $\text{\AA}$, which was obtained under the temporal assembling without an vibration isolation system.

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1. INTRODUCTION

The resolution of the electron microscope has been improved by increasing the accelerating voltage. Recent high voltage electron microscopes (HVEM) have resolution less than 2 $\text{\AA}$ (1, 2, 3). With the increase of the accelerating voltage, however, the specimen is inevitably damaged by high energy electron irradiation. The critical voltage of the irradiation damage decreases with the decrease of the atomic number of elements. Then, the structure of materials is observed at the highest accelerating voltage under the critical voltage. It is, therefore, required to maintain the high resolution not only at the highest accelerating voltage but also at lower voltage.

An atomic resolution HVEM has been constructed, which is specified by the National Center for Electron Microscopy (NCEM) at the Lawrence Berkeley Laboratory, University of California. Typical features of the microscope are: (1) high stability of high voltage (1×10^{-6} /min), (2) low spherical aberration coefficient C_s (2.3 mm at 1000 kV), (3) high resolution (less than 2 $\text{\AA}$) in every accelerating voltage between 400 and 1000 kV achieved by a newly developed height control goniometer and (4) a clean high vacuum around specimens created by sputter ion pumps, titanium sublimation pumps.

2. ATOMIC RESOLUTION ELECTRON MICROSCOPE

Fig. 1 shows a cross section of the atomic resolution HVEM. The microscope consists of a high voltage generator (1-7 in the figure), a specimen stage and a goniometer (9, 10), lens system (8, 11, 12), an image observation and a recording system (13, 14, 17) and an evacuation system (15, 16).

2.1. High Voltage Generator

Figs. 2 (a) and (b) show arrangements of the high voltage generator on the plane perpendicular to the optical axis for a previous HVEM and the present HVEM, respectively. In the previous high voltage generator, there are 6 columns: one accelerating column (ACC), one Filter column, two direct current columns (DC) and two alternating current columns (AC). In this generator, the electric field distribution in each column can be hardly unified when discharge occurs and electric parts are often destroyed due to an anomalous high voltage caused by the discharge. In the present high voltage generator, however, DC columns and Filter are assembled in one column to reduce the probability of discharge and to keep the uniform electric field distribution even after discharge. The standard resistors are covered by shielding cases in order to homogenize the electric field around the resistor. In the previous high voltage generator, filament power is resultantly changed when the high voltage is changed, because a different standard resistor is activated for an individual high voltage, thereby, gain and phase of the feed-back circuit inevitably changes and this produces the fluctuation of high voltage. In the present high voltage generator, on the other hand, the standard voltage is changed through transformers and highly stable high voltage (1×10^{-6} /min.) is obtained even after the change of the high voltage.

2.2. Optical Property of Objective Lens and Height Control Goniometer

Design procedure and optical properties of the objective lens are already described (4, 5). Slim lines of Fig. 3 shows C_s depending on the specimen position Z_0 . Bold line is the C_s giving $C_{s\lambda} = 0.02 \text{ mm}\text{\AA}$. The values of C_s (and Z_0) are 2.3 (4.2), 1.9 (3.8), 1.6 (3.2), 1.4 (2.8) and 1.2 mm (2.3 mm) for 1000, 800, 600, 500 and 400 kV, respectively, which data are put into the memory of microcomputer.

This HVEM is provided with the adjustment mechanism of the specimen position (Z-control) giving the optimum C_s for each accelerating voltage. Fig. 4 shows the top and side views of the Z-control goniometer. When the screw is rotated by a motor, a carriage fixed on the roller is moved up and down. The rotation angle of the screw is transmitted to a voltage signal and put into the microcomputer. The Z-control goniometer fixed on the carriage moves automatically so as to set the specimen on the optimum plane with the change of accelerating voltage.

The accuracy of the Z-control goniometer was checked by the image shifts (for X, Y plane) and change of the focussing excitation (for Z direction) after the Z-movement. The maximum image shift by the change of specimen position of 2 mm was $17 \text{ }\mu\text{m}$. The reproducibility of Z-position was high with an error of less than $4 \text{ }\mu\text{m}$, after the movement of 2 mm and returned back state. It was very difficult to obtain a high anti-vibration property in the Z-control goniometer. At first, we manufactured a stage without two springs A and C of Fig. 4. In this first model, lattice image of $1 \text{ \AA}$ of Au could not be observed because of the vibration of the goniometer. After attaching these springs, lattice lines of $1 \text{ \AA}$ can be photographed.

2.3. Vacuum System

Fig. 5 shows the vacuum system diagram of this HVEM. Each chamber in the

whole column is cleanly evacuated to a switching pressure of 0.1 Torr, by a turbo-molecular pump TMP2 backed by a mechanical rotary pump RP3. A differential evacuation system is established between the accelerator, the column chamber, and the viewing and camera chambers. The accelerator and the column chamber are finally evacuated by a sputter ion pump and a titanium sublimation pump, independently. The viewing chamber, connected to a camera chamber is evacuated by a diffusion pump (DP) with a cold trap (t2) to pump out a large amount of water vapor evolved from photographic films.

Degassed Viton O-rings and perfluoropolyether grease were employed. The grease can withstand vacuum bake-out and is not polymerized by electron beam irradiation (6). Excitation current of electron lens is used to a mild bake-out of the column. The lens coils and the deflection coils are positioned outside the vacuum. A residual gas spectrum in the main pipe line for the specimen chamber is presented in Fig. 6, where typical gases are identified. The spectrum shows a very clean vacuum with hydrocarbon partial pressures of less than 3×10^{-10} Torr except methane (CH_4). Recorded ultimate pressure is 4×10^{-8} Torr for the column chamber.

3. RESOLUTION OF THE MICROSCOPE

There are two methods for determining the resolution of high resolution electron microscopes. A conventional method uses the optical transforms from micrographs taken with thin film of amorphous carbon or silicon (7). The other method used in this investigation compares the structure image of crystalline material with the image obtained by the computer simulation (8). Fig. 7 shows the structure image of $\alpha\text{-Si}_3\text{N}_4$ ceramic taken with (001) incidence at 1000 kV. The image has a trigonal symmetry. Dark bands correspond to clusters of Si and N atoms in the projected model. The image computation was made by changing the thickness of the specimen, defocus and resolution. The resolution is taken into the simulation as the effective aperture size (8). The spherical and chromatic aberration coefficients C_s and C_c are 2.3 and 3.4 mm, the stability of the high voltage is 1×10^{-6} and resolution is 1.4 Å. The structure model and calculation method of $\alpha\text{-Si}_3\text{N}_4$ are already described by Hiraga et al. (9).

Insert image of Fig. 7 shows computed one selected from through focus series of 20 Å step. The image of defocus 700 Å coincides fairly good with the observed image, though a difference is noticed. In order to obtain better coincidence calculations were made by changing resolution and C_s . Fig. 8 (a) and (b) show the computed results. When the higher order waves are cut by the aperture, triangles become bright, while dark bands separate to two spots. The degree of separation of dark bands is good coincidence with the image of resolution 1.6 Å. By increasing the C_s , triangles become bright without separating the dark bands into two spots. The computed images gradually change from $C_s = 2.3$ mm to $C_s = 2.8$ mm and hardly change from $C_s = 2.8$ to 4.2 mm and then suddenly changed above $C_s = 4.5$ mm. Thus, it is concluded that the image shown in Fig. 7 has the C_s of 2.8 mm and the resolution of 1.6 Å, respectively.

The reduced resolution is considered to be due to the vibration of the specimen relative to film. In our factory, no vibration isolation system is provided for the HVEM. In the NCEM Berkeley, vibration isolation system is set under the microscope which is made of concrete block of 100 ton in weight

which is supported on many air-mounts. The vertical and horizontal frequencies of vibration are 1.15 Hz and 0.64 Hz which the acceleration of it is less than 0.2 gal. So that, after installation of the HVEM on Berkeley, the resolution will reach the expected value of 1.3 Å.

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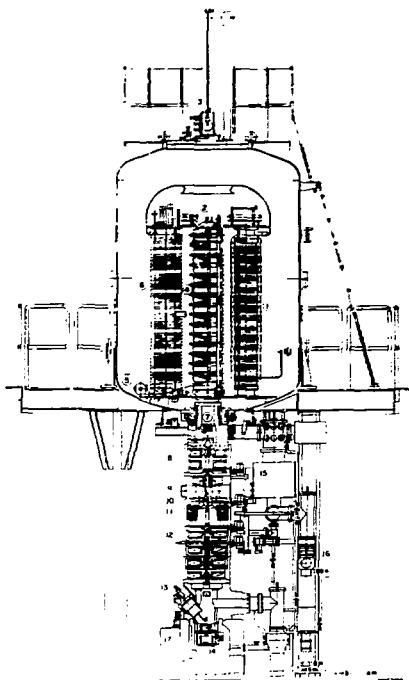


Fig. 1. Cross section of atomic resolution HVEM. 1) High voltage generator, 2) Electron gun, 3) Emitter exchanger, 4) Accelerator, 5) Conditioning mechanism, 6) Reference resistor, 7) Beam detector, 8) Condenser lens, 9) Specimen chamber, 10) Goniometer, 11) Objective lens, 12) Intermediate and projector lens, 13) Viewing chamber, 14) Camera, 15) Ion pump, 16) Turbo pump, 17) Operation panel.

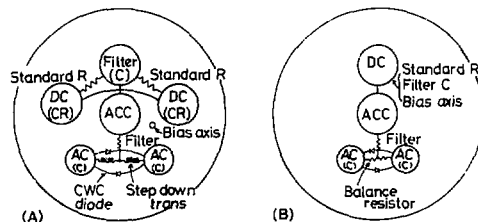


Fig. 2. Arrangement of high voltage generator of previous (A) and present (B) HVEM.

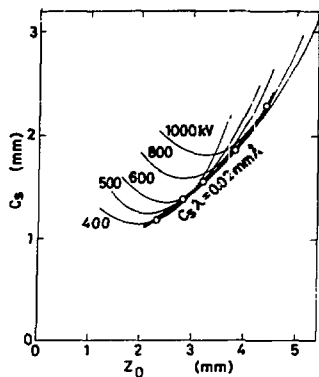


Fig. 3. Spherical aberration coefficient depending on the specimen position for each accelerating voltage. Bold line indicates the C_s giving $C_s \lambda = 0.02$ mmA.

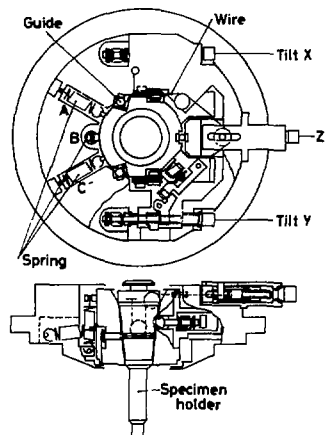


Fig. 4. Mechanism of Z-controlled goniometer.

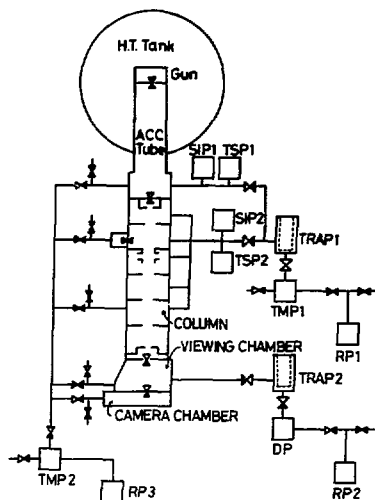


Fig. 5. Vacuum system diagram of the HVEM. SIP 1, 2: sputter ion pump with $1000 \text{ l} \cdot \text{s}^{-1}$, TSP 1, 2: titanium sublimation pump with $510 \text{ l} \cdot \text{s}^{-1}$, TMP 1, 2: turbo molecular pump with $270 \text{ l} \cdot \text{s}^{-1}$, EC: exchange chamber, DP: Diffusion pump, RP: Mechanical rotary pump.

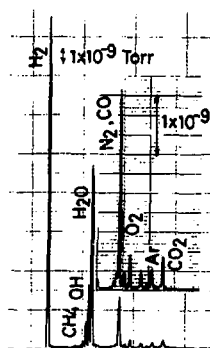


Fig. 6. Residual gas spectrum measured by mass spectrometer.

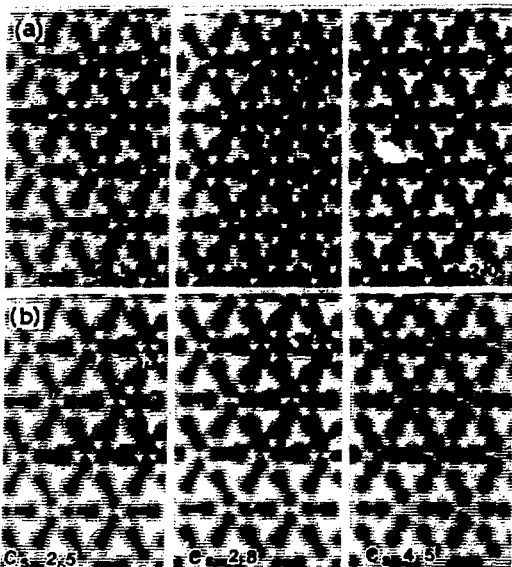
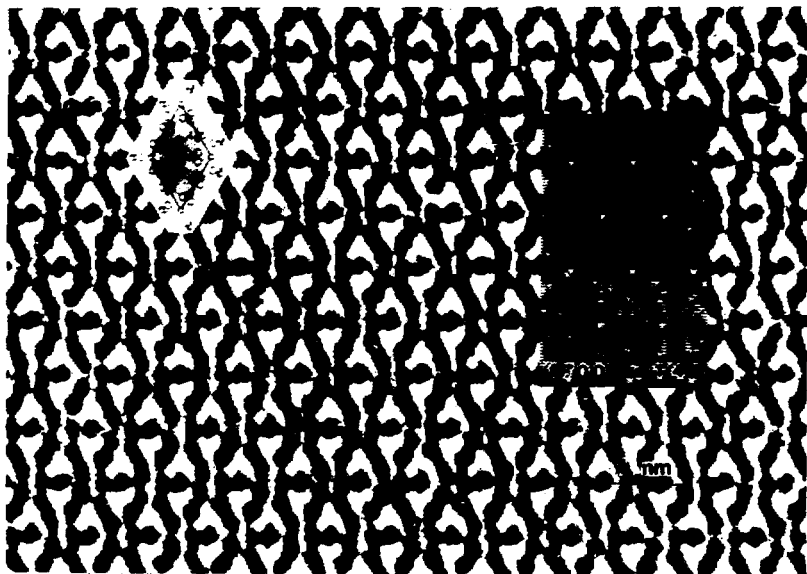


Fig. 7. Structure image of α - Si_3N_4 with (001) incidence taken at 1000 kV. Insert figures are a projected model and computed image obtained by $C_s=2.3$ mm, $C_c=3.4$ mm, stability of high voltage $\Delta V/V=1 \times 10^{-6}$, resolution 1.4 Å and defocus 700 Å. The specimen was offered by Nippon special ceramics Co., Ltd.

Fig. 8. Computed images of α - Si_3N_4 .

(a) $C_s=2.3$ mm, $C_c=3.4$ mm, $\Delta V/V=1 \times 10^{-6}$, resolution 1.6 Å, C_s (defocus) 2.5 mm (730 Å), 2.8 mm (750 Å) and 4.5 mm (860 Å) from left to right.

(b) $C_c=3.4$ mm, $\Delta V/V=1 \times 10^{-6}$, resolution 1.6 Å, C_s (defocus) 2.5 mm (730 Å), 2.8 mm (750 Å) and 4.5 mm (860 Å) from left to right.

STRUCTURE IMAGES TAKEN BY A HIGH RESOLUTION LMV ELECTRON MICROSCOPE

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ABSTRACT

An ultra-high vacuum high resolution LMV electron microscope(HU-1250), whose objective lens parameters measured are 2.5mm(C_s), 3.5mm(C_H) and 2.6mm(C_A), is used to obtain high resolution structure images. A point to point resolution of about 0.16-0.17nm is obtained. The lens of smaller C_s value than the previous ones gives not only higher resolution images but also structure images under wider defocus ranges.

INTRODUCTION

High voltage and high resolution electron microscopy(HV-HREM) with point to point resolutions about 0.2-0.23nm has been used for the analyses of crystal structures and defects[1-4]. However, to apply the HREM to various crystals especially to practically important materials such as metals and semiconductors of small lattice parameters, much higher resolution is needed.

To improve the resolution a new UHV LMV HREM was constructed[5,6]. It was designed to have a objective lens with C_s of 2.5mm at LMV to get a resolution of 0.14nm. A UHV condition of 10^{-6} Pa level without use of cold traps in the specimen chamber reduced contamination of specimen which is one of the practical problems in HREM. The microscope was so designed that the same pole piece can be used for top- and side-entry holders. This capability together with the UHV condition can extend application field of HREM, because HREM with use of various kinds of top- and side-entry holders(heating, cooling...) can be done routinely without contaminations and reactions of specimens with residual gases. HREM of surfaces by the present microscope is given in separate papers[7,8]. In the present paper a basic performance and HREM images by the top-entry stage are given.

PERFORMANCE

As mentioned in the previous communication[6], the pole piece was measured to have the following lens parameters at LMV: $C_s=2.5$ mm, $C_H=3.5$ mm and $C_A=2.6$ mm. Resolution expected from the C_s value is 0.14nm. However, optical diffractograms showed a resolution of 0.16-0.17nm as shown in Fig.1. Reduction in resolution is mainly due to the chromatic aberration. Mechanical vibrations due to three turbomolecular pumps for dry evacuations are reduced by bellows connection and sound proofs. 0.1nm lattice fringes are resolved(Fig.2).

STRUCTURE IMAGES

A top-entry tilting holder($\pm 30^\circ$) was used to take structure images.

W8Nb18069

Figures 3a and b) are the structure model and a structure image of the 5x5

block structure of WgNb18069 crystal, respectively. Individual strings of metal atoms in the corner or edge sharing metal oxygen octahedra are clearly resolved. An X-ray structure analysis showed that a distance between the corner sharing ones is 0.384nm, while a distance in the projection between the edge sharing ones is 0.237nm[9]. The ratio is 0.71. The ratios measured from the image are in a range of 0.65-0.71 and agree well with the X-ray datum. The X-ray analysis showed that tetrahedral positions were occupied by tungsten atoms. In the micrograph these sites(indicated by small arrows) are seen to be relatively broad and not so dark as the octahedral sites. A defect is seen along a line indicated by a big arrow head. There, dark dots of metal atom positions separated by about 0.18nm are resolved. The defect may be a step of a crystallographic shear plane along the electron beam direction.

Figure 4 shows a series of through focus images. It is noted that in a defocus range from (b) to (g) strings of the metal atoms in the corner and edge sharing octahedra and those at tetrahedral sites are well recognized. This is because of the small C_s value of the microscope: The distances of metal atom strings concerned are 0.384 and 0.237nm much longer than the resolution expected from the C_s value. However, details of the images change by defocus: The above mentioned ratios measured in large defocus images are larger than that of X-ray datum. The defect images(0.18nm distance) seen in Fig.3 lose their contrast by slight change of defocus(~ 20 nm). In the other area small tunnels formed by crossing of two perpendicular shear planes(Fig.5) are observed. This kind of defect structure is recognized in a small defocus range of ~ 40 nm. These ranges are consistent with the values simply estimated from transfer function for various defocuses. From (e) to(g) bright contrast is seen at the center of the octahedral metal atom strings. This is more clearly seen in an enlarged micrograph(Fig.6) which was taken at 40nm underfocus condition from Fig.3b. The bright contrast is seen only in this crystal regions. The bright contrast may be due to the strong interference effect of higher order reflections under large underfocus conditions. The bright contrast is not seen at the tetrahedral site metal strings as indicated by arrows in Fig.6.

Nb3Sn AND V3Si

Figure 7 shows a [001] projection of atoms in the A-15 type crystal(A_3B : Nb3Sn,V3Si). Big holes with a string of A atoms at the center of each hole and small holes at the corners of the unit cells surrounded by four A atom strings are noted. The lattice parameters of Nb3Sn and V3Si are 0.52 and 0.472nm, respectively. The nearest neighbour distance in the projection is a separation distance of three strings(A-B-A atom strings) along the cube edge, and it is 0.13nm for Nb3Sn and 0.12nm for V3Si. The second nearest neighbour distances are between the strings around the small holes and are 0.18 and 0.17nm for Nb3Sn and V3Si, respectively.

Figure 8 shows a structure image of a Nb3Sn crystal. The large holes with Nb atom string in the center are seen. A small holes are also seen. The small holes were not recognized in a previous observation with use of a 200kV electron microscope[10]. However, the three atomic strings between the small holes are not resolved and are seen to be black lines in the image. This is because the nearest neighbour distance is smaller than the resolution of the microscope. The fact that the small holes are contrasted indicates that the resolution is close to 0.18nm. This kind image is taken only in a narrow defocus range(less than 20nm). Images similar to that in Fig.6 were taken in the case of V3Si crystals.

OTHER SUBSTANCES

The microscope was also used to observe Fe-C crystals[11], WO_3 , Si crystals and $NaNbO_3$ - $SrNb_2O_7$ solid solutions[12] and clean surfaces of metals[8].

CONCLUSIONS

A point to point resolution of about 0.16-0.17nm was obtained with use of HREM. Due to the small C_s value structure images are observed in wide defocus ranges when we are concerned with distances of 0.2-0.3nm which is longer than the resolution limit 0.14nm expected from the C_s value. This is practically important especially when HREM is done with use of various kinds of specimen holders such as a heating specimen holder[8].

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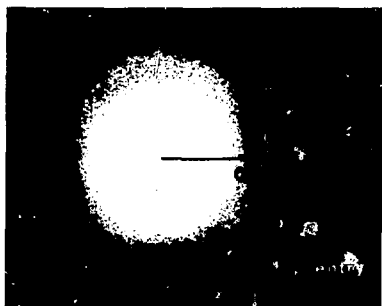


Fig.1 An optical diffractogram from an image of an amorphous carbon film.



Fig.2 0.1nm lattice fringes of Au(001) film (axial illumination).

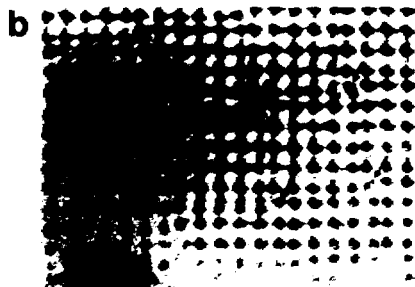
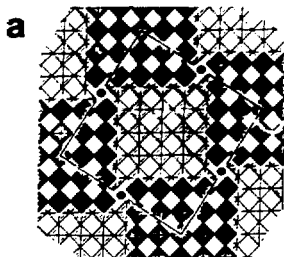


Fig.3 Structure model (a) and a high resolution structure image (b) of a $W_8Nb_{18}O_{69}$ crystal.

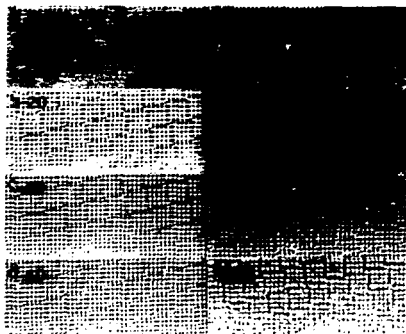


Fig.4 Through focus images of $W_8Nb_{18}O_{69}$.

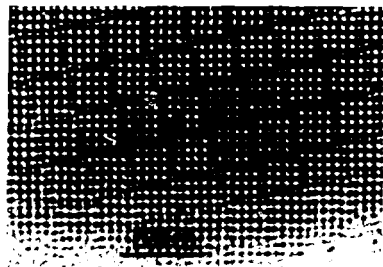


Fig.6 Under focus image of $W_8Nb_{18}O_{69}$.

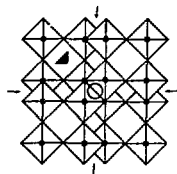


Fig.5 A defect formed by a crossing of shear planes.

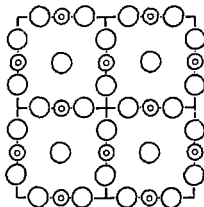


Fig.7 [001] projection of atoms in the A-15 type crystal (A_3B structure).
A atom: single circle
B atom: double circle

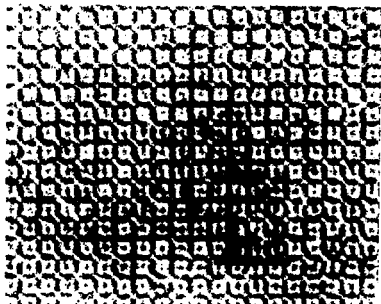


Fig.8 Structure image of Nb_3Sn crystal, [001] incidence.

CONSTRUCTION OF A 400KV ANALYTICAL ATOM RESOLUTION ELECTRON MICROSCOPE (AARM)

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ABSTRACT

A 400KV high resolution electron microscope which has the systems of analysis of materials and images and aims resolution limit of $1.5\text{\AA}$ has been constructed and the features of TEM are described. Oil free clean vacuum system, stable power supply, bright illumination and computerized operational function provide the easy observation of atomic structure of the specimen. The microscope has been constructed by the sponsorship of Japanese Ministry of Education, Science and Culture.

INTRODUCTION

It is now well understood that high resolution electron microscopes become the powerful tools for studying the atomic structure of the substances. For obtaining the high resolution, the electron waves accelerated by high voltages such as 1MeV are now being used because the short wave length of electrons produces the high resolution theoretically. However, with increasing the accelerating voltage, the electrons will give the heavy radiation displacement damage the specimen, which destroys the original atomic arrangement in crystal and becomes more serious than contamination for the study of atom position. Operational uneasiness, maintenance and cost-performance ratio are also become more serious than in low voltages.

In 1982, the present authors constructed 300kV high resolution electron microscope[1] as the appropriate microscope to obtain the high resolution without heavy radiation damage. After one year operation of 300kV microscope, the present authors noted that 400kV electron microscope with operational easiness is more useful in the field of materials science, because the high resolution such as $1.5\text{\AA}$ (point to point) can be obtained easily.

Using the fund from Japanes Government, we have constructed a 400kV electron analytical microscope which has functions of identification of the specimen materials and image processing system and enables us to see the images of atoms directly on the fluorescent screen and the TV screen. The present paper describes only the features of high resolution electron microscope. The functions of analysis of the specimens and the images will be shown elsewhere.

INSTALLATION

As shown in Fig.1, the electron microscope column is installed in front of the high voltage power supply tank and directly coupled with short cable. The height, width, depth and weight of the main console are 3.1m, 2.24m, 3.565m and 3100kg.

CONSTRUCTION OF ELECTRON MICROSCOPE

Figure 2 shows the cross section of the electron microscope column, which consists of electron gun, condenser lens, specimen chamber, objective lens intermediate and projector lenses, viewing chamber and recording system. The microscope column is evacuated by Balzers TPU270 turbo molecular pump.

Electron Gun

The electrons which are emitted from the tip of single crystal of LaB₆ are accelerated with seven steps, 100kV, 150kV, 200kV, 250kV, 300kV, 350kV and 400kV. The brightness is 1×10^7 amp/cm²ster at 400kV. Stability of accelerating voltage is 2×10^{-6} /min. Minimum beam diameter is 50nm and max beam tilt angle is $\pm 2^\circ$ (X,Y). The accelerating tube is evacuated by 60 l/s sputter ion pump and kept at 10^{-7} Torr.

Specimen Chamber

The number of specimens which can be mounted are six and two for ultrahigh resolution and analytical modes. The specimen can be tilted with $\pm 15^\circ$ and moved 2mm, 2mm and 1.5mm for X, Y and Z direction. The clean specimen environment is prepared by the use of 140 l/s sputter ion pump and at present 2×10^{-7} Torr is obtained without using liquid nitrogen in cold trap. Tensile stress, heating and cooling devices can also be fabricated.

Imaging Lens

For standard ultra-high resolution observations, using top entry goniometer ($\pm 15^\circ$), the pole piece for objective lens with focal length 2.6mm, spherical aberration coefficient 1.0mm and chromatic aberration coefficient 1.7mm is used. This lens pole piece provides the resolution limit of $1.55\text{\AA}$. Another lens pole piece with spherical aberration coefficient 0.8mm can be used, which gives the resolution limit of $1.5\text{\AA}$. Some phase contrast transfer function in optimum focussing are shown in Fig.3. Magnification range is from 100 to 1,000 times with fourteen steps and from 1,200 to 1,800,000 times with thirty one steps. An example of observed images is shown in Fig.4.

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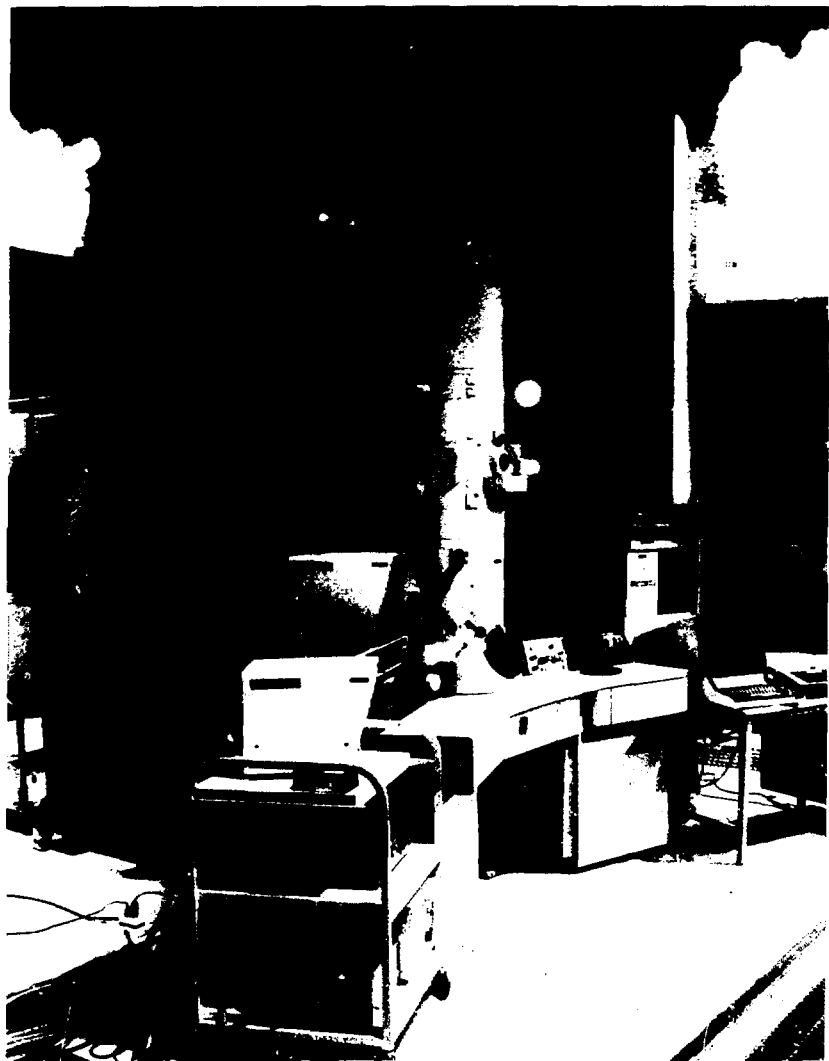


Fig.1 Outer view of AARM.

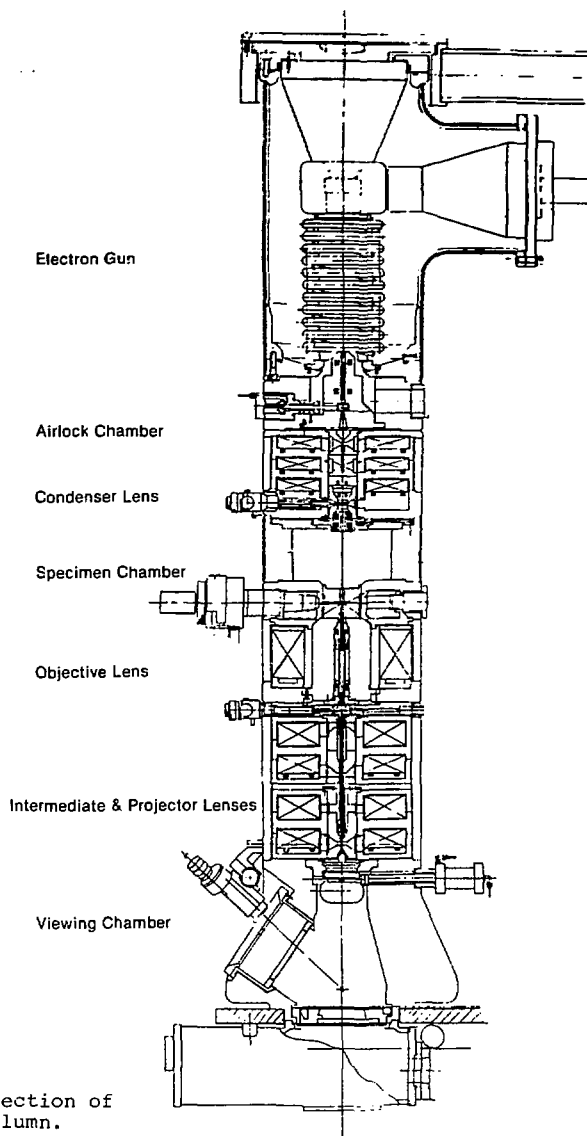


Fig.2 Cross section of
AARM column.

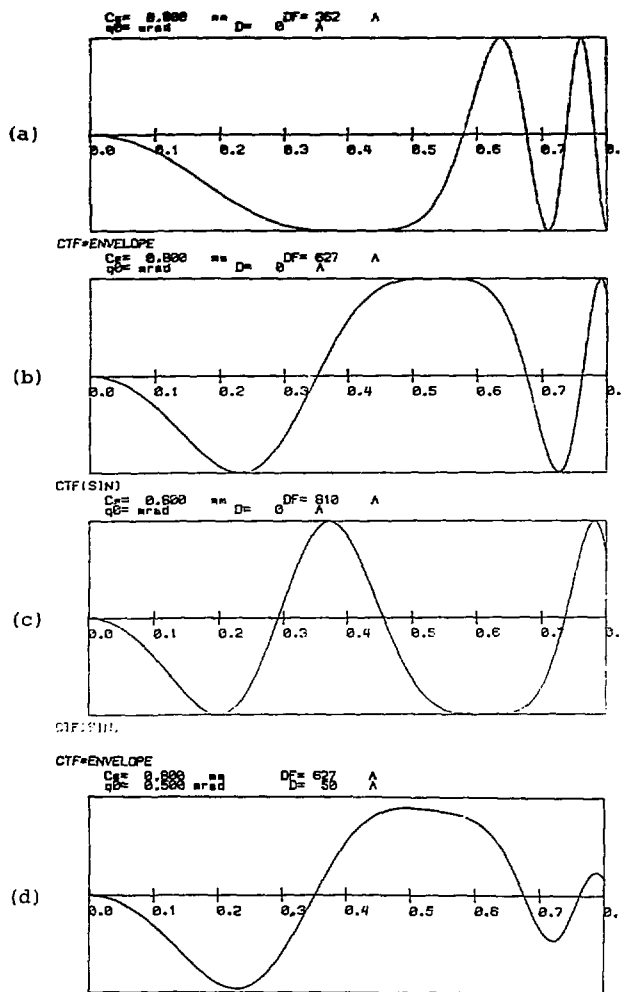


Fig.3 Phase contrast transfer function of objective lens $C_s = 0.8$ mm
 (a) $\Delta f = 362$ Å, (b) $\Delta f = 627$ Å, (c) $\Delta f = 810$ Å, (d) $\Delta f = 627$ Å, beam divergence
 $q_0 = 5 \times 10^{-4}$ rad., chromatic defocus spread $D = 50$ Å



Fig.4 Electron microscope image of silicon of $1000\text{\AA}$ thickness in 110 symmetry position taken at 350kV. Radiation displacement damage produces the point, line and plane defects.

CHARGE DENSITY DISTRIBUTION FROM HIGH RESOLUTION MOLECULAR IMAGES

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ABSTRACT

The possibility to determine the degrees of ionization of the individual atoms by combining micrographs to enhance the effect of ionicity on the image contrast which is more distinctive at a low scattering region has been studied. Two images taken at the Scherzer and a further underfocus positions are combined in the reciprocal space. Although the case of 200kV ($C_s=0.8\text{mm}$) has considerable information about the ionicity even on the Scherzer focus image, the determination of the individual ionicities is difficult since each atom is not well resolved. The case of 500kV ($C_s=1.1\text{mm}$) gives the best results, and the intensity change of 5.8% due to the ionization of copper ($0 \rightarrow +1/2$) is expected at the specimen thickness of 38A. For the case of 1000kV, the combined image recovers only a part of information at the low angle region, and the image reconstructed by combining three or more micrographs may be useful. Since the defocus conditions are not so critical, this method is easily applicable. The effects of the specimen thickness through the dynamical interaction should be considered for the quantitative interpretations of the high resolution images except for very thin specimens. Although low angle reflections only reflect general feature of the molecular shape, they should be included in the image formation to represent the structure faithfully.

INTRODUCTION

The scattering factors of ionized atoms for electrons are very much different from those of neutral atoms at low scattering angles. Therefore it is possible to estimate the degrees of ionization of individual atoms in a crystal by the precise measurement of the electron diffraction intensities. Anstis *et al.*[1] have tried to determine the atom ionicities in the tungsten niobium oxide crystal from the diffraction intensities obtained through n-beam dynamical calculations. The diffraction method can be applied only to crystal specimens, while the analysis based on high resolution images can also be applied to aperiodic objects such as defects in the crystals. The recent remarkable developments of the electron microscope and the observation techniques make it possible to discriminate even the medium atoms by the image intensities, e.g. copper and chlorine atoms in chlorinated Cu-phthalocyanine (ClCuPc)[2]. We have studied the possibilities to determine the ionicity based on the contrast of the combined image of two high resolution micrographs taken by Kyoto 500kV HREM[3]. In the present paper we will discuss the general effect of combining the images and the effect of the specimen thickness on the determination of the ionicity. The applicability of HV-HREM to determine the ionicity will also be discussed.

FUNDAMENTALS

Since the atomic scattering factors of ions for electrons drastically differ

from those of the corresponding neutral atoms at the low angle region ($\leq 0.2\text{\AA}^{-1}$) as compared with X-ray atomic scattering factors as shown in Fig. 1, the electron microscope images might show more clearly the degree of ionization than the electron density maps in X-ray analysis. However, the contrast transfer function (CTF) at the low angle region attenuates from unity for a Scherzer focus. This effect becomes more severe as the instrumental resolution increases. In order to retrieve the information on the ionicities of the individual atoms, the image including low angle reflections should be synthesized with the Scherzer focus image. This might be done by combining two images taken at the Scherzer focus and a further underfocus respectively. The best combinations of the defoci for different accelerating voltages as well as electron optical conditions are listed in Table 1. The region where $\sin\chi \geq 0.7$ at the Scherzer focus extends between q_0 and q_1 , while the corresponding region of the combined image covers from q_0 to q_2 . An example of the combined CTF including the partial coherence effect is shown in Fig. 2 for a case of 500kV.

Table 1. The best combination of defocus for image synthesis.

Acc. (kV)	Cs (mm)	Defocus (Å)	$q_0(\text{\AA}^{-1})$ $d_0(\text{\AA})$	$q_1(\text{\AA}^{-1})$ $d_1(\text{\AA})$	$q_2(\text{\AA}^{-1})$ $d_2(\text{\AA})$	$\Delta(\text{\AA})$	$\alpha(\text{rad})$ $\alpha/\lambda(\text{\AA}^{-1})$
200	0.8	546+1545	0.445 2.25	0.141 7.09	0.081 12.35	100	5.97×10^{-4} (0.0238)
500	1.1	482+1364	0.630 1.59	0.200 5.00	0.114 8.77	100	4.78×10^{-4} (0.0336)
1000	2.8	602+1704	0.719 1.39	0.228 4.39	0.131 7.63	100	3.35×10^{-4} (0.0384)

q_0 and q_1 are upper and lower limits of spatial frequency on the Scherzer focus image, where $\sin\chi \geq 0.7$. q_2 is a lower limit of the corresponding region of the combined image. Δ and α are energy spread and illuminating angle, respectively.

RESULTS AND DISCUSSIONS

Role of Low Angle Reflections

Simulated images of ClCuPc on the condition of 500kV are shown in Fig. 3, where (a) and (b) are the Scherzer focus image and the combined image respectively. Here all atoms are assumed as neutral. The corresponding thickness is one unit cell, so that the kinematical approximation might be valid. The molecular shape of phthalocyanine is more clearly recognized in (b) than in (a). Moreover the contrast of benzene rings is improved in the combined image (b). The condition of defocusing is not so critical, since a small defocus error does not produce significant effects on $\sin\chi$ at the low angle region, and since the image change with defocusing is minimum around the Scherzer focus. Thus any real image with defocus error less than 50Å from the best defocus combination given in Table 1 can be used to synthesize the combined image. This makes the method practicable.

Effect of Ionicity on Image Intensity

The combined images were calculated for different degrees of ionizations. Carbon and nitrogen atoms are assumed as neutral although they might have some

ionicities. The ionicities of one copper and sixteen chlorine atoms are assigned to hold the neutrality in total; e.g. +1 and -1/16 are assumed for the copper and each chlorine respectively. The atomic scattering factors for partially ionized atoms are estimated by the appropriate combination of the atomic scattering factors for electrons of neutral and fully ionized atoms tabulated in the International Tables for X-ray Crystallography[4]. The peak intensities in the image of copper and chlorine atoms are given in Table 2 for two specimen thicknesses. Here the incident beam is assumed as one. The image intensities for the degrees of ionization preliminarily estimated by kinematical calculations are compared with those of the neutral atoms. The intensity at the ionized copper increases, while the intensity change of the chlorine ions is very much small since the degree of ionization of chlorine is one-sixteenth of that of the copper. The combined images simulated at ten unit cell thickness are shown in Fig. 4 for neutral and ionized models in the case of 500kV. Here the assumed ionicities are +1/2 and -1/32 for the copper and chlorine respectively. Both images show almost same intensity distribution except for the position of the copper. This indicates that the resolution is sufficiently high, and the degrees of ionization of the individual atoms will be determined independently.

Table 2. Image intensities of copper and chlorine atoms.

Acc. Volt.	Unit cell (Thickness)	Scherzer focus image				Combined image			
		Cu ⁰	Cu ^{1/2+}	Cl ⁰	Cl ^{1/32-}	Cu ⁰	Cu ^{1/2+}	Cl ⁰	Cl ^{1/32-}
200kV	1 (3.8Å)	.937	.925	.921	.922	.928	.908	.922	.923
	10 (38.0Å)	.487	.416	.391	.393	.426	.355	.402	.397
500kV	1 (3.8Å)	.906	.900	.906	.907	.909	.897	.904	.905
	10 (38.0Å)	.386	.354	.307	.310	.472	.414	.297	.301
1000kV	1 (3.8Å)	.884	.880	.886	.881	.881	.872	.884	.882
	10 (38.0Å)	.319	.301	.200	.201	.384	.351	.225	.225

Detectability of Ionicity

The differences of the image intensities between the neutral and the ionized models are summarized in Table 3. The possibility to determine the ionicity becomes high if the difference is large. It is evident that the thick specimen has the advantage over the thin one to detect the ionicity. For example, the intensity of the copper changes from 1.2% to 5.8% when the thickness increases from one unit to ten unit cells for the case of 500kV. However the dynamical effect will make the quantitative determination of the ionicity difficult as will be discussed later. In the case of 200kV, the gains of the intensity changes by combining the images are negligible. This might result from two reasons: 1) the effect of the ionicity is considerably included in the Scherzer focus images, 2) the resolution is not sufficient to resolve each atom and to detect the degree of the ionization of the individual atom. For the case of 1000kV, on the contrary, the combined image recovers only a part of the information at the low angle region, and the image reconstructed from three or more originals will make it feasible to determine the ionicity.

Table 3. Intensity change by ionization.

Acc. Volt.	Unit cell	Scherzer focus image		Combined image	
		Cu	Cl	Cu	Cl
200kV	1	.012	-.001	.020	-.001
	10	.071	-.002	.071	.005
500kV	1	.006	-.001	.012	-.001
	10	.032	-.003	.058	-.004
1000kV	1	.004	.005	.009	.002
	10	.018	-.001	.033	.000

Dynamical Effect on Image Intensity

It is almost impossible to determine the absolute intensity of the experimental image compared with that of the incident beam, so that we have to use some ratio of the image intensities. In the preliminary experiment to determine the degrees of ionization by comparing the reconstructed image with the theoretical one, we therefore take the ratio of the image intensity of the copper to that of the chlorine. However, in the dynamical scattering region, the image intensity will nonlinearly vary with the specimen thickness, and the intensity variation depends on the atom species. The intensities at the copper and the chlorine atoms on the Scherzer focus image(S) and the combined image(C) for the case of 500kV are plotted against the specimen thickness in Fig. 5. The intensity changes are almost linear up to the thickness of five unit cells. The ratio of contrast (defined as one minus the image intensity) of the copper to that of the chlorine on the combined image is 0.95 at one unit cell thickness, while 0.75 at ten units. The dynamical effects on the general appearance of the molecular images are demonstrated in Fig. 6. First, it can be recognized that the intensity changes of the copper and the chlorine with the specimen thickness are different. Secondly, the contrast of the light atoms gradually increase with the specimen thickness, and these atoms behave like medium atoms at the thick region. It is worthwhile to note that the contrast and also the ratio of peak intensities in the combined image are different from those in the Scherzer focus image especially at the thick region. The intensity of image does not have a simple relation to the scattering power even in the Scherzer focus, if the specimen is not thin enough. Thus the specimen thickness is the most important factor to discriminate the atom species and determine the degree of the ionization from image intensities.

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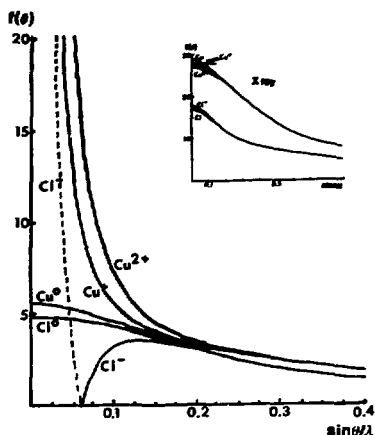


Fig. 1. The atomic scattering factors of ions and neutral atoms for electrons and X-rays. A dotted line indicates the negative.

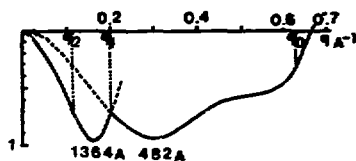


Fig. 2. A solid line shows a combined CTF including partial coherency for the case of 500kV. $\sin \chi$ takes 0.7 at q_0 , q_1 and q_2 .

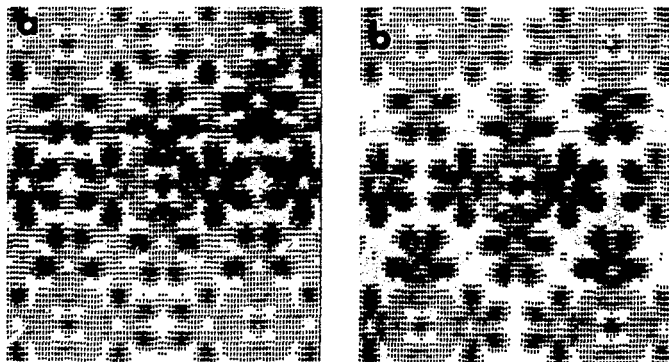


Fig. 3. Simulated images of ClCuPc showing the role of low angle reflections. (a) and (b) are the Scherzer focus image and the combined image, respectively, for 500kV electrons.

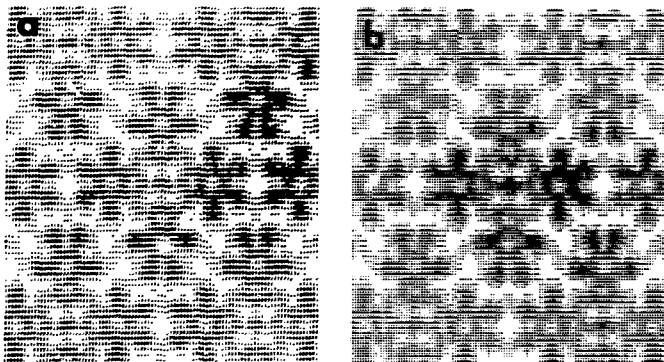


Fig. 4. Combined simulation images which show the effect of the ionicities. (a) corresponds to non ionized structure. The ionicities of $+1/2$ and $-1/32$ are assumed for copper and chlorine atoms in (b).

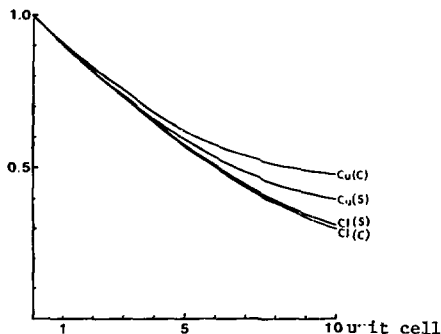


Fig. 5. The intensities at copper and chlorine atoms on the Scherzer focus image(S) and the combined image(C) against the specimen thickness. All atoms are assumed as neutral. The thickness is expressed in number of unit cell which is equal to $3.8\text{\AA}$.

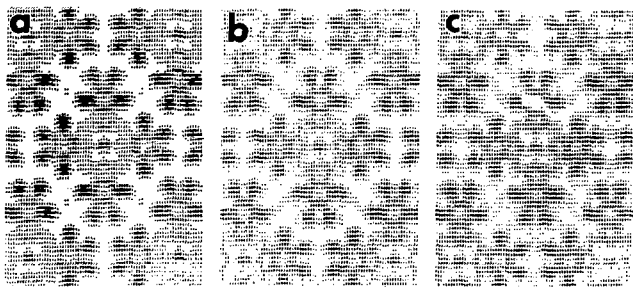


Fig. 6. The dynamical effects on the general appearance of the molecular image. (a), (b) and (c) correspond to the thickness of one, five and ten unit cells, respectively.

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ABSTRACT

In the course of high resolution observation of N-niobium pentoxide crystal wedge oriented with the b-axis parallel to the incident beam, extra images regarded as interstitial niobium ions were sporadically found in the cube-octahedral sites of some regular 4×4 arrays of NbO_6 octahedra, showing diffuse X-type features at the optimum focus position. The appearance of image varies in a through focus observation. The images were reasonably interpreted in terms of the thermal oscillation of the interstitials by the comparison with series of simulated images based on the multislice calculations.

INTRODUCTION

In the previous paper¹, we reported that the position of niobium ions observed in N-niobium pentoxide crystal with Kyoto 500kV HREM coincided to a considerable extent with that determined by Anderson² on the basis of X-ray diffraction analysis, indicating that the attainment of sufficient enough resolution is the fundamental requirement for the structure study. It was also briefly referred to that anomalous images were sporadically present in the central space of 4×4 arrays of NbO_6 octahedra to be regarded as interstitial niobium ions. Recently, a comparative study was performed for the detailed interpretation of those images on the basis of multislice computer simulation which has verified the former assumption on the presence of interstitial ions.

HREM IMAGES OF MATRIX LATTICE OF N-NIOBIUM PENTOXIDE

The specimen of N- Nb_2O_5 crystal furnished by Dr. Hiraga, Tohoku University, was prepared by thermal decomposition of niobium fluorate. The crystal is wedge-shaped and on actual observation the incident beam was parallel to the b-axis so that the high resolution images taken with Kyoto 500kV HREM consisted of square arrays of Nb ions as reproduced in Fig. 1 for a rather thin area near the crystal edge. The two images a and b in Fig. 1 are taken at different focus positions with respect to different areas of the same crystal. In order to compare the real with theoretical images, the through focus image simulation was performed on the basis of multislice calculations for two slice numbers of 6 and 10, where each slice thickness was assigned to be equivalent to the unit cell dimension. Fig. 2 show several examples which are considered to reflect the real images better. The effect of thickness does not seem to be too strong in this range although the simulation with the dynamical effect taken into account indicates that the sharpness of atomic image is rather enhanced at the position slightly overfocused from the optimum condition ($\Delta f = 450 \text{ \AA}$). The effect is more apparent in a thicker area although no serious deviation in the atomic position was caused by this focus shift as far as the present specimen crystal is concerned.

HEEM IMAGES OF INTERSTITIAL ATOMS COMPARED WITH SIMULATIONS

The anomalous contrast which is regarded as the image of interstitial niobium ion is clearly detected in the enlarged photomicrographs reproduced in Fig. 3. These extra images are statistically distributed with varying contrast in the area slightly far from the thinnest crystal edge. They are always located in the central holes of 4x4 standard square arrays of NbO_6 octahedra which in turn leave 3x3 arrays of rather large cube-octahedral space among them. Since the central hole in particular is known to give the minimum potential for an interstitial atom to situate, the origin of these contrasty images is most plausibly ascribed to the presence of extra heavy atoms. In view of the process of the specimen preparation, no heavy atoms other than niobium are considered to come in as the inclusion. Thus, the further image interpretation is performed in terms of niobium interstitials.

The image of such interstitials show cross-like features at the optimum focus position, although the darkness, weaker than that of nearby Nb ions, varies from position to position, indicating the variation in occupancy factor in the hole column seen normal to the image plane. The appearance changes with the focus position as shown in Fig. 3 a through c. For instance, the dark dots including both regular and interstitial ions appear as white discs in dark background at a overfocus position of $\Delta f = -250\text{\AA}$, while at deeper underfocussed position of $\Delta f = 600\text{\AA}$, both holes and Nb ions show bright contrast and a dark ring surrounds the position of the interstitial ion. While the regular Nb ions are rather tightly bound at the center of oxygen octahedra which are known to assume somewhat deformed arrangements², a fairly large space is allocated for the interstitial ion to move by thermal oscillation. For the interpretation of the anomalous image, the computer simulation was also performed by applying the multislice formula under the same conditions as in the case of the regular matrix lattice, although the effect of thermal motion had to be duly taken into account.

For this purpose, however, a simple maneuver of Debye-Waller factor, for instance, by assigning a large B coefficient may not be appropriate, since the equation is defined with very small strokes of atomic displacement. In the present case, the calculation was based on a statistical distribution of the interstitial atom over the whole central room which may be regarded as a cube octahedron surrounded by 8 NbO_6 octahedra in conventional sense. For the practical approach, this space can be defined as a room allocated for the center of interstitial atom to occupy, although in this case the size of constituent atoms must be taken into account. Since the interstitial Nb ion is surrounded by 16 oxygen, the allowance space can be limited by 16 intersecting spheres with their center located at these oxygen positions and with their radii equal to the sum of both ions as shown in Fig. 4a. In this case, ionicity of the interstitials was tentatively assumed to be equivalent to those of the regular ones so that the radius is equal to one half of the nearest Nb-Nb distance. A set of sampling points (N) were defined three-dimensionally in the waternut like space and the interstitial ion is assumed to occupy each sampling point at a probability of $1/N$. When projected to the image plane as in Fig. 4b, the sampling points are arranged in a two dimensional array. The image simulation was performed by locating the interstitial atom with the existence probability assigned to each projected column of sampling points. The results were shown in Fig. 5 in respect to two slice numbers, 6 and 10, at focus position, Δf : -400, 300 and 750Å. Although a certain effect of thickness change is apparent, the variation of image feature follows a similar

tendency for both defocus series. As to the real images, enlarged photomicrographs were prepared to examine the detailed feature of the interstitial and its environment. In order to eliminate the photographic noise which is inevitable in the enlarging process, the spacial averaging was operated by applying the multiple exposure technique as shown in Fig 6. The characteristic feature of image variation due to the through focussing is clearly reproduced in the series. When compared with the set of simulated images, the appearance show fairly good coincidence in the tendency of image variation in particular with the series of slice number 6. some image details are found to show close resemblance as well. In the images for the near optimum focus (Δf 300A), Nb ions almost look like a square rather than a sphere, while in the overfocussed image it becomes round although the total contrast is reversed. As to the most underfocused image in the series, the striking feature of the central part is very well reflected, especially by the octagonal appearance of outer periphery of the thick dark ring. By such a comparison, the overall status of real images is then fairly well interpreted in qualitative sence in terms of the presence of interstitial ions in the central space. The formation of such an interstitial structure may indicate that the crystal must have been produced somewhat oxygen deficient environment.

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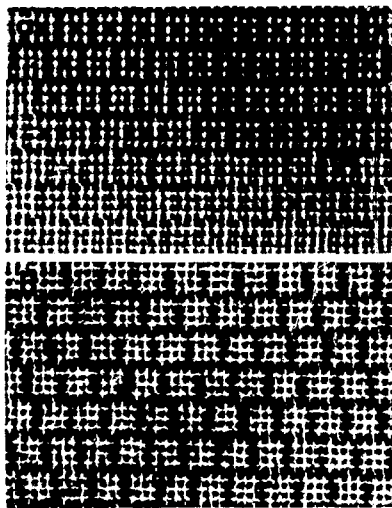


Fig. 1. HREM images of N-Nb₂O₅ at optimum focus (a) and under focus (c) positions.

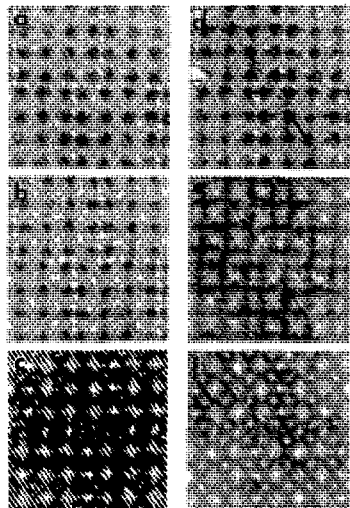


Fig. 2. Simulated images of matrix of N-Nb₂O₅ for slice numbers in unit cells (a-c: 6; d-f: 10) and defocus positions (a,d: 300A, b,e: 400A, and c,f: 600A).

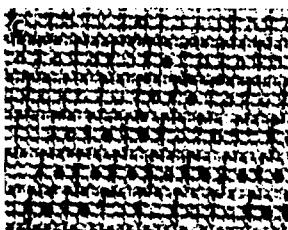
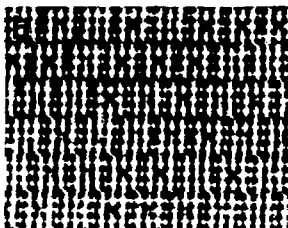
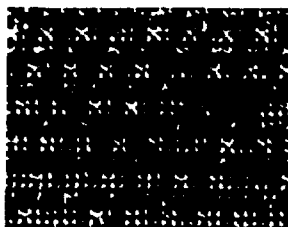


Fig. 3. Through focus images for interstitial ions.
(a: overfocus, b: optimum focus, c: underfocus)

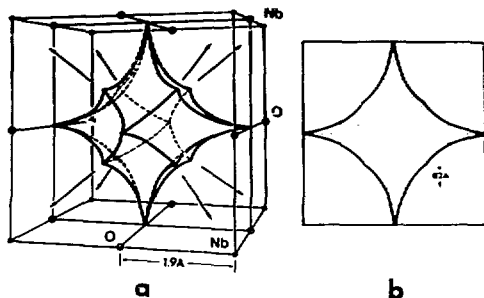


Fig. 4. Three dimensional configuration of interstitial space and two dimensional sampling points for the position of interstitial ion.

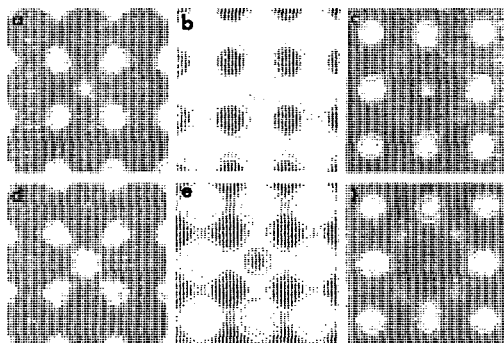


Fig. 5. Multislice simulations of interstitial ion for slice number in unit cell (a-c: 6 and d-f: 10) and defocus position. (a,d:-400A, b,e: 300A and c,f: 700A)

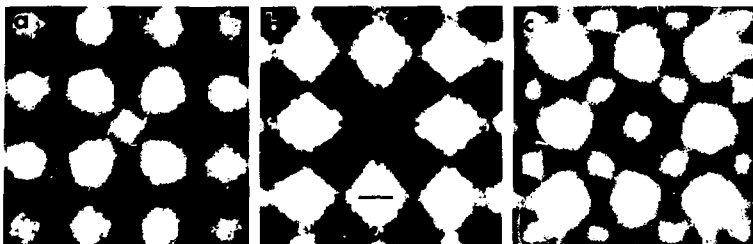


Fig. 6. Spatially averaged through focus images of interstitial ion and its environment. (a: overfocus, b: optimum focus and c: underfocus) Scale: 2A.

HIGH VOLTAGE HIGH RESOLUTION ELECTRON MICROSCOPY OF COMPOUND SEMICONDUCTORS

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ABSTRACT

Several II - VI compound semiconductors have been observed with a 500kV high resolution electron microscope. The lattice defects occurring in ZnTe and ZnSe are described and compared with those found in CdTe.

INTRODUCTION

Characterisation of the structural defects found in compound semiconductors is becoming of increased interest because of their importance in device applications. Conventional TEM and lattice imaging methods at 100kV have already provided considerable useful information [1,2], but it is clear that observation at higher voltage and resolution should provide further details about these defects: more beams contributing to the image make the effects of Fourier imaging less confusing and recognition of the optimum defocus becomes easier; more of the diffuse scattering from the lattice defects is transferred without phase reversals to the image; and thicker specimens can be imaged before extinction effects become important. In this paper, we describe our recent 500kV high-resolution studies of the zinc-based materials ZnTe and ZnSe and compare the defects observed with those found in CdTe [2,3].

METHODS

Specimens were prepared in the usual manner. First, slices were cut from the bulk crystal with faces approximately parallel to a {110} plane. Then, after mechanical polishing, ion-beam-milling with 5kV Argon ions was finally used. All observations were made with the Cambridge University High Resolution Electron Microscope (HREM) [4], operated at 500kV, with typical image magnifications of 600,000x. This HREM is equipped with a $\pm 30^\circ$ double-tilt goniometer making it straightforward to locate the {110} zone axis; it also has an image pickup/viewing/recording system which makes it possible to document the dynamic events which often occurred during high magnification operation [5].

RESULTS AND DISCUSSION

The defect microstructure of CdTe has been comparatively well-documented by earlier high-resolution studies [2,3]. The predominant defects appear to be intrinsic stacking faults (single, double, multiple), although extrinsic stacking faults, complicated fault intersections and dissociated dislocations (relating to the intrinsic stacking faults) are also observed. In many cases, the partial dislocations associated with the faults can be determined directly by reference to the experimental high-resolution images: intrinsic faults are generally terminated by Shockley partials, $\frac{1}{2}\langle 211 \rangle$, and the extrinsic faults by

Frank partials, $\frac{1}{2}\langle 111 \rangle$. Complete vacancy loops are rare (only one has been seen in CdTe) but several examples of perfect interstitial, or Frank, loops have been recorded and one of these is shown in Fig.1. At both the optimum defocus (Fig.1a), and the approximate "reverse contrast" defocus position (Fig.1b), it is obvious that the dislocations at either end of the fault are not equivalent. This non-equivalence is, in fact, as expected because of the crystal polarity [6]. Image simulations are in progress to verify the expected atomic configurations around these fault terminations.

The defect morphologies of both ZnTe and ZnSe are remarkably similar, although somewhat different from CdTe, and this may be due, in part, to the different susceptibilities of the two Zn-based materials to ion-beam damage in the sample preparation process [6]. Relative to CdTe, there is generally a higher density of stacking faults, but many of these defy easy classification since they do not appear to be "simple" extrinsic or intrinsic stacking faults. Fig.2 shows a typical low magnification image of ZnSe. Some faults are obviously inclined, but note the terminating (interstitial) planes (arrowed) and the interstitial loop at A. Fig.3 shows another of these interstitial loops in ZnSe at higher magnification. Interstitial loops were also observed in ZnTe and, as shown in Fig.4, these were comparable in size and appearance to those seen in CdTe.

Finally, it should be noted, as we have described elsewhere [3,5], that many of these defects are observed to alter because of local annealing by the electron beam. For example, in CdTe, slip of Shockley partials occurs at intrinsic stacking faults, and diffusional climb is associated with extrinsic stacking faults. Movement of terminating partials has also been seen in ZnTe [3]. Video-tape recordings of these events at the lattice resolution level, allow the lattice dynamics of these defects to be studied directly.

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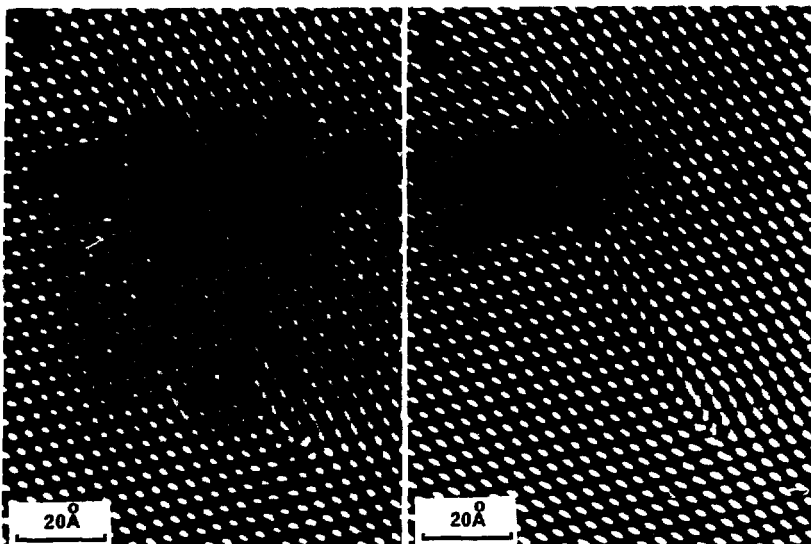


Fig.1 Small interstitial dislocation loop in CdTe (a) optimum defocus (black atomic columns) ; (b) reverse contrast (white atomic columns).



Fig.2. Typical region of ZnSe. Note the terminating planes (arrowed) and the interstitial loop at A. (110) projection.



Fig.3. Interstitial dislocation loop in ZnSe.

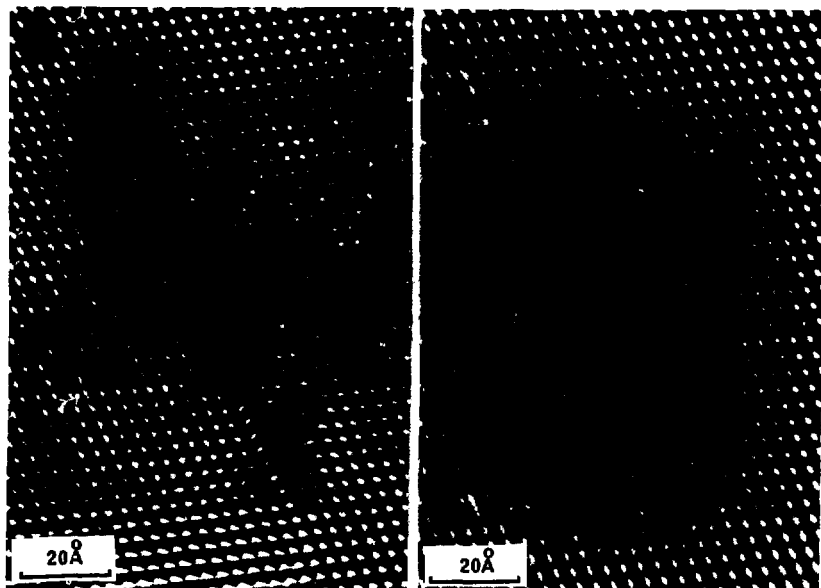


Fig.4. Comparison of interstitial dislocation loops in (a) ZnTe and (b) CdTe.

SUBSTITUTIONAL DISORDER IN MgSb_2O_6 OBSERVED BY 1 MV HRTEM*

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ABSTRACT

Structure images of trirutile-type MgSb_2O_6 crystal taken by 1 MV high-resolution transmission electron microscopy (HRTEM) reveal that nearest neighbouring Mg and Sb are mutually substituted and the structure becomes slightly disordered. The site of the substitution seems to be at random except small preference along $[110]$. The probability of substitution is estimated to be less than 10 % from the comparison between the real and calculated images for relatively thick crystals of about 100 Å. 4 cation-site clusters are necessarily formed by the substitution and excite weak diffuse scattering along $\langle 110 \rangle$.

INTRODUCTION

Many crystals with a trirutile-type structure have so far been reported [1]. A magnesium antimonate, MgSb_2O_6 , belongs to such a group. Fig.1 shows the crystal structure of MgSb_2O_6 [2]. It is composed of three subcells of rutile-type structure. The position of oxygens is the same as that in a rutile-type structure. Mg and Sb are arranged in a long-range order, i.e. magnesiums tend to be apart as far as possible from each other. In the present study, we have found point defects in a MgSb_2O_6 crystal, which has been prepared by a flux method, by means of 1 MV high-resolution transmission electron microscopy.

EXPERIMENTAL

The preparation of crystal is as follows: 0.4 g of powdered MgSb_2O_6 [3] and 4 g of $\text{Na}_2\text{B}_4\text{O}_7$ were mixed and heated in a Pt-crucible at 1100°C for 4 hr, followed by cooling through 750°C at a rate of 4°C/hr. Transparent crystals smaller than 0.3 mm have grown in the flux. Their powder x-ray diffractogram is identified as MgSb_2O_6 , which has a tetragonal symmetry with lattice parameters $a=4.65$ and $c=9.23$ Å.

The crystals were crushed in an agate mortar. The fragments obtained were examined by a high-voltage electron microscope (H-1250 type) operated at 1 MV [4].

EXPERIMENTAL RESULTS AND INTERPRETATION

Electron diffraction

Series of electron diffraction patterns were taken from several fragments, tilting them inside the microscope. okl reflexions are excited for $k+l=2n$, in accordance with the space group of $P4_2/mnm$ [2]. It is found in some of diffraction patterns that weak diffuse scattering occurs along $\langle 110 \rangle$.

Structure images

* A related paper is published in Trans.JIM (1983).

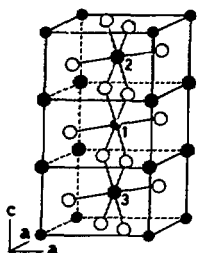


Fig. 1. Unit-cell of a trirutile-type MgSb_2O_6 crystal. Open circles represent oxygens, dark small ones magnesiums and dark large ones antimonies. Tetragonal, $a = 4.65$ & $c = 9.23$ Å. Nearest neighbouring cations are at the sites 1 & 2 or 1 & 3.

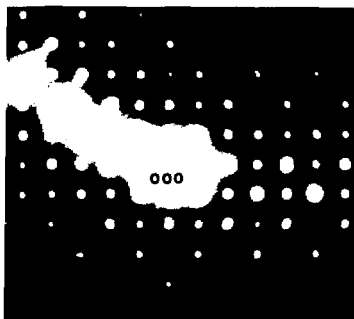


Fig. 2. Electron diffraction pattern of MgSb_2O_6 . Electrons are incident nearly parallel to the $[001]$ direction. Diffuse scattering occurs along $\langle 110 \rangle$.

Fig.3 is a 1 MV HRTEM image taken at about 700 Å underfocus, which is in the range of the optimum defocus for getting crystal structure images [4]. The electrons are incident along the $[001]$ direction. As is known from Fig.1 both Mg and Sb are included in each cation row along this direction. The projection of cation rows -Mg-Sb-Sb-Mg- is inserted in Fig.3 with the same magnification as that of the photograph. It is noted that each projected site is imaged as dark dot.

Fig.4(a) is an image from a different crystal, in which electrons are incident along $[110]$. In this case the crystal is rather stable against electron irradiation. Dark lines elongate parallel to the c axis. A thin area at the edge of the fragment is enlarged in (b), in which the arrangement of dark and bright sites is irregular; the contrast is darker at the parts marked by upward arrows, while brighter at downward ones. In the inner, thicker area, on the other hand, the contrast makes a regular pattern, as noticed in an enlarged photograph in (c).

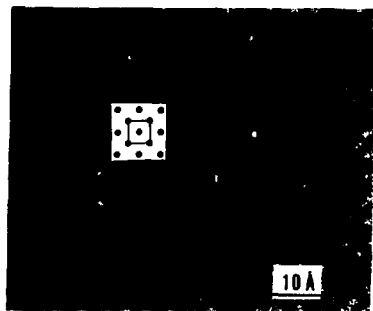


Fig. 3. 1 MV HRTEM image of MgSb_2O_6 with the 001 zone axis parallel to incident electrons. The figure inserted shows a projection of cation rows. $a = 4.65$ Å.

In order to interpret this contrast anomaly we have performed a computer simulation; in this projection Mg and Sb are arrayed in different rows, unless there are lattice imperfections, and the projected sites of Mg show a slightly dark contrast while those of two adjoining Sb elongated dark one (Fig.5(a)). In the calculation dynamical interaction among 140 waves are taken into account according to the multi-slice method. The spherical aberration coefficient of the objective lens is taken as 10 mm, the mean fluctuation of defocus due to chromatic aberration 200 Å and the beam convergence 8×10^{-4} rad [4]. The

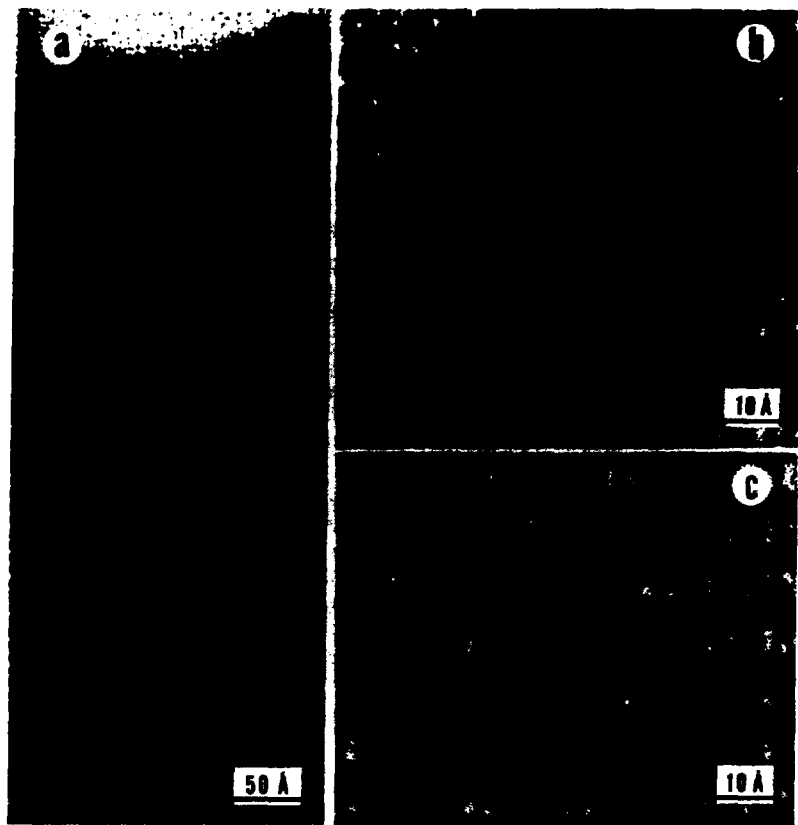


Fig. 4. (a) 1 MV HRTEM image of wedge-form MgSb_2O_6 with the 110 zone axis parallel to incident electrons. Thin and thick areas are enlarged in (b) and (c), respectively. $c = 9.23 \text{ \AA}$.

thickness of crystal is assumed to be $19.7 \text{ \AA}$.

A possible origin of the contrast anomaly is that Mg and Sb are locally substituted between the nearest neighbouring cation sites like 1 and 2 or 1 and 3 in Fig.1. It should be noted that even after this substitution two Mg never adjoin at the nearest cation sites. First we assume for a thin fragment that the substitution occurs only between the sites 1 and 2. The change in contrast due to the substitution is calculated and some of the results are shown in Fig.5(b) and (c). In (b) and (c) 1 and 2 among 3 cation-pairs are assumed to be substituted in the whole thickness of $19.7 \text{ \AA}$ (6 slices), respectively. It is clear in (c) that the site 1, which has been occupied by Mg in the ideal

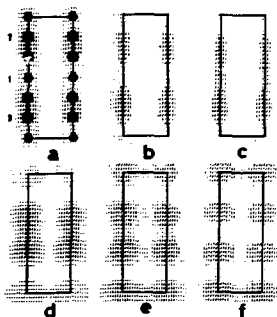


Fig. 5. Calculated images of MgSb_2O_6 with the 110 zone axis parallel to incident electrons. Frameworks correspond to those in Fig. 4(b) & (c). Dark circles and figures in (a) have the same meaning as in Fig. 1. The thickness of crystal is 19.7 and 88.8 Å for (a) to (c), and (d) to (f), respectively.

the real one. In (f) it is composed of the contrast of three rutile-type subcells, which are mutually identical. Similar images as (d) are obtained in the thickness range between 70 and 120 Å unless α exceeds 0.1. Based on these results we may conclude that the substitution occurs with the probability less than 0.1. In this calculation the probability is introduced through the change in the scattering amplitude for phase grating.

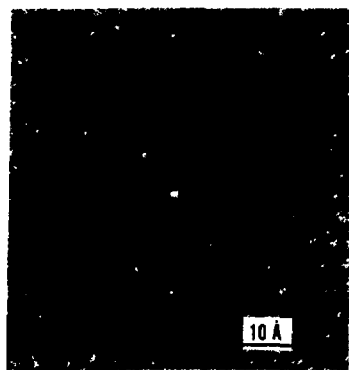


Fig. 6. 1 MV HRTEM image of a thin MgSb_2O_6 crystal with the 100 zone axis parallel to incident electrons. $a = 4.65$ & $c = 9.23$ Å.

structure, is slightly darkened, while the site 2, which has been by Sb, brightened. Although the calculation is performed on a simplified model, we may say that the contrast anomaly in the thin area must be related to the substitution of cations, i.e. locally concentrated occurrence of the substitution causes the irregular change in contrast.

In reality the substitution must be possible at any cation site. In the calculation for thicker area like in Fig. 4(c) we may assume that the site of the substitution is statistically at random, since the image contrast is apparently regular. The calculation has been performed on this assumption with changing the values of the substitution probability α and the crystal thickness. For examples, Fig. 5(d) to (f) are obtained for $\alpha = 0.05, 0.15$ and 0.33 , respectively, with the crystal thickness of 88.8 Å. The image (d) well fits the real image in Fig. 4(c). In the higher range of probability (e) and (f) the calculated image contrast no longer coincides with

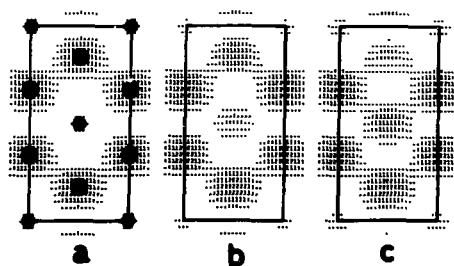


Fig. 7. Calculated images of Fig. 6. Dark circles and figures have the same meaning as in Fig. 1. The crystal thickness is taken as 27.9 Å.

Fig.6 is the structure image taken from a thin crystal area by the incident electrons parallel to [100]. Calculated images corresponding to this orientation are shown in Fig.7. No substitution is assumed to occur in (a). The substitution between the sites 1 & 2 in Fig.1 occurs in 2 and 4 among 6 slices (27.9 Å) in (b) and (c), respectively. Although the crystal with this orientation is rather sensitive to electron irradiation and, therefore, the image is not so clear as in Fig.4, we may say that the real image fits the calculated ones in (a) and (b).

DISCUSSION

Image contrast of the substitutional disorder in thin areas

The image in Fig.6 seems more regular than that in Fig.4(b). This suggests that the substitution does not occur completely at random. In other words, it must occur along any [110] direction with small preference. The situation is schematically shown in Fig.8; we consider the arrangement of cations in the (110) plane. Dark circles mean Sb while open ones Mg. The cation-pairs, which have been substituted, are marked by dotted lines. When these arrangements are observed along the direction parallel to the sheet plane, the site indicated by the arrow 1 must be darker, since it has a higher projected potential as a result of the substitution. The site 2 is also darker, while the site 3 brighter.

Clusters giving the $\langle 110 \rangle$ diffuse scattering

The substitution between the nearest neighbouring Mg and Sb causes each (001) plane to include two species of cations. This necessarily results in the formation of clusters, as schematically shown in Fig.9; each cluster occupies 4 cation sites. The clusters excite the diffuse scattering [5,6],

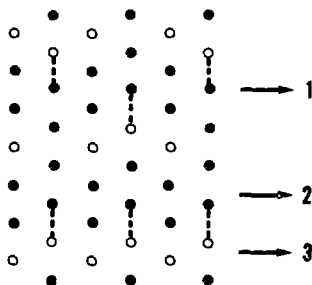


Fig. 8. Atomic arrangement in the plane parallel to (110) to MgSb_2O_6 , which qualitatively accounts for the contrast irregularity in Fig. 4(b). The contrast in the direction marked by arrows becomes darker at the site 1 and 2, while brighter at 3.

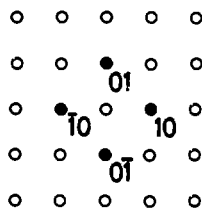


Fig. 9. Model of 4 cation-site cluster, which can explain the origin of diffuse scattering along $\langle 110 \rangle$. All cation sites in the (001) plane of MgSb_2O_6 are shown.

whose intensity locus is defined by

$$f(g) = \sin \pi(h+k) \sin \pi(h-k) = 0 \quad (1)$$

$$\text{Then } h+k = m \quad (2)$$

, where m is integer. The equation (2) explains the origin of the diffuse scattering along $\langle 110 \rangle$ found in Fig.2.

The cluster relation [5] is

$$\sigma_{10} + \sigma_{\bar{1}0} - (\sigma_{01} + \sigma_{0\bar{1}}) = 0 \quad (3)$$

, where σ_j is the Flinn operator. For the (001) plane, which has been composed of Mg in the ideal structure and includes a small amount of Sb after the substitution, σ_j has a value of $-\alpha$ for the site occupied by Mg, while $1-\alpha$ for the site Sb.

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STRUCTURE IMAGE OF THICK MgO CRYSTAL
TAKEN AT 80KV-1MeV

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ABSTRACT

Using 100kV, 200kV, 400kV and 1MeV electron microscopes, the maximum observable thickness of MgO crystal in 110 orientation which gives the atomic structure image has been studied. Observations suggest that the maximum observable thickness is proportional to (v/c) , where v and c are the velocities of electrons and light. Radiation displacement damage, which prevents the penetration of electrons, becomes predominant with increasing the voltage. Optimum voltage must be selected to take the image of beam sensitive thick specimen.

INTRODUCTION

Since the observation of thick specimen by an electron microscope is very important in the materials science, improvement of transmissive power of electron waves with increasing the accelerating voltage has been studied theoretically and experimentally using 300kV, 500kV, 1MeV and 3MeV electron microscopes [1] [2] [3] [4] [5]. At high voltages, it is well understood that the relativistic effect of electron mass to the elastic and inelastic scatterings becomes predominant. It is known that in the two beam situation the transmissive power of electron waves and the visibility of the images of inner structure of the crystal such as dislocations are proportional to $(v/c)^2$ and (v/c) respectively where v and c are the velocities of electrons and light [1]. However in many beam situation such as at the higher voltages than 500kV observed transmissive power of electron waves is different to each different observer and only rough tendency could be explained by the many beam dynamical theory of electron diffraction considering absorption [6]. The different observed values may be attributed to the effect of complex processes of elastic and inelastic multiple scattering, which are sensitive to the Bragg reflecting conditions of the specimens, aperture size and resolving power of the electron microscopes used in the observations. Although the observation of atomic structure of thick specimens is important, high voltage electron microscopes which have been constructed for these several years are confined to take the images of rather thin specimens [7]. Though the atomic structure images of thin specimens taken at high voltages can be interpreted by assuming the specimens as weak phase object, i.e. the images reflect the crystal potential, it is advisable to study the atomic

structure of thick specimen by using high resolution high voltage electron microscopes. The present paper concerns to study the maximum thickness which gives the atomic structure image by high voltage electron microscopes. Though the improvements of penetration of electron waves and image contrast are expected with increasing electron energy, the effect of radiation displacement damage in the specimen cannot be disregarded. Therefore, the determination of the optimum voltage which compromise the penetration and the radiation displacement damage is also necessary.

EXPERIMENTALS

Using high resolution electron microscopes, JEM 100kV, 200kV and 400kV high resolution electron microscopes in the Department of Applied Physics of Osaka University and JEM 1000kV high resolution electron microscope in Tohoku University, crystal lattice images of MgO crystal with wedge shape in 110 orientation were photographed. The specimen MgO crystal which was cleaved by a sharp knife edge so as to be surrounded by (100) (100) (010) and (011) was mounted on a grid by silver paste as shown in Fig.1. Electron beam illuminates the specimen from the direction parallel to [110]. The images were photographed in two specimen orientations, 110 symmetry and 200 Bragg reflecting conditions. The diffraction patterns from 200 Bragg condition is shown in Fig.2. The image of the specimen in 200 Bragg condition formed by using central undiffracted waves is shown in Fig.3, in which 200 bend contour can be seen. Thickness of the specimen is equivalent with the distance measured from the edge. Figures 4 show the images of MgO crystal which are photographed by 200kV electrons parallel to [110] and corresponding calculated contrast. Crystal lattice fringes can be seen clearly at the thickness of 2700Å. Figures 5 show the images of a MgO crystal photographed by illuminating 1MeV electrons. The low magnification image is shown in (a), which shows the formation of displacement damage. Long exposure to the beam forms much damage. (b) is the large magnification of the area shown in (a) by small square and (c) is its Fourier transform, which shows the existence of 111 lattice fringe in (b). Figure 6 shows the plot of measured energy dependence of the maximum thickness, observable of the lattice fringes. Figure 7 shows the calculated structure image at 400kV using the many beam dynamical theory considering absorption.

Above observations suggest that optimum voltage for studying MgO with less damage and high resolution is at 300kV~400kV which enable us to observe the atomic images of MgO of 3000Å thickness.

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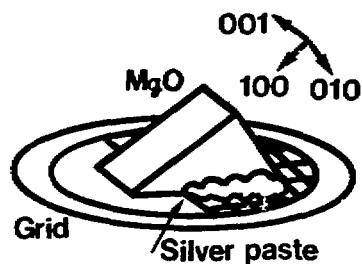


Fig.1 MgO specimen

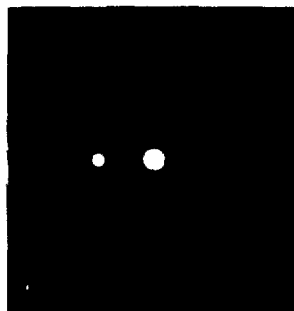


Fig.2 E.D. pattern in 200 Bragg condition

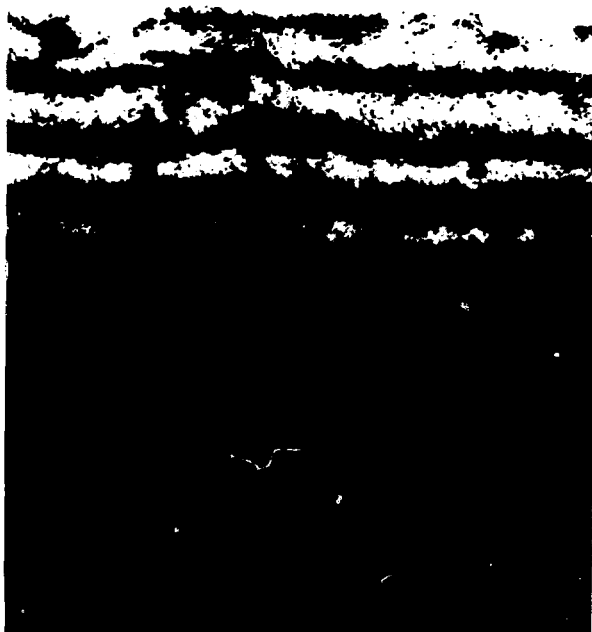


Fig.3 200 extinction contour parallel to the edge of MgO crystal is seen.

$$\theta_{200}(200\text{kV}) = 584.5^\circ$$

Disk spots are due to radiation displacement damage.

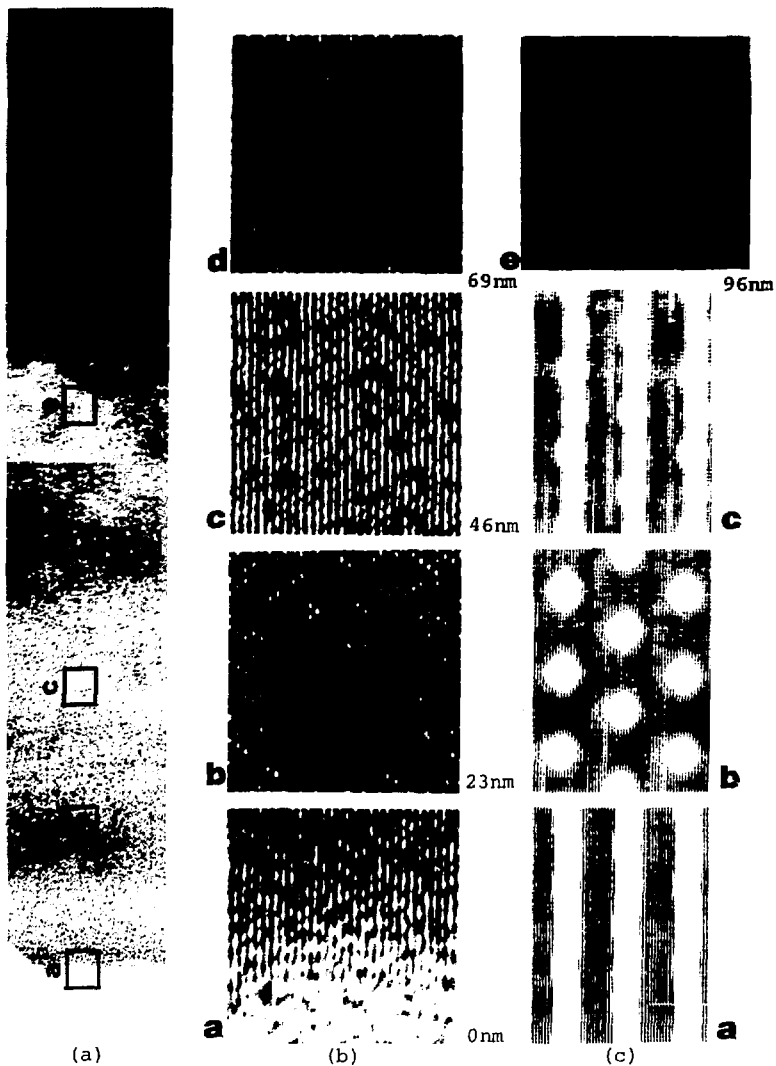


Fig.4 (a) Image of MgO crystal in 110 symmetry position taken at 200kV. (b) Magnifications of the areas shown in (a) by square. (c) Calculated contrast by MB theory.

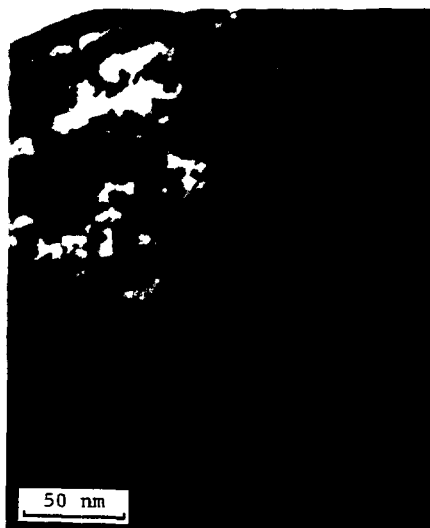


Fig.5 (a) Wedge shape MgO taken at 1MeV. Dark areas are due to displacement damage.



Fig.5(b) Large magnification of square in (a) (top). Fourier transform of the top image (bottom).

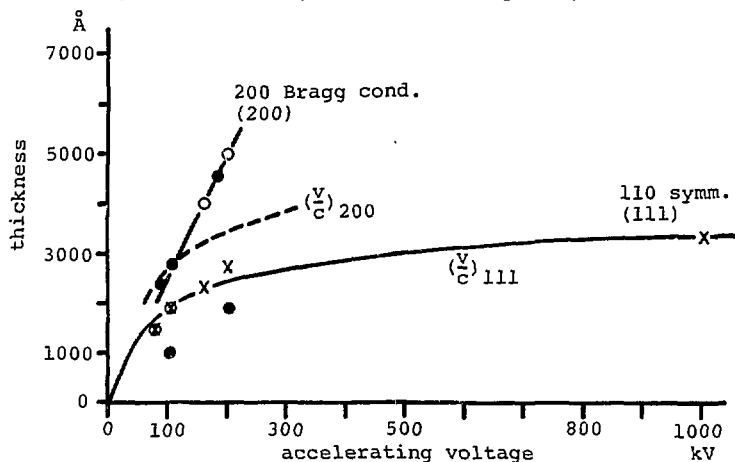


Fig.6. Measured maximum thickness observable of the lattice fringe. Curve represents (v/c) , v : velocity of electrons.

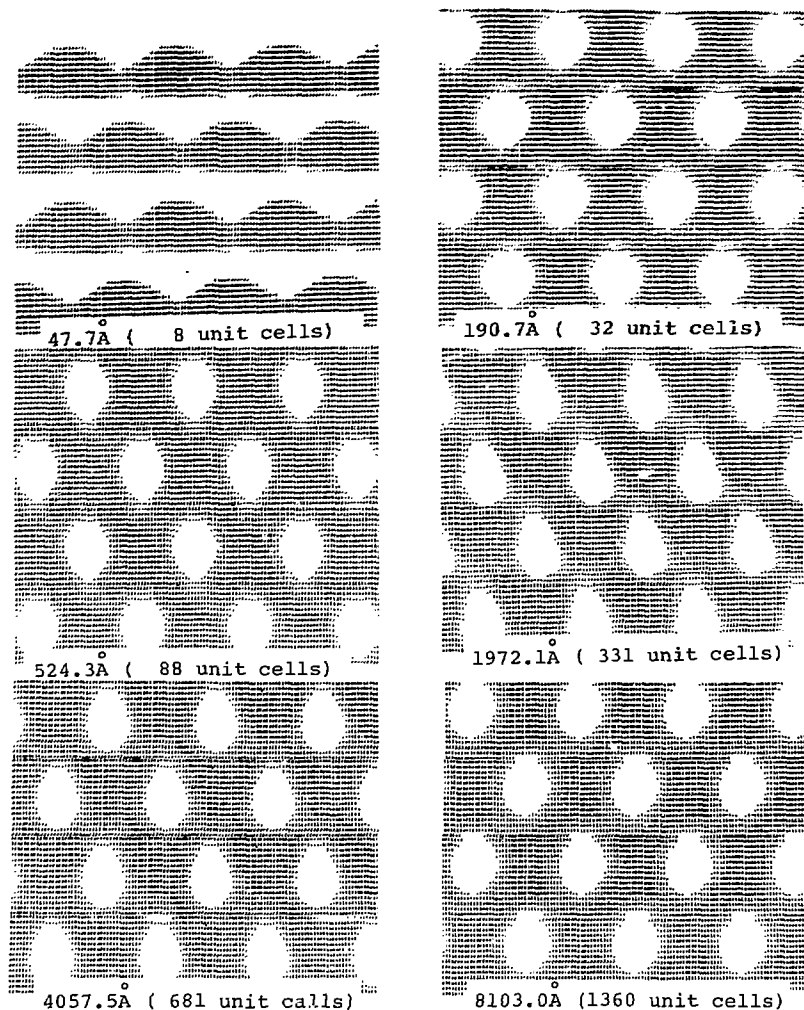


Fig.7 Calculated structure images at bottom face of MgO crystal in 110 orientation at 400kV. 129 waves excited, 000,111, 111,200 waves contributed. $\xi_0/\xi'_1=0.0323$, $\xi_{111}/\xi'_{111}=0.0011$, $\xi_{200}/\xi'_{200}=0.0269$, $\xi_{220}/\xi'_{220}=0.0261$. Thickness are indicated in the figures.

SURFACE STUDIES BY HIGH-RESOLUTION IMAGING

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ABSTRACT

Surface imaging of Ag(111) and (001) was done by an UHV-1MV high resolution electron microscope (HU-1250). Clean and well-defined surfaces of Ag crystallites were prepared by deposition on graphite films in-situ in the electron microscope at 4×10^{-6} Pa. Images of the (111) and (001) surfaces were obtained by the forbidden reflections of the indices $\{10.0\}_{\text{hex}}$ and $\{110\}$, respectively. The surface images of the (001) film were seen by filtering out the $\{200\}$ Bragg reflections of the bulk crystal.

INTRODUCTION

High resolution electron microscopy(HREM) has been applied mostly to the studies of crystal structures and defect structures. One of new applications of HREM is imagings of clean surfaces and atoms condensed on the surfaces.

Imaging of surfaces of Au(001) [1] and Au(111) films [2,3] was claimed previously. However, the observations could not reveal images of "clean and well-defined" surfaces. They were done for post-mortem specimens with contaminations on the surfaces with use of microscopes of dirty vacua. We have studied phenomena on clean and well-defined surfaces at monatom-high level by developing ultra-high-vacuum(UHV) electron microscopy and in-situ techniques [4]: Monatom-high terraces of Ag(111) surface [5], monolayer adsorption process of Pb on Ag(111) [6] and reconstructed surface structures of Au(111) [7] were revealed.

As an extension of these works, we developed an in-situ deposition system and a cryogenic pumping system for the UHV-1MV electron microscope [8,9] and made HREM imaging of surface atoms. One of the present author(K.T) had shown a possibility of the imaging of monolayer atoms by computer simulation [10]: Contrasts of 3~10% for the structure images of Pb adatoms on Ag(111), Ag(111)-($\sqrt{3} \times \sqrt{3}$)R30°-Pb, were suggested.

The present paper describes experimental results of HREM of clean and well-defined surfaces of Ag(111) and Ag(001).

IN-SITU PREPARATION OF CLEAN AND WELL-DEFINED SURFACES

Ag(111) and (001) films were prepared in-situ by deposition on a graphite film at 4×10^{-6} Pa [9]. The graphite film was air-cleaved and heated up to 800° C in the 1MV electron microscope before the Ag deposition. The (111) and (001) surfaces of Ag platelets were parallel to the (001) graphite surface. There was no definite epitaxy of their azimuthal orientations, however. The size of the Ag crystallites were 50~500nm after the deposition of 50nm in mean thickness which was monitored by a quartz oscillator. The platelets were estimated to have 5nm thick from extinction contours. The bottom surfaces of Ag platelets in

contact with the graphite surface are atomically flat, while the top surfaces have surface terraces bordered by monatom-high steps.

SURFACE IMAGES

Ag(111) SURFACE

Figure 1a) shows a dark-field micrograph of a Ag(111) platelet taken by a forbidden $\{10.0\}_{\text{hex}}$ * reflection [5]. Areas of different contrasts are surface terraces of monatom-height (0.23nm). Figure 1b) schematically depicts a diffraction pattern from a Ag(111) platelet and a graphite film. The forbidden reflections of the indices $\{10.0\}_{\text{hex}}$ from the Ag(111) (triangles) are connected by dashed lines. The $\{10.0\}$ reflections from the graphite (solid circles) are connected by chain lines. The $\{10.0\}_{\text{hex}}$ reflections appear at slightly smaller diffraction angle side than the $\{10.0\}$ reflections; $\{10.0\}_{\text{hex}} = (0.25\text{nm})^{-1}$ and $\{10.0\} = (0.22\text{nm})^{-1}$.

Figure 2a) shows a HREM image of an Ag(111) on a thin graphite film. The incident beam is normal to the (111) surface. Only the six $\{10.0\}_{\text{hex}}$ reflections were included in the objective aperture. Hexagonally arranged bright dots are seen in an area marked A, while they are obscure in an area marked B. The periods of the bright dots are around 0.28nm in each of the three $\langle 110 \rangle$ directions (the spacings of the fringes along three $\langle 110 \rangle$ are around 0.25nm). The values are close to the nearest neighbour distance of atoms in the (111) surface layer. The slight difference is due to the deviation of the incident beam from the [111] normal of the Ag platelet. An optical diffractogram of the image of the region A, shown in Fig. 2b), gave diffraction spots corresponding to the $\{10.0\}_{\text{hex}}$ lattice planes of the surface layer. The region B gave no diffraction spots. A (111) film of ABC stacking gives a certain intensity to the forbidden reflection points if the film thickness is $3N \pm 1$ layers (N is an integral number), while no intensity if it is 3N layers. Therefore, the region A and B are supposed to have thicknesses of $3N \pm 1$ (or $3N - 1$) and 3N layers, respectively. The bright dots in Fig. 2a) (formed by an interference of the three fringe lines) correspond to an image of one surface layer.

Ag(001) SURFACE

Figures 3a) and b) show a high resolution image of an Ag(001) platelet on a graphite and its optical diffractogram. The image was taken at an overfocus condition without an objective aperture. In Fig. 3a), lattice fringes spaced 0.28 nm are seen along the $[110]$ and $[\bar{1}\bar{1}0]$ directions as indicated by arrows. The fringe spacing corresponds to the nearest neighbour distance of atoms in the (001) surface layer (see, Fig. 4). The optical diffractogram in Fig. 3b) shows four spots corresponding to the $\{110\}$ forbidden reflections. In addition to the $\{110\}$ spots, the (200) and (200) Bragg reflections from the bulk Ag(001) layers appear. An amplitude distribution in the back focal plane of an object is given by

$$Q(u,v) = \delta(u,v) + \sigma \Phi(u,v) (\sin \chi - i \cos \chi), \quad (1)$$

where a phase factor χ arises due to an objective lens aberration and a defocus and $\Phi(u,v)$ is a Fourier transform of the projected potential of the (111)

*The value of ℓ was in a range 0.5-2, but the precise value was not determined.

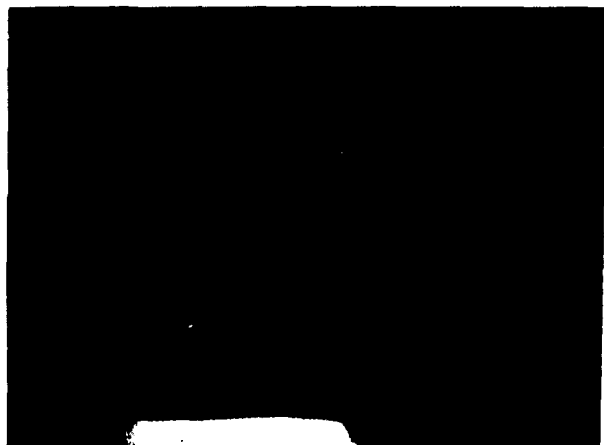


Fig. 1a) A dark-field image of an Ag(111) platelet grown on a graphite thin film. The regions of different contrasts are surface terraces whose steps are monatom-height.

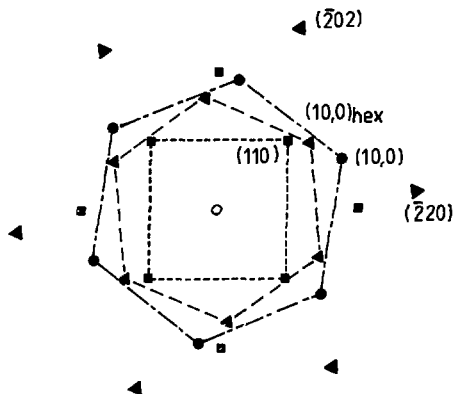


Fig. 1b) A scheme of diffraction pattern from an Ag(111) platelet on a graphite film. Diffraction spots from an Ag(001) platelet are also shown. Solid circles are the spots from graphite. Triangles and rectangles are the spots from the (111) and (001) platelets, respectively.

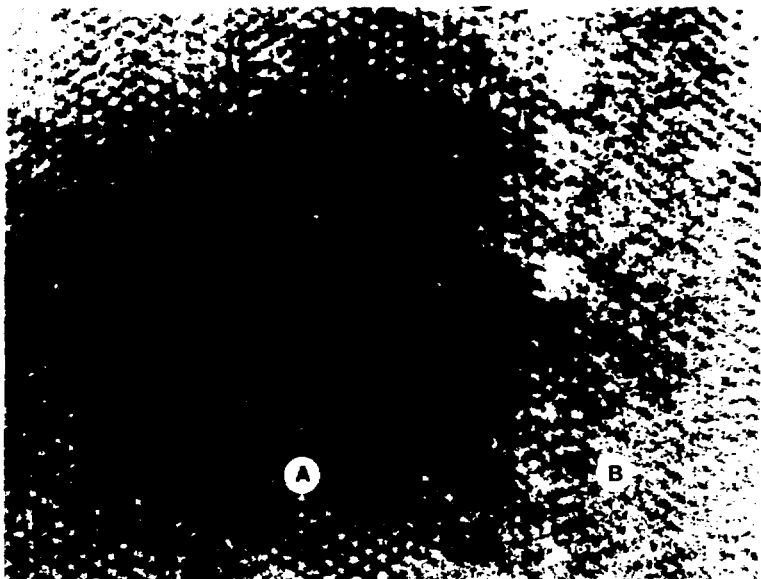


Fig. 2a) A HREM image of an Ag(111) platelet on a thin graphite film.

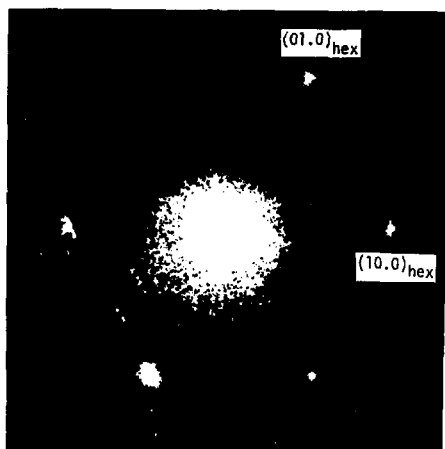


Fig. 2b) An optical diffractogram obtained from the region A in Fig. 2a).



Fig. 3a) A HREM image of an Ag(001) platelet on a thin graphite film. See the image from a grazed direction.

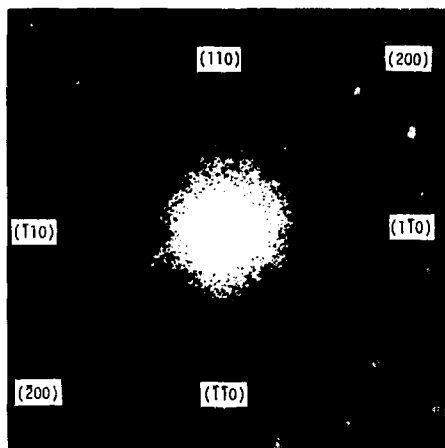


Fig. 3b) An optical diffractogram from Fig. 3a).

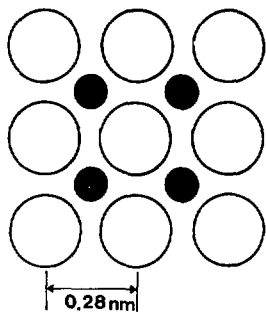


Fig. 4 An atom arrangement of the (001) surface (top view). Open and solid circles represent atoms in the top and the next lattice planes from the surface.

planes. The phase factor of the over focused image ($\Delta f=25\text{nm}$) almost satisfies the condition, $\sin\chi=1$ for the forbidden reflections ($(u,v)=(1,1)$) and $\sin\chi=0$ for the (200) Bragg reflections ($(u,v)=(2,0)$) (see Fig. 5), so that the main contribution to the image intensity comes from $\phi(1,1)$ of eq.(1) in the case of the weak phase object. The (200) Bragg reflections are, thus, filtered out and the image of Fig. 3 reveals surface lattice image by the $\{110\}$ forbidden reflections. The image of the same Ag platelet as in Fig. 3a) showed the (200) lattice fringes at under focus condition (see Fig. 5).

CONCLUSION

Imaging of the surface layers were done by HREM by preparing clean and well defined surfaces in-situ in the UHV microscope. The forbidden reflections from the surface layers were used for the imaging. The filtering of the Bragg reflections was made to get the surface image. The UHV-1MV HREM is useful for surface studies when it combined with the dark-field microscopy by the UHV-100kV microscope.

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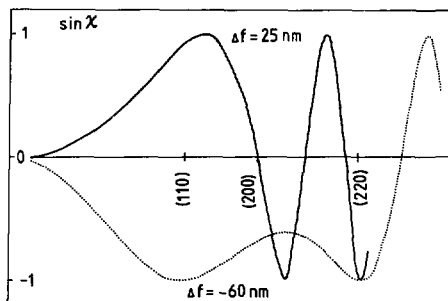


Fig. 5 A phase factor $\chi(u,v)$ at an overfocus condition ($\Delta f=0.25\text{nm}$). The position of the $\{110\}$ forbidden and the $\{200\}$ Bragg reflections are indicated. A dotted curve shows the phase factor for an under focus condition ($\Delta f=-60\text{nm}$).

SURFACE STRUCTURE IMAGING OF SMALL GOLD PARTICLES

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ABSTRACT

The surface structure of small metal particles, including details of surface steps and faceting, has been imaged directly at the atomic level using a 600kV high resolution electron microscope. Computer simulations confirmed the interpretation of images in terms of atomic columns and also showed that the detailed atomic structure and surface relaxations of reconstructed metal surfaces have been recorded.

INTRODUCTION

A variety of methods, such as Low Energy Electron Diffraction (LEED), Auger spectroscopy and Reflection High Energy Electron Diffraction (RHEED) are available for the characterisation of surfaces, but most are essentially bulk techniques and are thus unable to provide localised information at anything approaching atomic scale. However, under certain circumstances, images can be obtained in the electron microscope which do show surface details at this level. Surface steps in projection in MgO [1], gold [2,3] and silicon [4] have been observed in the transmission mode for example, and also in silicon using reflection techniques [5]. These various electron microscope results have recently been reviewed [6].

Details of the surface morphology of small metal particles can, in principle, provide a bridge between the various theoretical mechanisms for heterogeneous catalysis (where the performance is attributed to the presence of active sites such as surface steps) and the experimental characteristics of a particular system. In this paper we report details of our recent observations of small metal particles which have been tilted to bring their surfaces parallel to the incident beam direction. Axial bright field imaging has been used, which made image interpretation much more straightforward, and information on the atomic scale about surface morphology including reconstructed surfaces and relaxations could then be obtained directly [7]. Further details of the surface relaxations observed on "free" surfaces are given elsewhere [8].

METHODS

Samples were prepared by evaporation of silver or gold onto heated alkali halide substrates cleaved *in situ* under UHV conditions, followed by deposition of amorphous carbon. Observations were made with the Cambridge University 600kV high resolution electron microscope (HREM) [9], operating at either 500 or 575kV. With recent improvements, this HREM now has an interpretable resolution of better than 0.2nm [10] giving high signal-to-noise ratios for the primary lattice spacings of 0.235nm (111 beams) and 0.204nm (200 beams). Computer calculations, carried out using the multi-slice approach, were used to confirm the image interpretations. However, considerable care was needed to avoid any periodic continuation or sampling effects [11].

RESULTS.

In both experimental images and computer simulations we have concentrated on the (110) pole, although preliminary calculations indicate that comparable results are applicable to other projections. This has meant that, for looking along the surfaces of the square pyramids which occur under UHV conditions, specimen tilts of 45° from the horizontal were usually required (since epitaxy was [100]).

The typical edge appearance of the small particle is illustrated by the two icosahedra of silver partially shown in Fig.1. These images were recorded at 575kV at the optimum defocus position with axial illumination where the atomic columnar positions appear black (see later). The surface morphology is readily apparent, including the small region of twinned structure arrowed in Fig.1b. Fig.2 shows two particles of gold imaged at 500kV; (a) was recorded near optimum defocus ($\sim 60\text{nm}$) so that column positions are black whilst (b) was recorded at the reversed contrast position ($\sim 100\text{nm}$) giving white atomic columns. Whilst the well-developed faceting of the surface is clearly visible in both cases, it is particularly so in the former particle where the supporting carbon film has been locally etched away. As we will show below, it is also under such etching conditions that surface reconstruction and surface relaxations have been observed. In some circumstances, the presence of "rafts" or ledges on the particle surfaces can also be established. In Fig.3(a), recorded in reversed contrast ($\equiv$ white atom columns), a ledge is shown arrowed; in Fig.3(b), recorded at optimum focus ($\equiv$ black atom columns), the contrast of several areas suggests small rafts sitting on the surface.

In order to confirm our image interpretation in terms of atomic columns, and also to investigate the possibilities for detecting surface "contaminants" such as carbon or silver, extensive simulations have been carried out and these will be reported in detail elsewhere [11]. Initially, it proved difficult to obtain a good match with experiment at crystal edges because of the step discontinuity between the crystal of finite thickness and vacuum, and uncertainties over an appropriate form for the surface potential. These problems were eventually resolved and Fig.4 shows through-focal series of simulations for particles of thicknesses 2.1 and 4.3nm at an accelerating voltage of 500kV. Note the close similarity in appearance between the simulated images at -67.5nm and -97.5nm and those shown in Figs.1 and 2.

The planar 110 gold surfaces were normally of the (1x1) type meaning that there was no suggestion of any re-ordering, and this is as expected for particle coated with carbon. However, under the etching conditions referred to above, this carbon coating was removed and the development of superlattices, albeit irregular, was observed. Figure 5 illustrates this behaviour: Fig.5(a) shows the normal (1x1) type surface structure, Fig.5(b) shows a region where the surface has partially reconstructed to a (2x1) surface (i.e. having a double periodicity along a 100 direction). Fig.5(c) shows a strip of the 111 surface and an apparent (100) structure recurs periodically. Analysis indicates that this is possibly a (22x1) surface (see, for example, [3]). Moreover, the appearance of Fig.5(b), which has been matched by image simulations [7], agrees with the so-called "missing-row" model for this reconstructed surface [12] and further confirmatory experimental evidence for this particular model has also been obtained by scanning tunneling microscopy [13] and X-ray diffraction [14]. However, the present images represent the

first time that reconstructed surfaces have been imaged directly on the atomic scale. (Note that a complete image match requires either carbon atoms or a partial gold occupancy of about 10% along the channels - partial occupancy would correspond to inhomogeneities or disorder parallel with the electron beam [11]).

Another surface phenomena observed in these gold particles in the absence of carbon has been surface relaxation. Without the constraining influence of the carbon layer, the outermost row of atomic columns on the 110 surface is invariably observed to be displaced slightly away from the bulk lattice. Careful measurement, confirmed by image simulation, demonstrates that, in the case of the (2x1) reconstructed surface, the outermost gold atoms are relaxed outwards by about 20% and those in the channels by about 40%. A through-focal series of a very small region of (2x1) surface is shown in Fig.6; in the inset image simulations a relaxation of 23.5% has been used [14]. Note that relaxations have also been measured for clean (1x1) surfaces with a typical figure of ~10%. For comparison, the relaxations for coated surfaces are certainly less than about 3%.

CONCLUSIONS

Our results, from what is an idealised model system, clearly demonstrate that surface morphology can be directly characterised at the atomic level by high resolution electron microscopy. Local information about surface reconstruction is available which compares favourably in surface sensitivity with the macroscopic results produced by essentially bulk diffraction techniques. Moreover, detailed information on surface relaxations is available. Fundamental insights into surface science as well as the structural aspects of heterogeneous catalysis should result from proper development of this technique.

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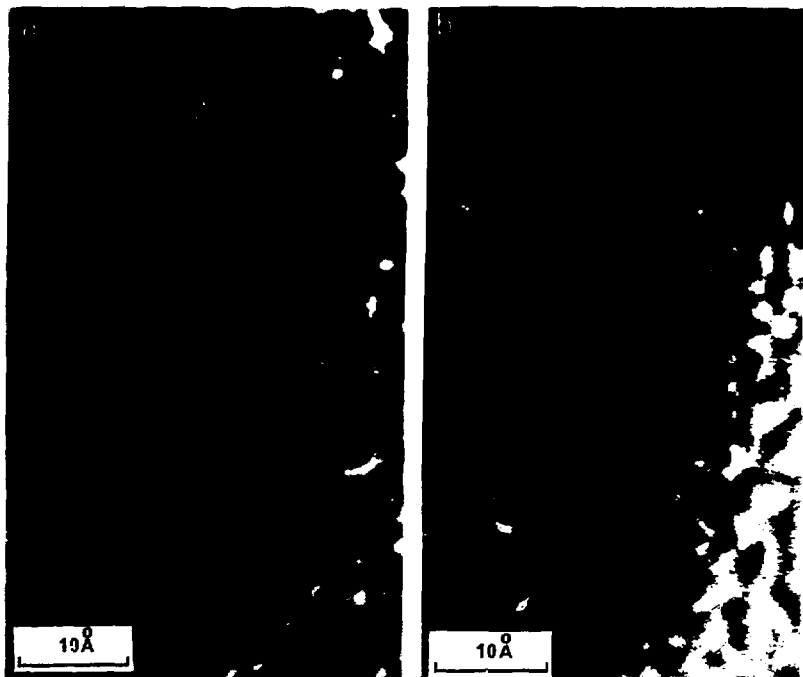


Fig.1. Parts of two icosahedral, multiply-twinned particles of silver recorded at optimum defocus (black atomic columns). Note surface morphology and micro-twin arrowed in (b). Recorded at 575kV.

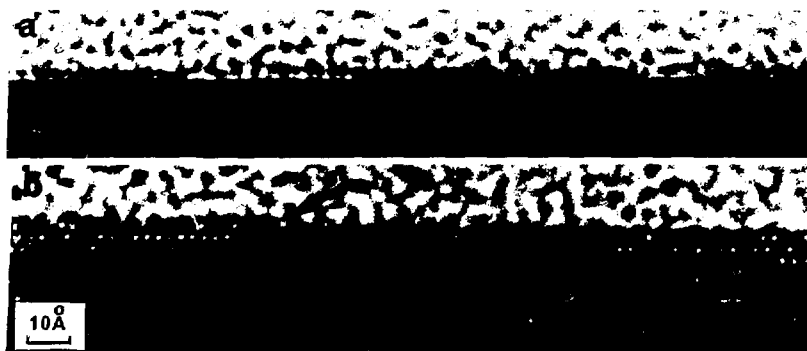


Fig.3. Large ($\sim 0.1\mu\text{m}$) gold particles showing evidence for surface "rafts" and "ledges" (a) optimum defocus; (b) "reverse" contrast.

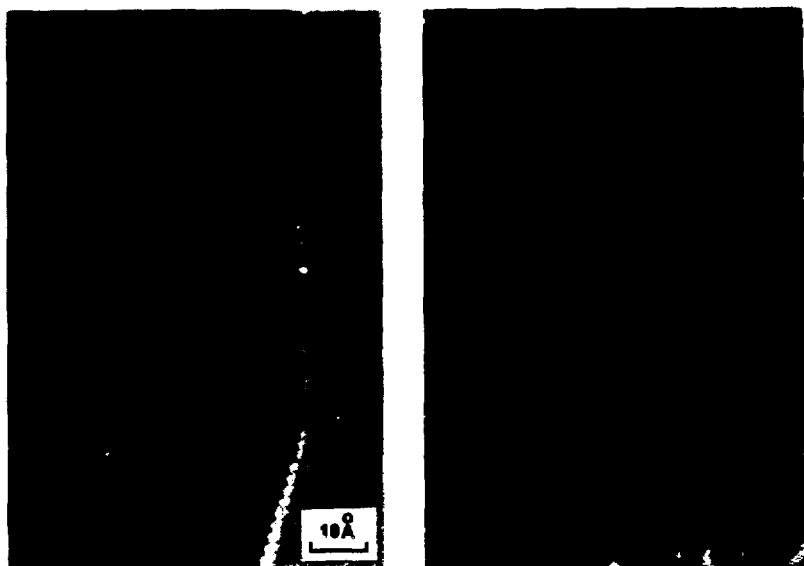


Fig.2. Small particles of gold showing well-developed surface facetting.
 (a) optimum defocus; (b) "reverse" contrast (white atomic columns).

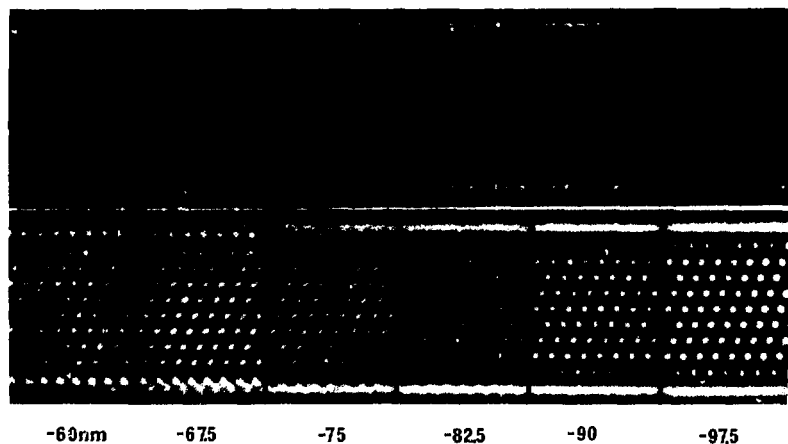


Fig.4. Through-focal series of image simulations for gold crystals
 of thicknesses 2.1 nm (top) and 4.3 nm (bottom) at 500 kV. Defoci shown.

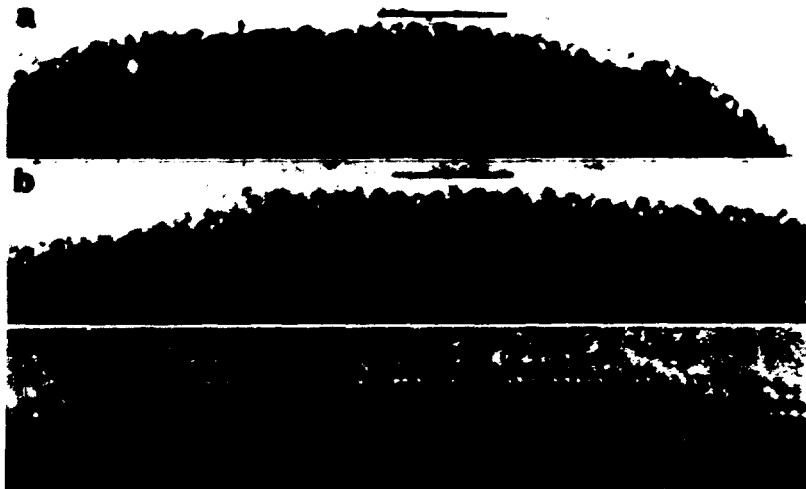


Fig.5. Images of gold 110 and 111 surfaces: (a) normal 110 (1x1)-type;
 (b) partial reconstruction to (2x1)-type in absence of carbon;
 (c) possible 111 (22x1)-type reconstruction.

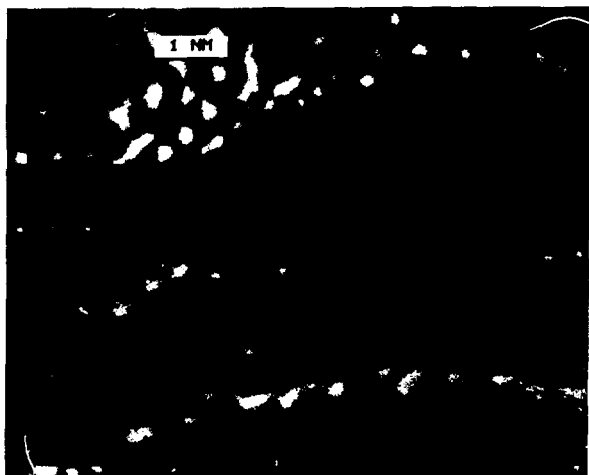


Fig.6. Direct evidence for surface relaxation. Through-focal experimental series of micrographs ($\sim 300\text{\AA}$ steps) with matching image simulations of partially-reconstructed surface. A relaxation of 23.5% of the outermost atoms was used in the simulation, whereas $\sim 20\%$ was estimated experimentally.

STRUCTURE OF WÜSTITE OBSERVED BY UHV-HR-1 MV ELECTRON MICROSCOPE

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ABSTRACT

The structure of P'' phase in wüstite $\text{Fe}_{0.90}\text{O}$ has been observed in the atomic level. Structure images show that clusters with size $2a_0 \times 2a_0$ (a_0 : lattice parameter of the fundamental cell) make a regular arrangement belonging to the two dimensional space group pg and giving a rectangular cell with dimensions $5a_0 \times 2.5a_0$. In the cluster tetrahedral iron atoms exist, but their arrangement is irregular. These results are compared with the structure model presented by Anderson and Sletnes.

INTRODUCTION

Wüstite Fe_{1-x}O ($x = 0.05 \sim 0.15$ at 1300°C) is a non-stoichiometric compound and stable above 570°C . Although its fundamental structure is of the NaCl type, some of iron atoms move to the tetrahedral interstices leaving octahedral vacancies in the quenched state. The tetrahedral iron atoms and associate vacancies aggregate to make a cluster, and such clusters make a periodic arrangement to produce superstructures [1]. There are three low temperature phases near $\text{Fe}_{0.88}\text{O}$ called P', P'' and P'''. Anderson and Sletnes [2] studied the crystal structure of P'' phase by electron diffraction and dark field electron microscopy, and proposed an orthorhombic structure model belonging to the space group $Abm2$. Iijima [3] observed the regular arrangement of clusters with high resolution electron microscopy.

In the present study, we made high resolution electron microscopic observations in the atomic level by using Ultra-High-Vacuum High-Resolution 1 MV Electron Microscope (UHV-HR-1 MV EM) recently installed at Tokyo Institute of Technology. This microscope has an ability to resolve individual atom rows in crystals. The results obtained are described in this paper.

EXPERIMENTAL

A pure iron plate was cold-rolled to a thickness of about 1 mm, oxidized at 1300°C for 12 h in a CO-CO_2 atmosphere with mol. ratio 1.50, and then quenched to room temperature by dropping on to a water-cooled iron base. The composition was determined to be $\text{Fe}_{0.90}\text{O}$ from the weight increase and by X-ray lattice parameter measurement, which gave $a_0 = 0.4287$ nm. The produced wüstite was crushed into fine powder in acetone to minimize oxidation, and thin flakes were scooped on a carbon-microgrid for observation.

RESULTS

Fig. 1 reproduce an electron diffraction pattern of $\text{Fe}_{0.90}\text{O}$ taken with the beam incident along the $[001]_f$ direction of the fundamental lattice. The superstructure spots and streaks connecting them are observed around not only

the incident spot but also the fundamental spots and the spots due to magnetite Fe_3O_4 . This is due to the effect of multiple reflection among the strong reflections. The distribution of superstructure spots can be interpreted by Anderson and Sletnes' orthorhombic lattice for the P'' phase with parameters $a = b = c = 5a_0$.

In the diffraction pattern taken with the beam incidence along [010], h (odd) spots are absent. From the consideration of the two dimensional space group, we can say that the superstructure projected along the [010] direction has the glide plane in the [100] direction.

Although the diffraction pattern shown in Fig. 1 comes from a single domain, the diffraction patterns are usually composed of spots coming from two types of domains oriented perpendicularly to each other. The diffraction spots from magnetite appear always with a definite orientation with the fundamental spots. In spite of the fact that the lattice parameter of magnetite a_0 (= 0.8394 nm) is slightly smaller than $2a_0$, the observed value was equal to $2a_0$ within the experimental error. These results indicate that magnetite grows coherently with wüstite without any mismatch.

Fig. 2 is a structure image of the P'' phase. An objective aperture used for UHV-HR-1 MV EM observations has a size corresponding to the large circle in Fig. 1. In the micrograph, spots with dark and white contrast pair are observed to make a fairly regular arrangement besides fine fringes with spacing $(1/2)a_0$. The spots are the cluster images and each has a size of $2a_0 \times 2a_0$.

Along the [001] direction the cluster arrangement is straight with inter-cluster distance $2.5a_0$, but along [100] it is zig-zag with amplitude $(1/2)a_0$, showing the existence of glide plane. Although the cluster arrangement is disordered frequently, the unit cell for the projected structure is rectangular with lattice parameters $a = 5a_0$ and $c = 2.5a_0$ as indicated in the micrograph. The projected structure belongs to the space group pg .

In Fig. 2, each cluster image gives the black-white contrast pair. This is due to the deviation of the incident beam direction from the zone axis. At the places indicated by arrows, the cluster images are very weak alternately along the [100] direction. This is also due to the deviation of incident beam direction from the zone axis. As was shown in a previous paper [4], when the projected structure has the glide plane, forbidden reflections appear and they produce a contrast modification with lattice period in the direction of glide plane.

Fig. 3 shows a highly magnified image and its optically transformed pattern. The dark dots corresponds to the images of iron-oxygen atom rows, while the white dots to the rows of tetrahedral interstices. The dark regions with size of about $2a_0 \times 2a_0$ are the cluster images. Although the image was taken under the optimum defocus condition, the contrast of cluster image is opposite to that in the structure image taken with the ordinary electron microscopes, which give the white contrast to the cluster image. This difference comes from the fact that the spots inside the small circle in Fig. 1 do not contribute to the cluster image formation in UHV-HR-1 MV EM. The details will be reported elsewhere.

Close inspection finds that in the cluster the tetrahedral interstices

show gray and dark contrasts. This indicates that iron atoms do exist at the tetrahedral interstices in the cluster. The inserted figure in Fig. 3 depicts schematically the distribution of iron atoms among the tetrahedral interstices.

DISCUSSION

When viewed along the [010] direction, the cluster has a size of $2a_0 \times 2a_0$, and its arrangement makes a superstructure with cell dimensions $a = 5a_0$ and $c = 2.5a_0$. Also the glide plane exist in the [010] direction. These results is in accordance with the results of Anderson and Sletnes and of Iijima. However, the distribution of tetrahedral iron atoms in the cluster is different from that proposed by Anderson and Sletnes. As was seen in Fig. 3, their distribution does not show any regularity. It is considered that the clusters can have various structures.

It must be added the fact that, in spite of many trials, we have not been able to obtain electron micrographs and diffraction patterns of the P" phase viewed along the [100] and [001] directions. The reason is not clear. Accordingly, we can not say whether Anderson and Sletnes's unit cell, space group and the three dimensional distribution of clusters are correct or not. Further studies are necessary on these points.

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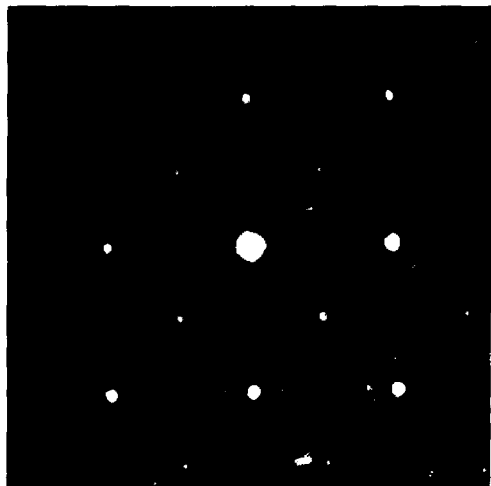


Fig. 1. Electron diffraction pattern of $\text{Fe}_{0.90}\text{O}$ showing the distribution of superstructure spots. The subscripts, f and m attached to the indices refer to the fundamental lattice and the magnetite lattice, respectively. The large circle corresponds to an objective aperture size used for UHV-HR-1 MV EM observations. The spots inside the small circle make almost no contribution to the structure image formation. (The pattern was taken with a 100 kV electron microscope.)

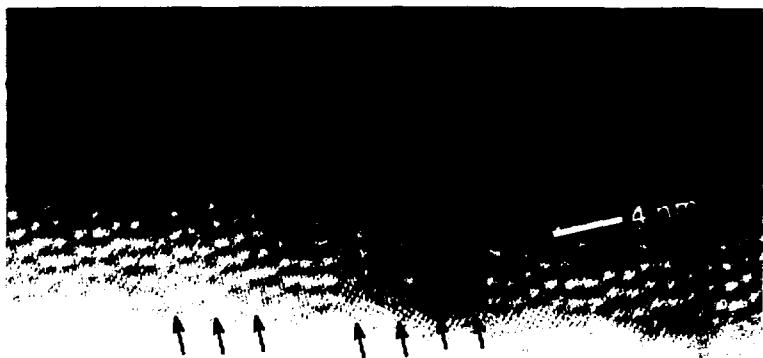


Fig. 2. Structure image of the P'' phase showing the cluster arrangement. Taken with UHV-HR-1 MV EM. Superstructure unit cell is indicated. At the arrowed places the cluster images almost disappear as a result of the deviation of the incident beam direction from the zone axis.

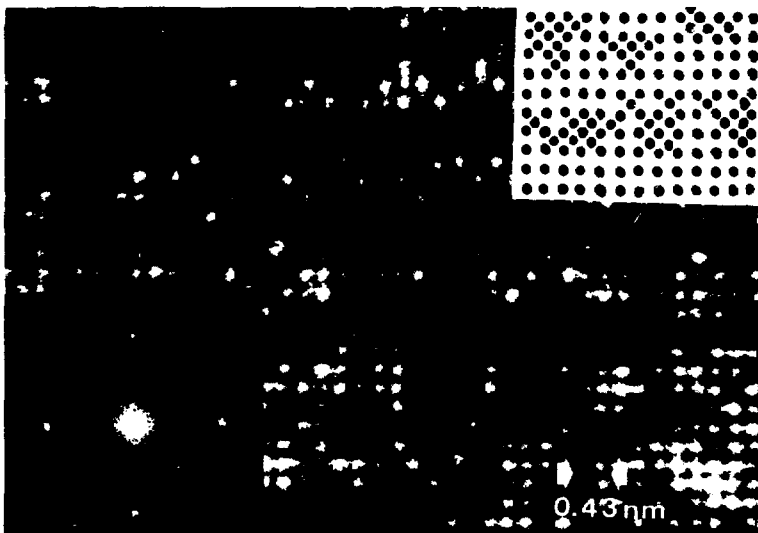


Fig. 3. High resolution structure image and its optically transformed pattern. The dark dots correspond to the iron-oxygen atom rows. The cluster gives dark contrast. The inserted figure illustrates schematically the distribution of iron atoms among the tetrahedral interstices.

DEFECT STRUCTURES IN HIGH TEMPERATURE IRON OXIDES

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ABSTRACT

The defect structures occurring in high temperature iron oxides have been studied using 500kV high resolution electron microscopy. Ordering of defect clusters was observed in wustite quenched from 850°C although details of the cationic distribution could not be obtained due to continual re-ordering caused by the electron beam. In slowly-cooled samples, "domains" of magnetite surrounded by wustite were visible at 850°C, but magnetite was the predominant oxide at 700°C and no wustite was observed.

INTRODUCTION

The oxidation of iron is characterised by a transition temperature (570°C) below which parabolic oxidation takes place at a slow rate and formation of the nonstoichiometric wustite (Fe_{1-x}O) phase is excluded. In contrast, above this critical temperature, rapid scaling occurs and all three oxides, wustite, magnetite (Fe_3O_4) and haematite (Fe_2O_3) occur [1]. The high rate of diffusion for wustite ($\sim 6 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ at 700°C) [2] results in a high rate of oxidation and this is normally associated with a high concentration of lattice defects. A number of techniques, such as electrical conductivity measurements [3], have been used to show that the nonstoichiometry in wustite is accommodated by octahedral iron vacancies which associate into tetrahedral complexes about ferric ion interstitials [4]. Several studies by high resolution electron microscopy (HREM) of the ordering of these defect clusters have been reported [5-7]. However, only superlattice details were revealed because of insufficient resolution ($\sim 3\text{-}4\text{\AA}$) of the microscopes used. We have previously demonstrated the usefulness of HREM (at $\sim 2\text{\AA}$ level) for providing structural information about deficit oxides in a comparison of growth processes in Fe_2O_3 and Cr_2O_3 whiskers [8]. We report here some observations of the defect structures occurring in high temperature iron oxides.

EXPERIMENTAL

Three different preparations have been used for the present study:

A. pure iron was oxidised by heating in air at 700°C for 24 hrs; part of the oxide scale was ion-beam-thinned in normal section, and spalled crystals from the same sample were also supported on holey carbon films; B. pure iron was oxidised at 850°C (2 hrs, in air) and allowed to cool to RT over ~ 10 mins; an edge-on specimen was made from the resulting scale using a method similar to that described elsewhere [9]; C. same treatment as B except that the sample was quenched in oil to RT and oxide crystals were supported on holey carbon films. Observations were made with the Cambridge University HREM [10] operated at 500kV.

RESULTS AND DISCUSSION

Sample A proved to be composed almost entirely of magnetite, with randomly-oriented grains in the approximate size range 0.1-2.0 μ m in the ion-thinned sample, although much larger grains were sometimes found. Figs.1(a) and (b) show typical fields of view. Grain boundaries are generally curved and often inclined to the beam, giving rise to moire fringe effects. Line defects are sometimes present, as arrowed in Fig.1(b). The higher magnification image of Fig.2 shows two adjacent grains, close to [110] normals. Note here the irregularity of the grain boundary and the marked absence of any defects in these grains. Also note the apparent superstructure at X, which is reminiscent of that observed earlier [5-7] although at much higher resolution here. Spalled crystals from this sample were almost invariably magnetite and the sizes of the bigger crystals made it easy to tilt to other zone axes.

Sample B had an unexpected domain structure, appearing to consist of regions of magnetite, embedded in wustite. This is clearly seen in both the image shown in Fig.4 and the diffraction pattern (inset) which corresponds to [001] normals of both materials, although rotated by 45° relative to each other. Note also the faint spots in the latter associated with the 020 beams suggesting the possibility of some superlattice ordering [7] although none is apparent in the image. The expected defect ordering of wustite was only observed in some crystals from quenched sample C, such as that shown in Fig.4. Most crystals instead appeared to be highly disordered, giving irregular lattice fringes and diffraction spots spread out into arcs. Furthermore, because of damage by the electron beam, observation of the ordering has been restricted to relatively low magnifications ($\sim 100,000\times$). Crossed 2.1Å lattice fringes can then be obtained but, because of uncertainties about the objective lens defocus, relating these to atomic positions is not straightforward, although work in this direction is continuing.

CONCLUSIONS

High resolution electron microscopy has been used to study the defect structures of magnetite and wustite as formed by the high temperature oxidation of iron. Although the grain sizes of the two oxides appear to be consistent with the different rates of formation of each layer, we have not observed a significant incidence of structural defects in air-cooled specimens. It is only by rapid quenching that we have been able to identify a superlattice structure in wustite, though specimens prepared in this way are susceptible to beam damage; it is not yet clear whether the defect ordering will be observable at the cation level. The nature of the defect structure of wustite would certainly favour its high rate of growth though we are currently investigating the properties of this material by observations of edge-on specimens.

We are pleased to acknowledge financial support from S.E.R.C., U.K.

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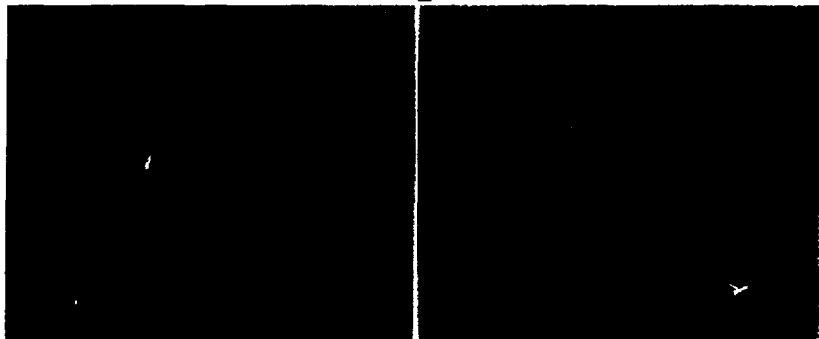


Fig.1. Fe_3O_4 formed on pure iron after oxidation for 24 hours in air at 700°C (Sample A) Planar defects are arrowed in b).



Fig.2. High magnification image of Fe_3O_4 (Sample A) at (110) showing $4.1\text{\AA}$ (200) and $4.8\text{\AA}$ (111) lattice fringes. An apparent superstructure in the oxide is shown at X.

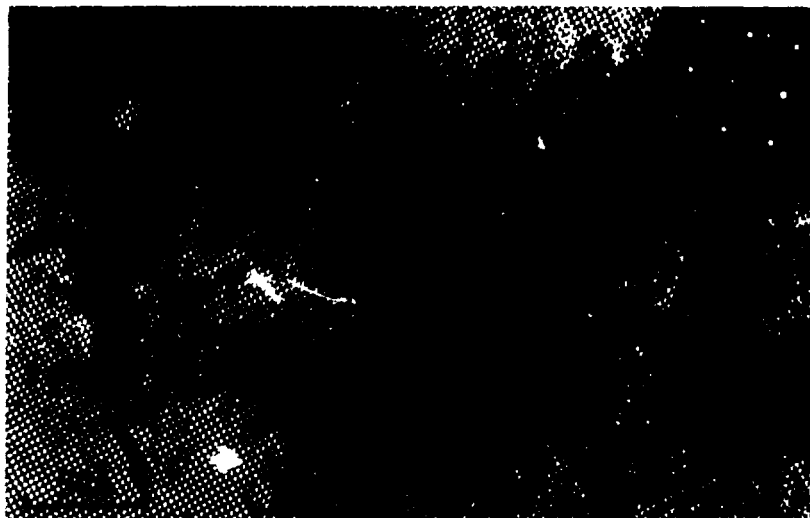


Fig.3. Irregular domains of magnetite in wustite (Sample B), with inset diffraction pattern showing the 45° relative rotation.

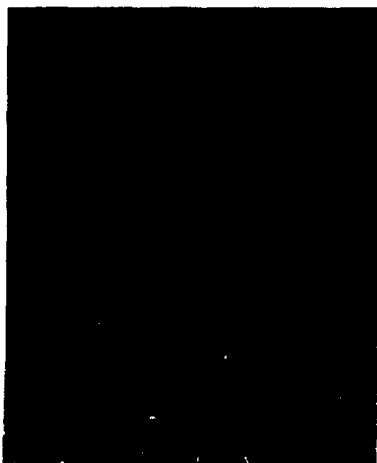
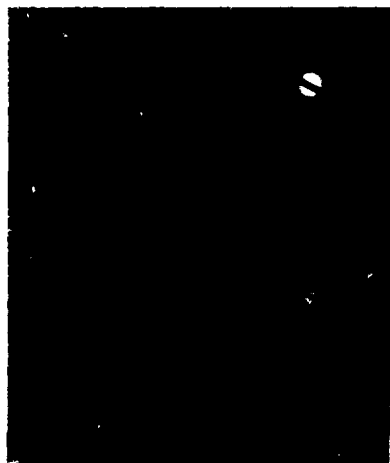


Fig.4. (a) Irregular cluster ordering observed in quenched wustite (Sample C) Note superlattice spots in inset (001) diffraction pattern; (b) Region of Fig.4(a) at high magnification showing crossed $2.1\text{\AA}$ wustite lattice fringes superimposed on coarse fringes from the micro-domains

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ABSTRACT

To survey the optimum condition for observation of a long period superstructural alloy the multibeam interference images were calculated for α' Ag-Mg by using the n -slice method. The multibeam dark field images, or MDFI, is found to be advantageous compared with the multibeam bright field image, or MBFI, with the following respects; (1) The atomic column of Mg gives a strong contrast in MDFI even for a rather thin specimen. (2) The image contrast in MDFI is not affected so much by the tilting of the specimen or the defocusing distance as in MBFI.

INTRODUCTION

α' Ag-Mg phase has a one-dimensional long period superstructure, or 1d-LPS, which can be derived from $L1_2$ order-cells by inserting antiphase boundaries periodically. The present authors [1,2] and other workers [3] reported that α' Ag-Mg consists of antiphase domains with $M=1$ and $M=2$, where M is the dimension of an individual domain referred to the $L1_2$. The feature was found to be common to other 1d-LPS such as α_2 Cu-Al[4] and α' Cu-Pd[5]. We have reported [1] that in MBFI with an axial illumination the sites for the minority atoms have a bright or dark contrast. But, it is expected that a high resolution image can be taken more easily by the MDFI technique than by MBFI, because a small objective aperture can be used. However, the deviation from the symmetrical diffraction and imaging conditions sometimes give rise to the distortion in the image contrast[2]. Thus, it is necessary to confirm the correspondence between the image and the actual structure. In this work, we examine the correspondence we calculated MDFI of α' Ag-Mg using a dynamic theory for various conditions of observation.

IMAGE CALCULATION

MDFI were calculated for α' Ag-Mg which is made of three domains of $M=2$ and one of $M=1$ in the unit structure, using the n -slice method[6] with the parameters listed in Table 1. The effects of the chromatic aberration and the divergence of the incident beam were taken into account by using the equation of reference [7]. The MDFI was observed for α' Ag-Mg using JEM-1000 at HVEM, Kyushu University.

RESULTS

Figure 1 shows the simulated MDFI for different thickness of the specimen, where white dots appear in a distinct contrast. Comparing the image with the structure-model which is illustrated in the inset, one can see that the white dots correspond to the minority atoms, or Mg. It is already reported [1] that MBFI has the similar contrast only for a rather thick specimen. In the MDFI, however, it is found that the image-contrast changes merely a little with the crystal thickness. Figure 2 shows the change in contrast of MDFI with the defocusing distance Δf . The "modified Scherzer focus" is about 120 nm for the present case. The white dots are found to be retained in MDFI corresponding to the

Mg-sites, even if Δf is deviated from the modified Scherzer focus by a considerable amount, while the image in MBFI is known to be dimmed[1]. Figure 3 shows MDFI for the specimen tilted by $\alpha_x=1.3$ mrad and $\alpha_y=1.3$ mrad, where α_x and α_y are the components of tilting angle along x and y directions, respectively. The present authors[2] reported that in MBFI the image contrast is distorted especially around antiphase boundaries. But one can see that the image contrast in Fig. 3 still correspond well to the actual order-structure.

In summary, it is found that MDFI is more advantageous than MBFI for observation of an order-structure in a binary alloy because the condition for taking the image which correspond to the actual structure is less restricted. Figure 4 shows an example of the observed MDFI where white dots appear indicating directly the positions of Mg-columns as expected from the present simulation.

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Table 1 Values of parameters used for calculations

*accelerating vol. $E=750$ kV	*radius of obj. aperture $k=1.05/a$
*Debye-Waller factor $0.6 \times 10^{-2} \text{ nm}^2$	*thickness of specimen $T \approx 41.2$ nm
*lattice parameter $a=0.412$ nm	*atomic scat. factor by ref.[8]
*region of rel-space $ h , k \leq 10$ or taken into account $h^2+k^2 \leq 14^2$	*absorption parameter $V_g/V_s = 0.05$
*thickness of a slice $\Delta z=a$ or $2a$	*spread in defocusing $\delta=20$ nm
*spherical aberration $C_s=10$ mm	*convergence angle $\alpha=0.54$ mrad
	*center of obj. aperture $(h, k)=(1, 1)$

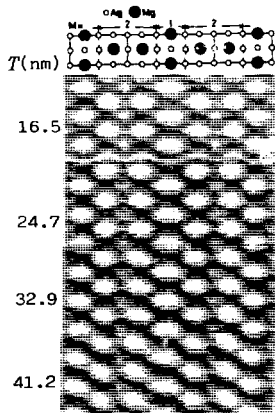


Fig. 1 Change in image contrast of MDFI with T

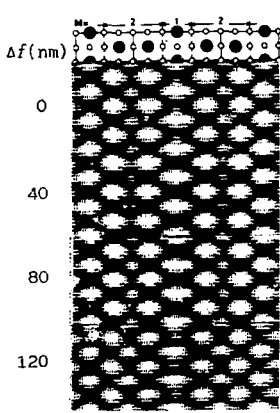


Fig. 2 Change in image contrast in MDFI with Δf

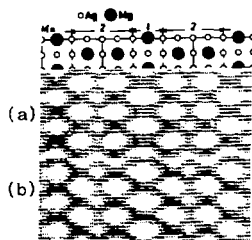


Fig. 3 Change in image contrast in MDFI with tilting angle $T=16.5$ nm, $\Delta f=80$ nm
(a) $\alpha_x=\alpha_y=0$
(b) $\alpha_x=\alpha_y=1.3$ mrad

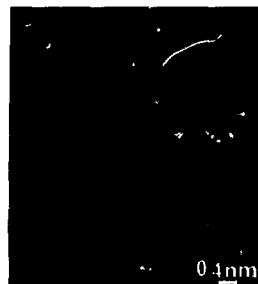


Fig. 4 Observed MDFI of α' Ag-Mg

IMAGE ANALYSIS OF STRUCTURE DEFECTS IN ALLOYS

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ABSTRACT

High-voltage, high-resolution images are analyzed with the use of a computer-aided image processing system. Many-beam images of Au-26at.% Cd alloy with incommensurate superstructures are processed with the Fourier transformation, and the incommensurate periodicity and the basic hcp cells are clearly revealed in the processed images. Autocorrelation functions of the images of partially ordered Au-Mn alloys containing 20.7 and 22.6at.% Mn are obtained. It is indicated that the partially ordered structure consists of small ordered domains of the $D0_{22}$ structure with out-of-phase configurations. The results demonstrate that the image processing is quite useful to analyze the atomic arrangements of incommensurate structure and imperfectly ordered structure of alloys.

INTRODUCTION

High-voltage, high-resolution electron microscopy provides useful information on structure defects in the atomic scale. It is scarcely possible, however, to propose the real atomic arrangements of structure defects directly from the observed images, because the image contrast is affected by the dynamical scattering interactions of the incident beam and a number of scattered beams. For the case of structure defects in many-component crystals such as alloys and ceramics, the situations are more complicated; the intensity distribution in non-periodic structure images can not be interpreted straightforwardly.

The purpose of this study is to present examples of faithful analyses of the many-beam images of non-periodic structures of alloys with the use of a computer-aided image processing system.

METHODS

The intensity distributions in either film or print of high-resolution images are first digitalized with 256 gray levels through a TV camera system. Then Fourier transformations or correlation functions are calculated with the digitalized data using a large computer (ACOS 1000).

RESULTS

Fig. 1 shows an example of the Fourier transformation of non-periodic images of alloys with incommensurate superstructures.

Fig. 1 (a) is an axial-illumination image of Au-26at.% Cd alloy, of which the basic structure is hexagonal close packed, and the superstructure has an incommensurate periodicity of $M=8.4$ in the unit of the basic hcp cell size $a=0.29$ nm [1]. The real structure of the incommensuration is scarcely possible to determine directly from the observed image of Fig. 1 (a), because the image is formed by many-beams of fundamental reflections and superlattice reflections as well as the incident beam, and no kinematical relationship holds among them. Fig. 1 (b) corresponds to a diffractogram, that is the Fourier transformation of Fig. 1 (a), where the amplitude of the central beam is much larger than the other beams, but set equal to the background level. There are two groups of reflections in the diffractogram; twelve spots inside the circle correspond to the superlattice reflections, and six spots outside the circle correspond to the fundamental ones as indexed as 100 and 010.

Faithful analyses of the observed image are obtained by the inverse-Fourier transformation of the diffractogram separating the two groups of reflections. Fig. 1 (c) is a Fourier image produced with the reflections inside the circle, and Fig. 1 (d) is produced with the central beam and the fundamental reflections outside the circle. The existence of domains consisting of the commensurate superlattice cells with $M=9$ can be seen in Fig. 1 (c) as indicated by the lozenges. An out-of-phase configuration is seen between the domains. In Fig. 1 (d), we may note a fine mesh of the basic hcp cells, of which the distance between the neighboring bright dots corresponds to $a=0.29$ nm.

The above results demonstrate the usefulness of the Fourier transformation by the image processor; we can reveal the configuration of the commensurate superlattice cells as well as the basic hcp cells which can not be recognized in the direct image.

Another example of the applications of the image processing system is the analysis by autocorrelation technique. The autocorrelation function $A(\vec{r})$ is a convolution given by

$$A(\vec{r}) = I(\vec{r}) * I(-\vec{r}),$$

where $I(\vec{r})$ indicates the intensity distribution of an input image. Figs. 2 (a) and (b) show the many-beam images of Au-Mn alloys containing 20.7 and 22.6at.% Mn, respectively. In these images, bright dots correspond to Mn atom positions projected down along the incident beam, and dark regions correspond to Au-rich portions [2]. If the kinematic relationship holds approximately among the superlattice reflections, the brightness of dots is roughly proportional to the occupation probability of Mn atoms in the columns [3]. Since the alloys are a partially ordered state, the distribution of bright dots shows no long-range periodicities. At first sight, however, there are local ordering based on the D0₂₂ type structure; the rectangles in the images correspond to the tetragonal unit cell of this structure projected down along

the incident beam. The atomic configuration averaged over the observed area may be visualized more clearly in the respective autocorrelation functions shown in Figs. 2 (c) and (d).

The central spot in both the images is the origin of the correlation function, and the intensity at a point of $\vec{r}$ from the origin indicates the occupation probability of Mn atoms in the two columns with the translation $\vec{r}$. In the autocorrelation functions of Figs. 2 (c) and (d), the cluster of bright dots around the origin indicates the short-range order of Mn atom distribution, which corresponds to the distribution of Mn atom columns of the D0₂₂ type structure indicated in Fig. 2 (e). We note that clusters of several bright dots with a similar shape to that around the origin are located around the translation $\vec{r} = 5/2\vec{a} + 7/4\vec{c}$ and other clusters of four dots exist around $9/2\vec{a}$. From the configuration of these bright dots, we see that the partially ordered structure consists of small ordered domains of the D0₂₂ type structure with lozenge shape of about 3×3 or 4×3 or 4×4 Mn atom columns, and the domains are separated each other at the translations $5/2\vec{a} + 7/4\vec{c}$ and $9/2\vec{a}$ in the average. Further we note that the occupation probability of Mn atoms at the primitive translation vector $\vec{c}$ is lower at the composition of 20.7at.% Mn than at 22.6at.% Mn. The above results are consistent with the atomic arrangement in the well ordered state of Au-Mn alloys observed by the 1 MV electron microscopy [2,4]. It is concluded, therefore, that the autocorrelation technique is useful to investigate the averaged atomic arrangement of partially disordered or short-range ordered structures using an experimental image taken from a very limited area in the specimen.

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Fig. 1. (a) High-resolution image of a Au-26at.% Cd alloy with the axial-illumination along [001]. (b) Absolute amplitude of the Fourier transformation of (a). (c) Processed image with the reflections inside the circle of (b). (d) Processed image with the central beam and the reflections outside the circle of (b).

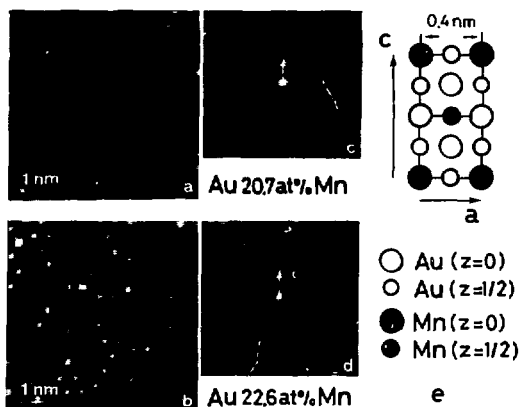


Fig. 2. (a) Superstructure image of Au-20.7at.% Mn. (b) Superstructure image of Au-22.6at.% Mn. (c) Autocorrelation function of (a). (d) Autocorrelation function of (b). (e) Atomic arrangement of the D0₂₂-type structure. a and c are the lattice constants of the tetragonal unit cell.

TECHNIQUES & INSTRUMENTATION



ON-LINE DIGITAL PROCESSING FOR HREM

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ABSTRACT

A system for the application of digital storage and processing techniques to high resolution electron microscopy is described. Examples of such applications are presented and discussed.

The previously described [1] image processing facility in Oxford has been further developed to provide a number of practical facilities for high resolution electron microscopy. The system consists of a Microconsultants Intellect 200 digital framestore and Fast-Fourier transform unit which together with associated output processor (look-up table) and various magnetic storage media is directly controlled by a DEC LSI 11/23 minicomputer. The input picture is obtained from a SIT low-light level T.V. camera focused via a pair of large aperture lenses, mounted nose to nose, on the image formed on a transmission screen mounted in the modified base of a JEOL 200CX HREM.

During the acquisition of images, simple algorithms may be applied to reduce noise by recursively processing the sequence of input television frames [1]. The result of this processing, together with contrast enhancement, also at T.V. frame-rate, is to provide a high magnification ($\approx 15MX$), high contrast display image of near photographic quality on a monitor at the microscope, with the added advantage of simultaneous clear viewing for several experimentalists. This has in a number of cases directly aided the taking of micrographs which would otherwise be difficult or nearly impossible to obtain [2, 3].

Of critical importance in HREM is the establishment of instrumental defocus, beam tilt and the correction of astigmatism. These, together with a knowledge of specimen thickness, orientation etc. are essential for a correct interpretation of the image contrast [4]. It is clearly of advantage if such information is made available to the microscopist during the course of an experiment within the time constraints set by stage drift and radiation damage (of the order of tens of seconds). The advent of digital framestore technology has made possible a number of attempts to extract the parameters of interest and these may be roughly categorised as frequency based [5], and spatially based [6].

Frequency analysis uses the calculation of the image Power Spectral Density to provide similar results at the microscope to those produced by optical diffraction on a laser optical bench. Figure 1 (a) shows a result from our system, obtained in $\sim 15-18$ s for a 256 point square image.

Attempts to extract accurate numerical values from such a result are made extremely difficult by the poor signal to noise ratio [7] - see fig. 1(b) - although some progress has been made by blurring the PSD with a 3×3 correlation mask. This adds 2-3 seconds to the processing time - see fig. 2. Spatial analysis either by dedicated correlation hardware or by using Fast-Fourier transforms is inherently much slower (at least a factor of 2) but provides a much better quality result. The calculation of the central correlation peak (image variance) is, however, much more rapid and may be used to extract useful information on defocus, beam tilt and astigmatism [8]. These methods and others under development are being evaluated on our system for speed, repeatability, robustness and uniqueness of solution.

The system at Oxford is extremely flexible and may be used for a wide variety of image processing operations. On-line facilities currently include gamma processing, noise reduction, and Fourier transformation. These are accessed via a keypad structure (fig. 3) which is simple and unobtrusive in use. Off-line (i.e. slightly slower than on-line but still interactive) facilities include file handling and archiving, histogram equalisation, auto- and cross-correlation, text addition etc., and are accessed via a combination of two character mnemonics and keypad operations. Also available are Fourier filtering and multislice image calculation. Although the computer (LSI 11/23) is comparatively slow, the presence of a 16 bit slice processor dedicated to FFT and similar operations and the availability of all facilities on one single-user system outweigh this disadvantage - indeed the speed may well be comparable to a larger, but multiuser, installation.

Fourier filtering as a technique for removing imaging noise and 'structural noise' such as an amorphous background is an established technique. The system we have developed is again keypad operated (fig. 4) and by the use of circular frequency apertures of varying size and position which may be added or removed, effectively any Fourier filtering operation may be performed. The limitations of the method have also been documented but may be usefully reinforced. Figure 5 shows the effect of applying a highly selective frequency mask to amorphous silicon. The result is easily mistaken for {110} silicon! The point to be stressed is that such a mask may never be used to reliably improve image quality. Careful filter design, however, can yield very useful results, and figure 6 shows the removal of structural noise from a lattice image of sodium 8" alumina (courtesy of R. Hull) where the structure of a twin has been clearly revealed without distortion.

In conclusion, we have seen that digital framestore systems can provide greatly enhanced viewing, useful information about operating conditions, and subsequent image analysis and processing. These techniques and their future development will greatly assist the experimental microscopist and enable better controlled experiments to be placed on a more quantitative basis.

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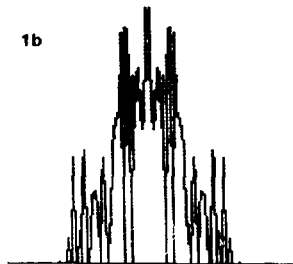
1a



2a



1b



2b

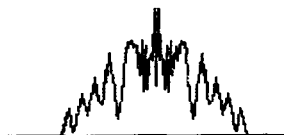


Fig. 1 (a) Power spectral density calculated by 2-D FFT. (b) Diametal trace across (a) along indicated line; note extremely noisy results.

Fig. 2 (a) PSD of figure 1(a) after smoothing by a 3 x 3 mask. (b) Diametal trace showing improved discrimination of maxima and minima.

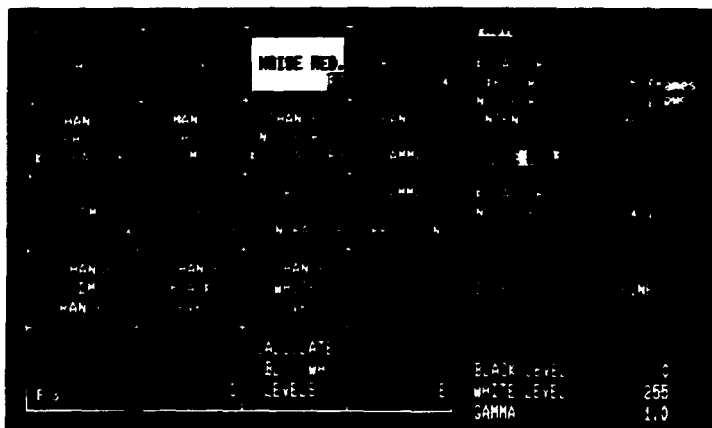


Fig. 3 Keypad for control of on-line image viewing, acquisition and calculation of power spectral density (ODM - optical diffractogram analogue).

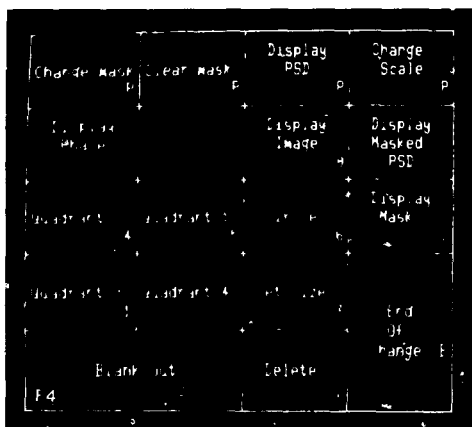


Fig. 4 Keypad for control of Fourier filtering facilities.

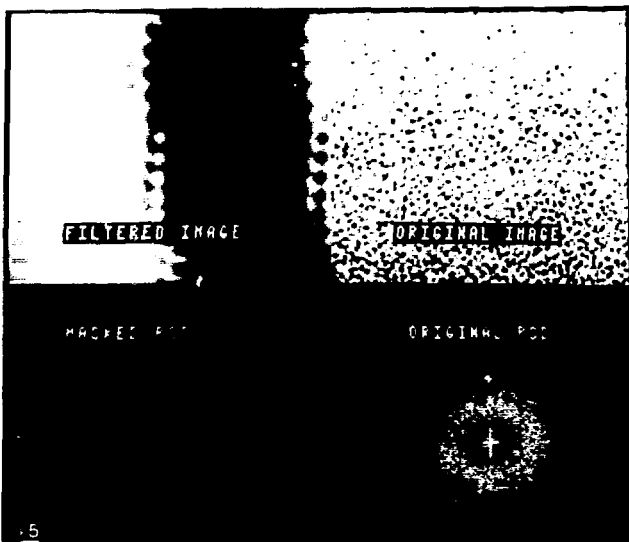


Fig. 5 Labelled segments showing how a particular filtering mask may produce as an artefact an apparently crystalline structure from an amorphous initial image.

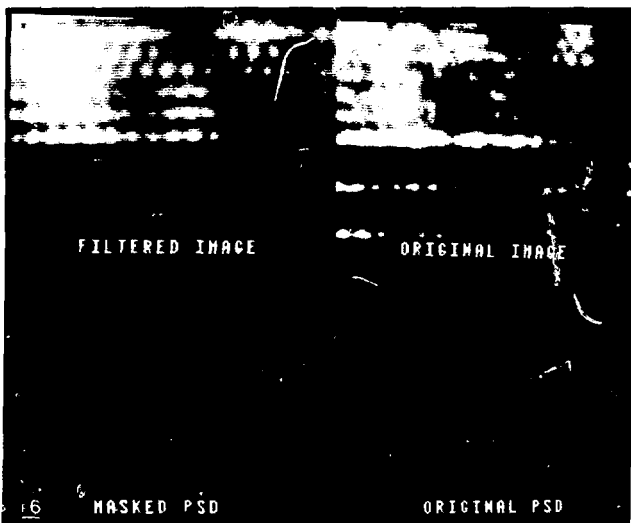


Fig. 6 Twinning present in a sodium β'' alumina specimen shown more clearly by use of a carefully chosen filtering mask.

NOTES

Duf

HIGH VOLTAGE ANALYTICAL ELECTRON MICROSCOPY

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ABSTRACT

The use of analytical and high voltage electron microscopies (AEM, HVEM) for microcharacterization is now well established as a powerful tool in both basic and applied materials research. There are, however, several fundamental limitations in the use of analytical electron microscopy in lower voltage instruments (100-200 kV) which restricts microanalysis - most notably multiple scattering. As a result of this, there is sufficient motivation to explore the merits of AEM-type microanalysis in the HVEM regime. This paper will discuss aspects of both qualitative and quantitative analysis at higher voltages, as well as the plans for upgrading the ANL 1.2 MeV HVEM (EM-7) for x-ray and electron energy loss spectroscopies (XEDS, EELS).

X-RAY SPECTROSCOPY

X-ray microanalysis in HVEM's has until recently received little serious attention, due in part to some severe instrumental problems associated with interfacing a Si(Li) detector to the microscope column [1-4]. There are, however, several factors which have overridden these difficulties: namely, the potentials for increased mass sensitivity [1,2] in XEDS and the decrease in multiple scattering in EELS. We shall begin this discussion by considering relevant aspects of quantification of XEDS data.

AEM-based x-ray analysis is usually approached using the thin-film standardless technique [5], where it can be shown that the relative intensity ratio of any two characteristic x-ray lines (I_A/I_B) from the elements A and B is directly related to the local composition ratio (C_A/C_B) by the equation:

$$\frac{I_A}{I_B} = \frac{(Q \cdot \omega \cdot \alpha)_A \cdot A_B \cdot \epsilon_A}{(Q \cdot \omega \cdot \alpha)_B \cdot A_A \cdot \epsilon_B} \cdot \frac{C_A}{C_B} \quad (1)$$

here ϵ_B is the relative detection efficiency of the characteristic line of element B, while Q, ω , α and A are respectively: the ionization cross-section, x-ray fluorescence yield, relative line intensity and atomic weight. Of these factors only the cross-section need be reevaluated for high voltage applications; however, we shall see that it also becomes relevant to consider alternate detectors to improve ϵ in the high x-ray energy regime.

Ionization Cross-section

The total ionization cross-section is usually expressed in the general form [6]:

$$Q = \frac{a_K b_K}{E_c U} \cdot \ln(c_K U) \quad (2)$$

where U is the overvoltage ratio (i.e. the ratio of the accelerating voltage to the critical excitation energy E_0/E_c with $E_0 = eV_0$) and the factors a_K , b_K , and c_K are constants. This expression has been used quite successfully for many years by the electron microprobe community, in instruments operating up to about 40 kV. In this situation, relativistic effects are small and the approximation that the electron energy is equal to eV_0 is nearly correct; however, its application to an AEM operating at 100 kV ($\beta = v/c \sim 0.5$) or higher, can result in serious errors. In order to see this, we must consider equation 2 in its more general relativistic form (5):

$$Q = \frac{a_K b_K}{E_c E_0} \cdot \left[\ln\left(\frac{E_0}{E_c}\right) - \ln(1-\beta^2) - \beta^2 \right] \quad (3)$$

with $E_0 = \frac{1}{2} m_0 v^2 = \frac{1}{2} m_0 c^2 \beta^2$. One can now see that the functional dependence of the cross-section varies as the electron velocity (v) not the accelerating voltage! Since the electron velocity has an upper limit (the speed of light), the cross-section essentially levels off as β approaches unity. At extremely high accelerating voltages (> 5 MV), the cross-section actually begins to increase again due to complex electron-atom interactions [7]. Figure 1 plots experimental values of the total ionization cross-section as a function of accelerating voltage for Al, Ni, Ag and Au taken from a variety of sources [8-14]. For comparison, also plotted on this figure are values calculated by the cross-section formulations proposed by Zaluzec [5] and Wood et al. [15]. The former (solid curve) incorporates the relativistic correction as shown above, while the latter (dashed line) uses the relativistic correction of Goldstein et al. [6] applied to equation 2. For nickel and silver, both these formulations yield nearly the same results at low accelerating voltages, however the use of a relativistic electron energy given by the equation $E_0 = E_c (1 + 9.785 \times 10^{-4} E_c)$ in the overvoltage term erroneously models the functional dependence at higher energies [6], and is simply incorrect. The expression of the form given by equation 3, clearly yields better overall agreement to the experimental data. For high Z materials such as gold ($Z=79$), however, this equation under estimates the cross-section, and the more complex calculations of Davidovic and Moisewitsch [16], or Kolbenstvedt [17] may be more relevant.

Another aspect of HVEM-based x-ray spectroscopy, arises when we consider the voltage dependence of the total characteristic x-ray production. The number of ionizations which occur at a particular set of operating conditions is given by the product of the cross-section (Q) and the incident probe current (i). Neglecting aberrations in the probe forming system, the incident beam current is related to the source brightness (β) and accelerating voltage (V) by the equations:

$$i = \frac{(\pi d_0 \alpha_0)^2}{4} \cdot \beta \quad (4), \text{ and } \beta = \left(\frac{J_c}{\pi k T} \right) \cdot eV \quad (5)$$

where d_0 is the probe diameter, α_0 is the convergence semi-angle, J_c is the emission current density of the source, and kT the effective energy spread of the gun. The relative number of ionizations as a function of accelerating voltage at constant electron-optical conditions (i.e. $d_0 \cdot \alpha_0 = \text{constant}$) is obtained by combining equations 3-5, and is plotted in figure 2 for Al, Ni, Ag and Au. As one can see, due to the fact that the gun brightness increases

with voltage, and the cross-section levels out, we get a continuous increase in the relative number of ionizations (and hence x-ray production) as the operating voltage of the microscope is increased.

Detector Efficiency

Typically microanalysis of high Z materials ($Z > 45$) is performed by analysis of their L shell x-rays, however, accurate cross-section measurements for these species at the accelerating voltages of AEM regime are scarce, coupled with the multiplicity of lines ($L\alpha$, $L\beta$, $L\gamma$, $L\delta$, $L\eta$) in the L series, and the results of figure 2 makes the concept of high Z analysis via K shell measurements an extremely attractive proposition. Unfortunately, as one can see from figure 3 the high energy detection efficiency of Si(Li) x-ray detectors begins to drop off rapidly above ~ 40 keV. This regime is more suitable to study through the use of high purity intrinsic germanium (IG) detectors, the calculated relative efficiency of which is shown in figure 4. Although the Ge dead layer causes severe absorption at the low energy end, the high energy characteristics of this type detector are excellent. Not accounted for in this calculation is the rather significant escape peak interaction, which will result in an additional loss in efficiency near the Ge K edge. Due to their efficiency below ~ 2 keV, IG systems have been ignored by the AEM x-ray microanalysis community; however, this may be compensated for, by using Si(Li) and Ge detectors in parallel. The advantage of such a dual detector arrangement would be the excellent overlap between the two systems. Alternatively, one can envision the construction of a composite detector where a thin Si(Li) detector is backed by a relatively thick intrinsic Ge crystal or a dual system with the detectors side by side in a single cryostat.

ELECTRON ENERGY LOSS SPECTROSCOPY

It is well known that multiple scattering decreases as the incident electron beam energy is increased, and that this is also the most important factor limiting EELS microanalysis. One method of determining the multiple scattering limit for EELS is to note that quantitative analysis can be cast in the same standardless format as is employed in XEDS analysis, and an expression of the form given by equation 1 is equally valid for EELS. Here $\epsilon = \omega = \alpha = 1$, while Q is simply the partial ionization cross-section of the desired atomic species for a given energy window, incident beam convergence, and collection solid angle [18-19]. Since this equation is thickness independent, one can immediately determine the limiting value for quantification by measuring the variation in the characteristic EELS intensity ratio of a homogeneous specimen as a function of thickness. Any departure from a constant value indicates a breakdown of the quantitative model. An example of this is shown in figure 5, for specimens of Boron Nitride (BN), Nickel Oxide (NiO) and Aluminium Oxide (Al_2O_3) as a function of $\ln(I_T/I_0)$, where I_T is the total energy loss intensity in the spectrum, and I_0 the zero loss integral [19]. The value of $\ln(I_T/I_0)$ is directly related to the ratio of t/λ , where t is the specimen thickness and λ the mean free path for inelastic scattering [20]. As one can see from figure 5 the limiting value of t/λ is ~ 1 . Deconvolution has been suggested as possible solution to this dilemma, [21], however, recent experimental work has shown that this may not be always applicable. On the otherhand, the mean free path for inelastic scattering varies as β^2 [22], and therefore, the relative specimen thickness

(t/λ) decreases as the electron velocity increases. Hence, in situations where multiple scattering limits microanalysis, one need only increase the accelerating voltage of the microscope and thereby decreases t/λ . We further note that for the case of light element analysis using XEDS the limiting factor is x-ray absorption [23], and in this situation one can only decrease the specimen thickness to eliminate absorption effects. Thus for XEDS, light element analysis is specimen limited while for EELS one can overcome the limitation by employing higher voltages. There is, however, a saturation effect to λ at very high voltages ($8 \sim 1$) which becomes the ultimate limitation for EELS. The advantages of increasing the accelerating voltage in decreasing multiple scattering can be further appreciated by reference to figure 6, which plots the experimental jump ratio for the carbon K edge in a 200 nm thick specimen as a function of accelerating voltage [24,25]. As can be clearly seen there is a continuous increase in the jump ratio as the accelerating voltage increases.

SUMMARY

From the standpoint of both x-ray and electron energy loss spectroscopies, there are clear motivations toward the further development and expansion of analytical techniques in both medium (300-500 keV) and high voltage (> 1 MeV) instruments. The current experimental program at the ANL-HVEM is in the process of interfacing both conventional x-ray detector systems to the column, as well as a $\pi/2$ magnetic sector energy analyzer beneath the camera chamber. This type of AEM, due to its relatively large probe diameters (~ 100 nm), will never compete in terms of spatial resolution with modern ~ 100 kV AEMs; however, it can provide valuable information on the physics of the electron solid interaction process, as well as limited low resolution microanalysis. With the commercial development of 300-500 keV analytical instruments in the immediate future, it is important to gain further insights into the higher voltage AEM capabilities in order that we can make optimum use and/or modification of these microscopes for materials research.

ACKNOWLEDGEMENTS

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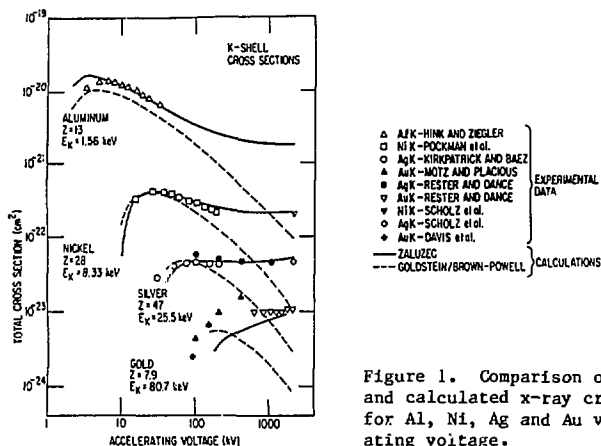


Figure 1. Comparison of experimental and calculated x-ray cross-sections for Al, Ni, Ag and Au versus accelerating voltage.

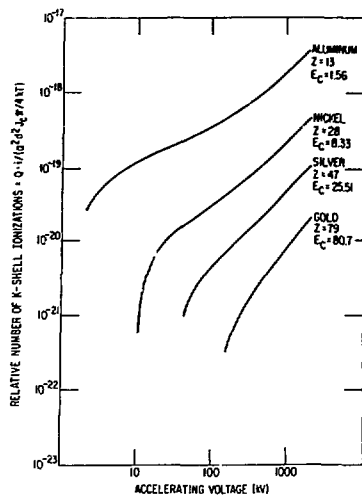


Figure 2. Calculated dependence of relative number of K-shell ionizations (x-ray production) for Al, Ni, Ag and Au versus accelerating voltage.

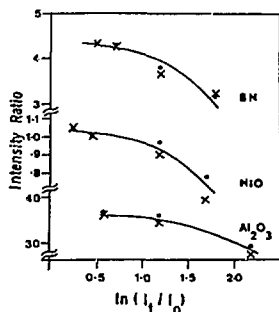


Figure 5. Experimental variation in EELS intensity ratio as a function of $\ln(I_1/I_0)$; $E_0 = 120$ kV, $\theta = 14.7$ mrad for specimens of BN, NiO, and Al_2O_3 .

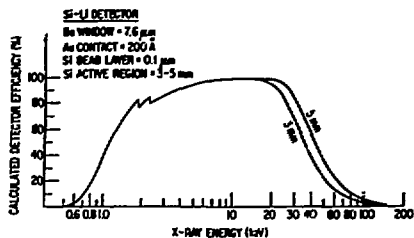


Figure 3. Calculated efficiency for a Si(Li) detector.

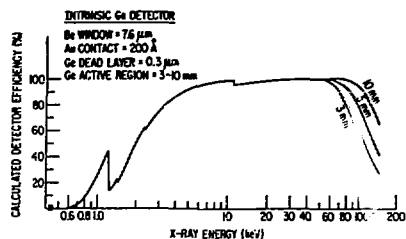


Figure 4. Calculated efficiency for a IG detector.

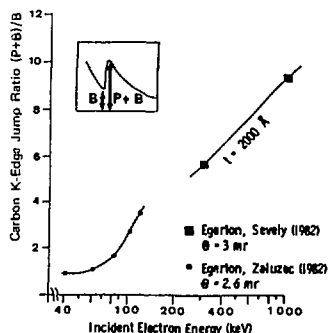


Figure 6. Experimental variation in Carbon K-edge jump ratio as a function of accelerating voltage.

ON THE INFLUENCE OF HIGH VOLTAGE IN ELECTRON ENERGY LOSS SPECTROSCOPY

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ABSTRACT

In the field of chemical microcharacterization, the use of electron energy losses associated with inner shell excitation of atoms, is becoming an important aspect of the development of electron microscopy. Experiments at low and high voltages, show that the specimen thickness t introduces one of the main limiting factors for the exploitation of the technique. We study here the influence of the t/λ_1 parameter, (defined farther) upon the ratio between the characteristic signal and the background intensities of a spectrum. We discuss then on the opportunity in the use of high accelerating voltage in electron energy loss spectroscopy. The results we present, have been obtained with a 1000 kV electron microscope equipped with an Ω system, [1]. They are compared with experimental results got at 80 kV with the same samples by R.F. Egerton, [2].

CONTRAST OF CHARACTERISTIC DISTRIBUTIONS.

The characteristic parts of a spectrum are made with electrons which have undergone single inner shell electron interactions. They are always superimposed over a background which is assumed to be produced by electrons which have suffered multiple inelastic interactions of various kinds. The relative importance of the characteristic signal can be evaluated by comparing it to the background intensity. We represent the characteristic signal contrast C by the jump ratio $C = I_M/I_m$. I_M is the maximum intensity of the characteristic distribution and I_m is the background intensity just before the inner shell ionization edge.

Assuming that the Poisson's statistics are applicable to the description of the scattering in the specimen film, the Fourier transform of the intensity $\hat{J}(E, t/\lambda_1, \theta_d)$ transmitted by the specimen through the objective lens aperture can be written:

$$\hat{J}(\omega) = \hat{G}_S(\omega) \left\{ 1 + \frac{t}{\lambda_1} F(\theta_d) \frac{\lambda_1}{\lambda_k} \hat{g}_k(\omega) \right\} \exp \left\{ \frac{t}{\lambda_1} F(\theta_d) \left\{ \hat{g}_1(\omega) + \frac{\lambda_1}{\lambda_2} \hat{g}_2(\omega) \right\} \right\}$$

In this relation, λ_1 is the mean free path for the main inelastic process (bulk plasmon excitations), λ_2 is the mean free path for a secondary inelastic process of minor importance than the preceding one, which also contributes to the background formation, λ_k is the mean free path for the inner shell excitation of the sample atoms. $\hat{g}_1(\omega)$, $\hat{g}_2(\omega)$, $\hat{g}_k(\omega)$ are the Fourier transforms of the energy loss functions $g_1(E)$, $g_2(E)$, $g_k(E)$, associated respectively with the inelastic processes defined previously, [3]. These latter normalized functions represent the probability for an electron to undergo a given energy loss E after an interaction of the corresponding kind. $F(\theta_d)$ is a function of the angle θ_d defined by the objective lens diaphragm and which reports the angular scattering in the specimen. $G_S(\omega)$ is the Fourier transform of the apparatus transfer function $G_S(E)$. This latter takes the energy fluctuations of the incident beam and the selecting slit effects of the dispersive system into account.

If we designate by $J_C(E, t/\lambda_1, \theta_d)$ the background intensity computed from the reverse Fourier transform of the function:

$$\hat{J}_C(\omega) = \hat{G}_S(\omega) \exp\left(\frac{t}{\lambda_1} F(\theta_d) \left\{ \hat{g}_1(\omega) + \frac{\lambda_1}{\lambda_2} \hat{g}_2(\omega) \right\}\right)$$

$J(E, t/\lambda_1, \theta_d)$ can be written:

$$J(E, t/\lambda_1, \theta_d) = J_C(E, t/\lambda_1, \theta_d) + \frac{t}{\lambda_1} F(\theta_d) \frac{\lambda_1}{\lambda_2} J_C(E, t/\lambda_1, \theta_d) * g_K(E)$$

where $*$ indicate the convolution product of two functions.

These relations allow to compute the energy loss spectra and to compare them to the experimental ones. The dotted curve, in figure 1, represents a computed spectrum fitted with an experimental spectrum (full curve) got with a 410 nm thick carbon foil at 1000 kV. The availability of the previous relations and of the models chosen to represent the energy loss functions, has been checked with various kinds of samples, various thicknesses and various experimental conditions: (accelerating voltage and selecting slit width). In any case, we have recorded a good fitting between experimental and computed spectra. [4].

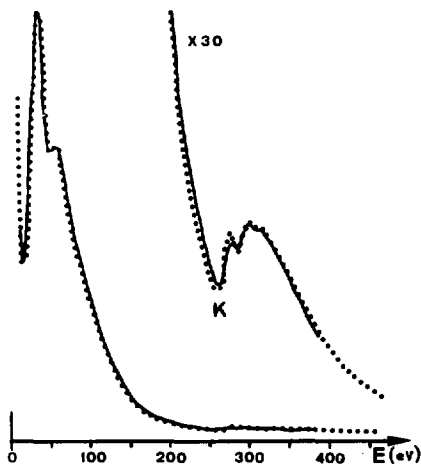


Figure 1 : Comparison of an experimental (full curve) and a calculated (dotted curve) energy loss spectrum for a 410 nm thick evaporated carbon film at 1000 kV.

The characteristic signal contrast has been measured from the computed spectra and compared with the experimental results. The full curve of figure 2 represents the variation of the computed contrast values as a function of t/λ_1 . The various points correspond to experimental values got at various accelerating voltages with carbon foils of various thicknesses. Taking the dispersion of measurements mainly due to signal noise into account, the experimental results are in good agreement with the theoretical ones. The contrast decreases when the thickness increases, then the best contrast got with the smallest t/λ_1 value.

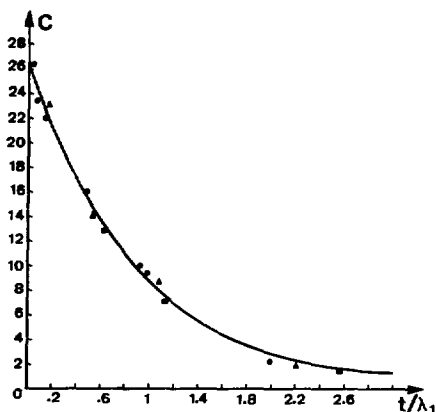


Figure 2 : Variation of the K-ionisation edge contrast as a function of t/λ_1 for carbon evaporated foils. Full curve: theoretical results. Points: experimental results got at 1000 kV($\circ$), 500 kV(Δ), 300 kV($\blacksquare$).

Since the mean free path of an inelastic process increases when the accelerating voltage increases,[5], it is better to work with high energy incident electrons, mainly when the specimen thickness cannot be got under control. Nevertheless, it will be necessary to keep the minimum intensity level widely above the level of the noise introduced by the recording system. These conclusions are in good agreement with the curves of the figure 3 which represent the experimental variation of the contrast as a function of the accelerating voltage for various thickness values of the sample.

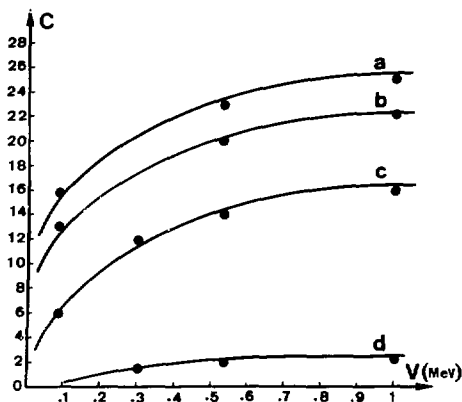


Figure 3 : Variation of the K-ionisation edge contrast as a function of the accelerating voltage for various thicknesses of carbon evaporated films. (a):16 nm, (b):32 nm, (c):100 nm, (d):410 nm.

APPLICATION TO CHEMICAL MICROCHARACTERIZATION

When the electron energy loss spectroscopy is applied to chemical micro-analysis, the energy losses used to characterize the elements of the sample can extend up to 2500 eV, which is enough to identify any of these elements. One of the main advantage in the use of high accelerating voltage, is to permit the chemical analysis of samples thicker than the ones investigated in a 100 kV electron microscope. The mean free path for the main inelastic process responsible of the background (generally bulk plasmons), is about three times greater at 1000 kV than at 100 kV. Experiments made in this field, with the 1200 kV electron microscope of Toulouse, show that chemical analysis of 200 nm thick biological samples is quite possible.

Figures 4 and 5 show spectra got with section of pathological tissues. Gallium has been located in the lysosomes of renal tubular cells and identified by its L_{23} ionisation edge at 1140 eV: (Figure 4)

Nickel has been detected on the periphery of tumoral cells. The edge of its L_{23} characteristic distribution appears in the spectrum at 860 eV. (Figure 5)

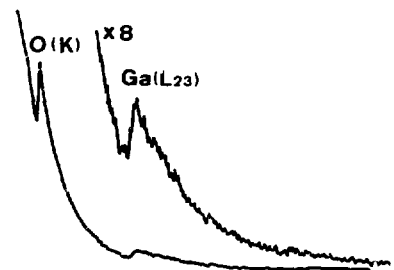


Figure 4: L_{23} -ionisation edge of gallium (1140 eV) from a 200 nm thick section of pathological tissues investigated at 1000 kV.

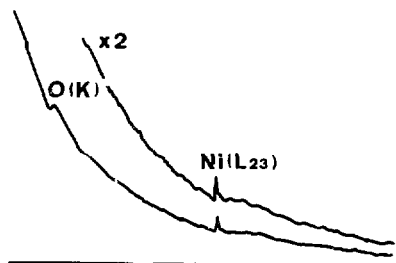


Figure 5: L_{23} -ionisation edge of Nickel (860 eV) located in tumoral cells at 1000 kV.

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CONVERGENT-BEAM ELECTRON DIFFRACTION AT THE CRITICAL VOLTAGE AND CONSIDERATIONS OF ANOMALOUS ABSORPTION IN CALCULATIONS OF ROCKING CURVES

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ABSTRACT

For the 333 reflection of silicon at the critical voltage the corresponding rocking curves have been calculated with different sets of absorption potentials. A special set could be found for which a very remarkable irregular modulation of the intensity in the vicinity of the Bragg position disappears. The rocking curves calculated for this set of data fit excellently to intensity patterns obtained in convergent-beam diffraction experiments which were done with a new, self-designed 1.25 MeV electron diffraction instrument.

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INTRODUCTION

In 1977, Moodie, Humphreys, Imeson and Sellar [1] reported on a very sharp extinction effect appearing at Bragg-satisfied reflecting positions in rocking curves calculated for the critical voltage V_c . A sensitive method for the registration of the angular variations of reflection intensities is the convergent-beam electron diffraction (CBED), introduced by Kossel and Möllenstedt [2]. Moodie et al. [1] proposed to combine the critical voltage effect and the convergent-beam diffraction technique in order to observe the theoretically predicted, fine extinction effect. This should be used for improved determination of structure factors. In 1980, Sellar, Imeson and Humphreys [3] published further experimental results: They did not observe the sharp central-peak extinction effect, which they had calculated, and they supposed this to be due to the limited angular resolution. In this paper, we report on corresponding investigations of the critical voltage effect appearing for the 333 reflection of silicon.

THE INFLUENCE OF ANOMALOUS ABSORPTION ON CALCULATED ROCKING CURVES

If a silicon single-crystal is set into 333 Bragg reflecting position, the Bloch waves #3 and #4 are most strongly excited. At the critical voltage V_c the wave vectors $\vec{k}^{(3)}$ and $\vec{k}^{(4)}$ degenerate and the contributions of the corresponding Bloch waves to the 333 reflection then interfere destructively. The contributions of the remaining Bloch waves can be summed up and, following Humphreys [4], form a small amplitude Δ .

If anomalous absorption is to be taken into account in many-beam calculations, the absorption potentials V_o^i and V_g^i must be given, but mostly the accuracy, with which these are known, is rather poor. As to silicon, several authors published theoretical or experimental values for the absorption potentials, differing from each other considerably.

In fig. 1 a convergent-beam diffraction pattern for the systematic row 111 of silicon is shown, which was recorded at the critical voltage $V_c \approx 1106$ kV. This value of V_c was measured by observing the vanishing and symmetry-reversal

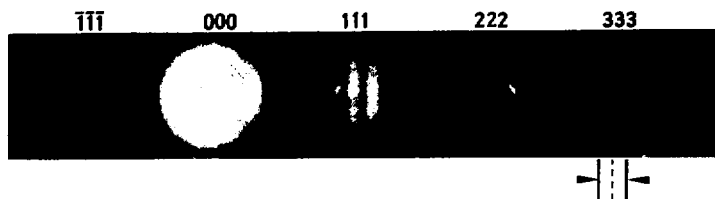


Fig. 1: Convergent-beam diffraction pattern recorded at the critical voltage $V_c = 1106$ kV for the Si 111 systematics, with 333 Bragg position satisfied. Crystal thickness: 7630 Å. Dashed line: position of 333 Bragg reflection. For the marked range of angles the rocking curves shown in the figures 2 and 3 have been calculated.

of Kikuchi lines at different crystal thicknesses. It is in good agreement with results published by Hewat and Humphreys [5].

For a small range of angles (see fig. 1) rocking curves were calculated by an exact solution of the corresponding full complex eigenvalue problem. Since the knowledge of the absorption potentials is rather poor, the consequences of variations of their values were investigated. For accelerating voltages near the critical voltage V_c , at the exact Bragg position a sharp peak in the intensity was found theoretically which splits by an extremely sharp minimum. Approaching V_c this double peak becomes higher and the central extinction effect becomes deeper and narrower (see fig. 2). A similar behaviour is reported by Sellar et al. [3] for their calculated extinction effect. The double peak is symmetrical only for certain crystal thicknesses. This remarkable modulation of the diffraction intensity depends very sensitively on the values of the absorption potentials, taken into account in the many-beam calculations. In particular, there are reasonable sets of absorption potentials for which the whole double peak does not appear at all (see fig. 3). Perturbation calculations yield the same results. In any case the sharp modulation can not be found, if absorption is neglected, so that it is clearly an absorption effect.

This theoretical intensity modulation is coupled with a discontinuity of the absorption coefficients of the degenerated Bloch waves. $q^{(3)}$ and $q^{(4)}$, given in fig. 4a as functions of the direction of incidence, are showing very sharp peaks at the critical voltage V_c . But for certain combinations of absorption potentials the irregularities do not appear at all. These combinations are clearly distinguished by the fact that at V_c the absorption coefficients of the two degenerated Bloch waves in question are exactly equal (see fig. 4b).

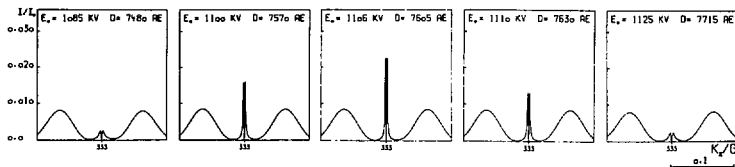


Fig. 2: Calculated rocking curves for the Si 333 reflection near $V_c = 1106$ kV. The absorption potential V_{111} is chosen to -0,125 volts.

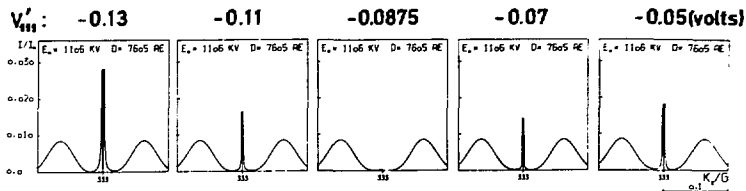


Fig. 3: Calculated rocking curves for the Si 333 reflection, exactly at the critical voltage for different absorption potentials V_{III} . For a certain value of V_{III} the sharp intensity modulation disappears.

Combined with the discontinuity of the absorption coefficients there is a deformation of the branches #3 and #4 of the dispersion surface in the vicinity of the 333 Bragg reflecting position. All these irregularities and their simultaneous disappearing for suitable sets of absorption potentials have also been found in other critical voltage configurations.

EXPERIMENTAL RESULTS

In approaching the critical voltage, the 333 Bragg reflection intensity decreases. But there need not exist a total intensity minimum. Due to the small contribution Δ of the weakly excited Bloch waves, the intensity at the exact 333 Bragg position oscillates with changing crystal thickness.

For the accelerating voltages considered here, the angular resolution of our new 1.25 MeV electron diffraction instrument is about 10^{-4} rad. This corresponds to the width of the finest diffraction fringes in fig. 1. Since in experiments an averaging of intensities over intervals of roughly 10^{-4} rad is unavoidable, the central sharp extinction effect can not be resolved in any case. The whole central pattern could only be detected by measuring its total intensity. In order to do this, one has to choose an appropriate crystal thickness, for which the contributions Δ of the weak Bloch waves disappear. This has been done, and the results are shown in the first column of fig. 5. There is no indication of any irregular intensity contribution. The experimental results excellently fit to the calculated curves based on the special set of absorption potentials. If a slightly different set is chosen, the outer parts of the rocking curves still fit to the experimental results, as is obvious in fig. 5.

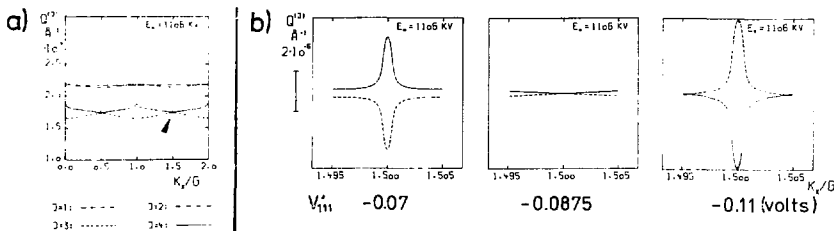


Fig. 4: a Bloch wave absorption coefficients for $V_{III} = -0.06$ volts at $V_C = 1106$ kV. The curves for $q^{(3)}$ and $q^{(4)}$ are sharply peaked.
b Absorption coefficients in the vicinity of the 333 Bragg position at the critical voltage for different absorption potentials V_{III} .

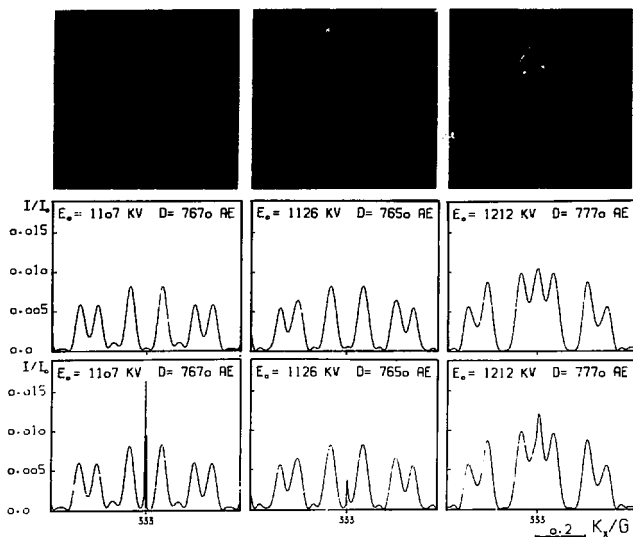


Fig. 5: Comparison of experimental 333 reflection discs with theoretical rocking curves. The curves in the middle row are calculated for $V_{111} = -0.0875$ volts and the curves in the lower row for an adopted value of -0.125 volts. In the pattern, recorded at $V_c = 1107$ kV, there is no indication of the existence of the sharp intensity modulation shown in the lower rocking curve. For voltages differing distinctly from V_c the rocking curves of the middle and of the lower row become similar.

SUMMARY

The extreme intensity modulations in the vicinity of the Bragg position which have been predicted theoretically as a peculiar effect at the critical voltage, could not be discovered experimentally. This does not contradict to the experimental results of other groups. For the critical voltage a set of absorption potentials could be found for which all irregularities disappear simultaneously and which fits excellently to our experimental results. This seems to indicate that the absorption potentials are related strongly to each other and to the structure potentials by requirements of consistence.

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TWO-DIMENSIONAL IMAGE DISPLACEMENT
BY ELECTROSTATIC DEFLECTOR IN TRANSMISSION H V E M

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Image visualization in transmission electron microscopy is accomplished by fluorescent phosphors and by photographic recording. While convenient and effective in general in producing the conversion from electron-optical to optical image, these processes suffer from several qualitative and quantitative deficiencies such as limited linearity of response, no direct specimen quantitation, no pixel accumulation to high statistics and no on-line image enhancement. At high accelerating voltages, furthermore, image contrast is reduced and cross talk in the phosphor makes for poor screen visibility and resolution.

To remove some of these limitations and to introduce electronic flexibility in the acquisition and manipulation of pixels in transmission HVEM a relatively simple scheme has been recently described [1,2,3]. In this scheme image pixels are defined by an aperture located at the bottom of the column below the camera in combination with the selected magnification. Electrons accepted by the aperture are further collimated and then bent through 90° in a magnetic field before reaching an electron detector in a shielded area. These latter features are necessary to remove the radiative component that accompanies high-energy electrons. By sweeping the beam across the aperture in a two-dimensional raster by means of two orthogonal pairs of electrostatic plates located in the column below the specimen the image is dissected into pixels that can be electronically detected, stored or manipulated at will.

It had been determined earlier with fixed beam [2,3] that the response of the detector adapted to a JEOL JEM-1000 is indeed linear and that beam intensity is stable within a few percent. With a single pair of plates image displacements of approximately 1.5 mm/V and 1.1 cm/V across the plates were obtained at magnifications 10,000 and 100,000, respectively, as well as transmission profiles of overfocus and underfocus Fresnel fringes at magnification 250,000 with a scanning spot size equivalent to 0.6 nm.

A two-dimensional deflector assembly consisting of two orthogonal pairs of plates 5 cm long and 1.5 mm apart was recently completed and installed inside the objective lens. Bench tests indicated that frequency signals from a function generator remained practically unchanged at the plates throughout the range tested (up to 1 MHz). An example of two-dimensional image displacement by fixed voltages at 1 MV and instrumental magnification 5,000 is shown in the figure. It should be noted that the image appears to remain undistorted in both directions and that the bottom plates are slightly less effective in displacing the beam, as expected, because in the fixed geometry of the microscope column they push the electron trajectory sideways slightly later than the top plates.

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As a simple application of this image-displacing scheme diffraction spots can be shifted to the axial electronic channel for direct quantitation or for determining their beam-induced attenuation. Complete two-dimensional images were displayed on a CRT by applying the ramp signals of a scan generator to the deflector plates. Recordings of such CRT images should be available soon.

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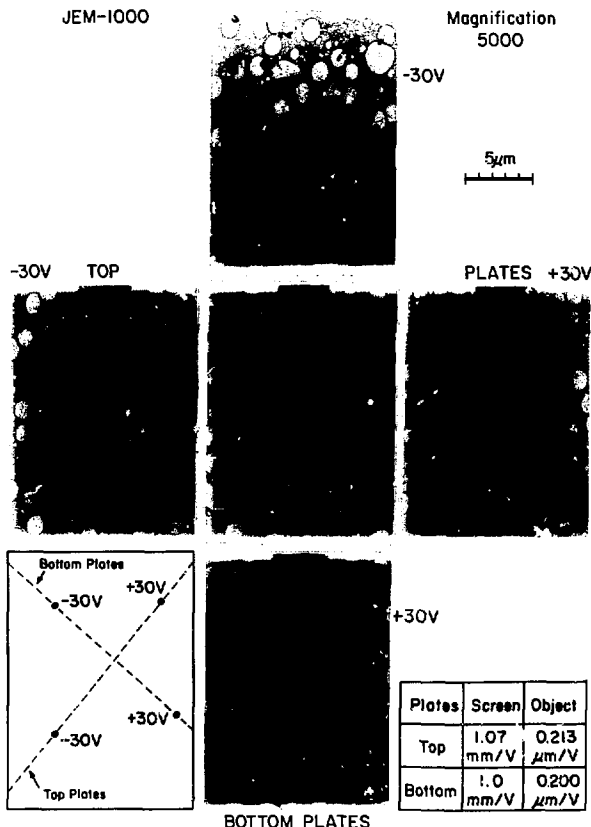


Image displacement in two orthogonal directions by uniform electrostatic fields inside the objective lens and perpendicular to the direction of the magnetic field. Each frame covers entire micrograph area. Specimen and stage positions fixed. Numbers near each frame indicates the voltage applied to the corresponding plates. Note lack of distortion in either direction. 1 MV. Instrumental magnification 5,000.

SCATTERING AND BACKSCATTERING OF 1 MEV ELECTRONS

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ABSTRACT

The spatial distribution of the electrons inside the interaction volume was determined experimentally in the HVEM. The corresponding intensity profiles were compared to the results of Monte-Carlo calculations. The difference was attributed to the fact that the interference among scattered electrons is not taken into account in those calculations. A simple model is presented which permit the introduction of the effects of interference in the Monte-Carlo calculations.

INTRODUCTION

A knowledge of the size and shape of the interaction volume in solids is essential in the study of the various phenomena related to the interaction of electrons with matter, such as X-ray microanalysis, resolution of detectors (phosphor screens) and the "top-bottom" effect which is one important factor limiting resolution in the transmission or scanning electron microscopes. Moreover, in the case of quantitative X-ray analysis, knowledge of the spatial distribution of the electrons inside the interaction volume is absolutely necessary when the particle size is smaller than this volume. The signal distribution would be strongly affected by the electron density at the centre of the interaction volume. In the worst situation, if this density is negligible, then the particle will not be detected.

Direct experimental visualization of the interaction volume has already been performed in certain targets such as gases (air [1] and N₂ [2]). The spatial distribution is obtained by Abel inversion of the experimentally obtained sideview intensity profiles. Indirect experimental visualization has also been made in luminescent materials [3] and in polymethylmethacrylate [4]. In this last case, the chemical etching following the electron beam interaction has revealed the extent and shape of the interaction volume. However, to our knowledge, no direct observation of penetration and scattering of electrons in metals have so far been published.

EXPERIMENTAL DETERMINATION OF THE SPATIAL DISTRIBUTION OF ELECTRONS

Due to the size of the interaction volume in light metals such as Al at high voltage (2 mm at 1 MV), it is possible to determine experimentally the spatial distribution of the electrons inside this volume. A metal target is bombarded by a fine parallel electron beam. This target is designed as follows (Fig. 1). A photographic film is placed between two metal plates, the emulsion being directed towards the incident beam. The metal plate which is placed over the film is thinner than the depth of the interaction volume, whereas the other plate is much thicker. Consequently, the film will intersect the interaction volume at a depth which is determined by the thickness of the upper plate. The density of electrons inside the interaction volume may thus be recorded at various depths. A microdensitometer trace will give the spatial distribution of the electron density inside the interaction volume.

In fact, two types of illuminations were used. In the case of a fine parallel beam, the spatial distribution (the point spread function) is obtained directly from the microdensitometer trace. However, even the finest beam will have a certain spatial extension and a certain angular aperture, and is only a rough approximation to a point illumination which can be mathematically represented by the unit impulse generalized function δ . Consequently, a step-pattern of illumination was also used. The line spread function F , which is the derivative of the response to the step-pattern of illumination, can be easily determined. The line spread function F is related to the point spread function f by the following integral equation :

$$F(x) = \int_{-\infty}^{\infty} f(x,y) dy$$

The point spread function may thus be determined from the line spread function since the two functions are related as Abel transform pairs.

If the response to the step pattern of illumination can be represented by an error function erf, then its derivative i.e. the spread function F is a gaussian function :

$$F(x) = K \exp - K^2 x^2$$

The parameter K is calculated by making the analytical form fit the microdensitometer trace. The point spread function is then equal to :

$$f(r) = K^2 \exp - K^2 r^2 \quad (r^2 = x^2 + y^2)$$

The spatial distribution of the electron density at various depths is indicated on Fig. 2. The two types of illumination i.e. the fine beam and the step pattern of illumination give very similar bell-shaped curves. At the bottom of the interaction volume, the width of the curve is smaller, which corresponds to the well-known pseudo-spherical shape of the interaction volume. The same experiments were also performed on an amorphous material (glass) and similar bell-shaped curves were obtained.

The intersection of the interaction volume with the surface corresponds to the lateral extent of back-scattering which may limit the resolution of the image in HVEM. A special transmission screen, designed in order to eliminate back-scattering effects was described in a previous paper [5]. A reflection screen taking advantage of back-scattering was also designed. At a voltage lower than approximately 800 KV, the lateral extent of back-scattering in a heavy metal (Pt) is comparable in size with the diffusion of light in a phosphor coating. A twofold increase in brightness may thus be obtained, the resolution being maintained.

The spatial distribution of the electrons inside the interaction volume directly affects the signal distribution in the case of X-ray microprobe analysis. This aspect is essential in the analysis of small particles in metallurgical specimens when the particles are smaller than the interaction volume. This is the reason for which those experimental determinations of the spatial distribution have been compared with the results of Monte-Carlo calculations which are frequently used to simulate the electron scattering process leading to X-ray production.

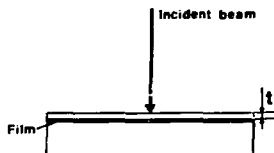


Fig. 1 - The experimental device.

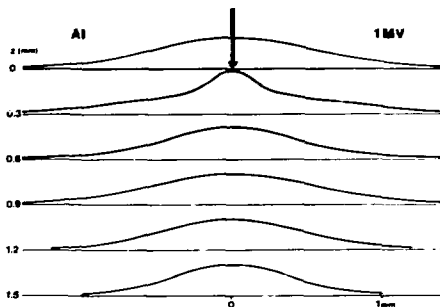


Fig. 2 - The spatial distribution of the electrons inside the interaction volume.

COMPARISON WITH MONTE-CARLO CALCULATIONS, CONCLUSION

The direct simulation of electron scattering by Monte-Carlo calculations schematically consists in dividing the electron trajectory into a number of steps, the step length being correlated to the mean free path of the electron at the energy of the step. The angular deflection of the electron by elastic scattering is generally selected from the screened Rutherford cross-section. The results of the Monte-Carlo calculations are usually represented by a projection of the trajectories of the electrons. This representation only gives the size and shape of the interaction volume and an idea of the sideview intensity. However, it does not provide any information regarding the density of electrons inside the interaction volume. This last type of information can only be obtained through histograms of the electron density inside the interaction volume. In fact, at a certain depth, these histograms do not present a maximum of intensity in the direction of the incident beam. This phenomenon has already been reported in a paper concerning Monte-Carlo calculations for high energy electrons in gold thin foils ([6] p 14). Consequently, a critical investigation of the Monte-Carlo method has been undertaken in order to explain this difference between the experimental determination of the spatial distribution of the electrons inside the interaction volume and the Monte-Carlo calculations.

The Monte-Carlo calculation consists in assimilating the target to a certain number of randomly distributed scattering centres. When the electron is scattered by one of these centres, the deflection angle is given by the scattering cross-section ($\sigma(\theta) = r^2(\theta)$) of the scattering centre e.i. the atom. However, the intensity of the diffraction pattern of N randomly distributed identical diffusing scattering centres is not only N times the intensity of the scattering cross-section, but the sum of this term $N r^2(\theta)$ and another term $N^2 r^2(0)$ which corresponds to a central peak (Fig. 3). This well-known phenomenon of optics and X-ray optics [7] may also be easily observed in the electron microscope. The diffraction pattern of an amorphous material (metglas) clearly shows the presence of the central peak (Fig. 4). The height and the area of this central peak may thus be determined experimentally, thereby giving for different thicknesses, the ratio of the electrons propagating in the direction of the incident beam to the scattered electrons. In fact, Monte-Carlo calculations may be considered as a convolution approach to represent N scattering events; consequently, the central peak $N^2 r^2$, which corresponds to the wave aspect of the interaction, cannot be taken into consideration.

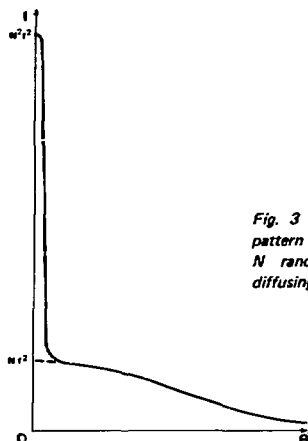
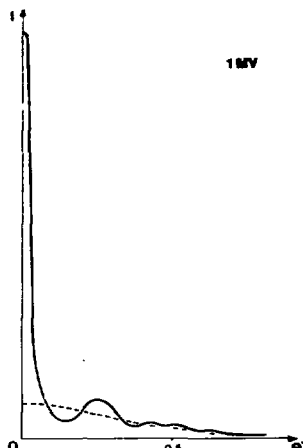


Fig. 3 - The diffraction pattern corresponding to N randomly distributed diffusing centres.

Fig. 4 - Experimental determination of the diffraction pattern of an amorphous material (metglas).



The Monte-Carlo method has to be modified in order to take into account this central peak phenomenon. One possible modification is to introduce a certain number of electrons propagating in the direction of the incident beam. The number of these electrons may follow an absorption law, for instance the familiar exponential decay and may be determined experimentally from scattering patterns of amorphous specimens of various thicknesses. The electrons leaving this direction will then be scattered in the same conditions than the other electrons.

As a conclusion, the discrepancy between the experimental bell-shaped intensity profiles and the histograms may be attributed to the fact that the interference among scattered electrons is not taken into account in the Monte-Carlo calculations. The wave aspect of the interaction corresponds to a central peak in the diffraction pattern of N randomly distributed scattering centres. This phenomenon may be taken into consideration in Monte-Carlo calculations by introducing a certain number of electrons propagating in the direction of the incident beam. This model is presently being tested and the parameters will be adjusted to make the histograms match the experimental spatial distribution of the electrons inside the interaction volume.

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THE 3-D RECONSTRUCTION OF CARBON BLACK IN THICK SECTIONS OF A POLYCARBONATE MATRIX

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ABSTRACT

The digital conversion of mass thickness images of carbon black embedded in thick sections of polycarbonate and the representation of these data points by computer graphics enables the morphology of the long chain molecules to be evaluated in much more detail than conventional stereo representations permit. The algorithms are quite straightforward and simply project the coordinates from individual micrographs, taken at different foil orientations, to provide a consistent three-dimensional image. The resulting digital image can be represented, totally or in part, in projection at any angle and the high density of detail that becomes an encumbrance in a straightforward stereo projection of a thick section can be readily deciphered.

A micrograph of an isolated chain of carbon black is shown in figure 1 and for the sake of example it has been simplified in figure 2 to a ball and stick model containing some of the carbonaceous spheres. The projections in figure 2 constitute a normal stereo pair and the rotation between them is 4° about the axis shown.

When the tilt axis is taken as the y axis the displacements perpendicular to it (x_1), induced by the rotation (α) are given by $r\{\cos\phi - \cos(\alpha + \phi)\}$ where ϕ is the angle which subtends the position vector (r) to the foil plane.

When a sufficient number of points can be identified between the two projections it becomes unnecessary to identify the angle of tilt or to establish the tilt axis on the micrograph and an iterative procedure can be used to determine them both. The simplicity of the image reconstruction from a technical point of view is however offset by the length of time needed for the computation of the coordinates.

The values of the x and y coordinates for the indicated spheres are shown in the Appendix in the format suitable for their computation by a simple program which calculates the z coordinates. The output from this program (program z) is in a coordinate system appropriate to the first projection and by using a similar program these points can be subsequently projected. Some examples of the alternative projection of the ball and stick model are shown in figure 3.

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Figure 1 Bright field micrograph of carbon black

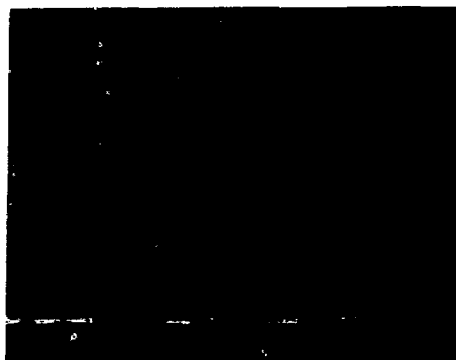
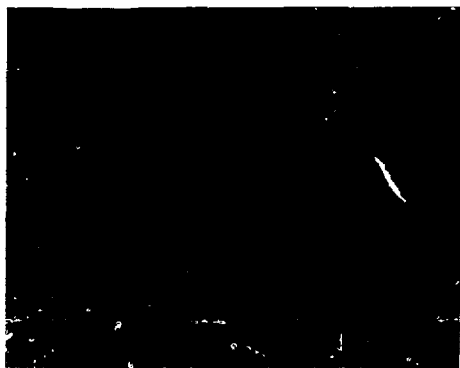


Figure 2 Stereo pair of the carbon black separated by 4°

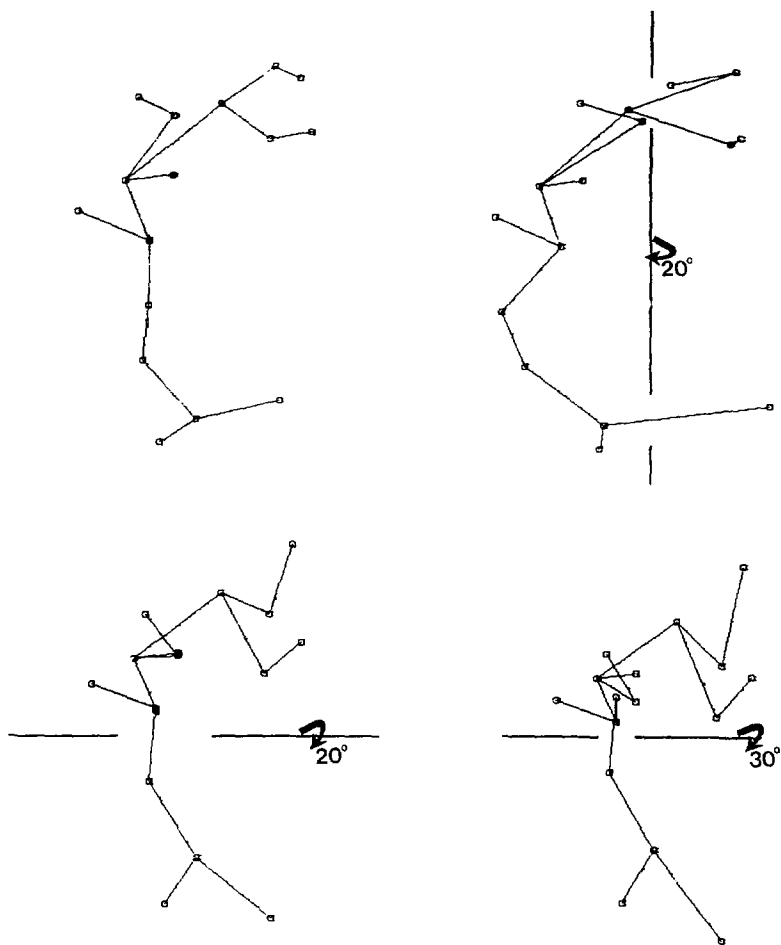


Figure 3 Reconstructed projections of the simplified chain outlined in figure 2

APPENDIX

```

      program Z
      common X1(100),X2(100),Y1(100),Y2(100),Z1(100),Z2(100)
      open (unit=2, name='XY.DAT', type='OLD')
      open (unit=3, name='XYZ.DAT', type='NEW')
      read(2,10) ALPHA
10    format(2x,f10.5)
      do 40 I=1,100
          read(2,20,FRR=50) X1(I), Y1(I), X2(I), Y2(I)
20    format(4(2x,f10.6))
          N=I
40    continue
50    close (unit=2)
      call ZFNDEK (ALPHA, N)
      do 60 I=1,N
          write(3,30) X1(I), Y1(I), Z1(I), X2(I), Y2(I), Z2(I)
30    format(6(2X,F10.6))
60    continue
      close (unit=3)
      stop
      end
c*****
      subroutine ZFNDEK (ALPHA, N)
      common X1(100),X2(100),Y1(100),Y2(100),Z1(100),Z2(100)
      ALPHA =ALPHA/57.29577951
      DO 50 I=1,N
          PHI = ATAN((1/TAN(ALPHA))-X2(I)/(X1(I)*SIN(ALPHA)))
          R2 = X2(I)/COS(PHI+ALPHA)
          Z2(I) = R2*SIN(PHI+ALPHA)
          Z1(I) = R2*SIN(PHI)
          PHI = PHI*57.29577951
          write(5,30) Z, PHI
30    format(' Z = ',F10.5,' PHI = ',F10.5)
50    CONTINUE
      return
      end
c*****
      Input Data in file labeled 'XY.dat'

```

4.00000				!1st line contains
7.00000	0.00000	6.50000	0.00000	!angle of rotation.
10.00000	2.00000	10.00000	2.00000	!The following lines
17.00000	3.50000	15.50000	3.50000	!of data are X1,Y1,X2
5.50000	7.00000	6.00000	7.00000	!and Y2 formatted as
6.00000	11.50000	7.00000	11.50000	!shown in line 20 of
6.00000	17.00000	6.00000	17.00000	!main program.
0.00000	19.50000	0.00000	19.50000	
4.00000	22.00000	4.00000	22.00000	
8.00000	22.50000	8.00000	22.50000	
16.00000	25.50000	15.00000	22.50000	
19.50000	26.00000	19.00000	26.00000	
8.00000	27.50000	7.00000	27.50000	
12.00000	28.50000	12.00000	28.50000	
5.00000	29.00000	4.50000	29.00000	
18.50000	30.50000	19.00000	30.50000	
16.50000	31.50000	15.50000	31.50000	

AN EVAPORATOR FOR IN-SITU STUDIES OF SURFACES AND THIN FILM GROWTH IN AN UHV 1MV HIGH RESOLUTION ELECTRON MICROSCOPE

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ABSTRACT

An in-situ deposition system for an UHV 1MV high resolution electron microscope(HU-1250), whose residual pressure in its specimen chamber is at 10^{-6} Pa level without use of cold traps, has been developed. The system is composed of an evaporator unit, a liq.He cooled cryogenic tip around the specimen and a side-entry heating specimen holder. The evaporator has two filaments from which two substances can be deposited successively. A deposition rate from each source is monitored by a quartz oscillator. 0.23 and 0.2nm spaced lattice fringes are resolved during and after depositions of Au and Ag, respectively. The technique to study surfaces and surface processes in-situ with atom resolution is basically established.(This work was supported by Grant-in Aid for Developmental Scientific Research 56850161)

INTRODUCTION

Bassett introduced an evaporator in an electron microscope and showed a usefulness of an in-situ deposition technique for thin film growth studies[1]. We have developed a technique of UHV electron microscope and in-situ deposition and clean substrate preparation techniques, and have shown details of various growth processes[2,3]. Recently, the techniques have been applied to studies of surface processes at monolayer level in both transmission and reflection modes of the microscope[4]. The results showed microtopography of surfaces such as surface atomic steps, motions of them due to sublimation and deposition, reconstructed surface structures and their domains and phase transitions and adsorption processes, which were hardly known by conventional surface analyzing techniques such as low energy electron diffraction, Auger electron spectroscopy.

The previous surface observations, however, were made under several tenth of nanometer resolution. To improve the resolution we have developed an UHV 1MV high resolution electron microscope(HREM). A base pressure in its specimen chamber is at 10^{-6} Pa level without use of cold traps. A high resolution pole piece with C_s of 2.5mm at 1MV is used for both top- and side-entry holders[5].

The present paper describes design and operational features of a new in-situ deposition system for the high voltage electron microscope(HVEM). HREM studies of clean surfaces are reported in a separate paper[6].

DESIGN FEATURES OF THE SYSTEM

The system is composed of an evaporator for depositions, a cryogenic tip and cryogenic plates to reduce a local pressure around the specimen and a side-entry specimen heating holder.

EVAPORATOR: The evaporator is UHV tight and exchangeable through an airlock system by a pneumatic drive. Figure 1 shows a vertical cross section of the specimen chamber and the evaporator, and Fig.2 shows another cross section per-

pendicular to Fig.1. In Fig.1(see also Fig.2), an evaporator head(1) with two filaments(details of which are shown in Fig.3) and water-cooled quartz thickness monitors(2,2') are at their working positions for depositions on to a substrate specimen(3). For an evaporant exchange the head(1) is removed to a left position indicated by dotted lines through a gate valve(4). Valves(5,6,7) are for an airlock system and for a double O-ring seal(8) to reduce a leak during the motion of the head. When the head is removed, the thickness monitors are also removed to positions indicated by dotted lines. Thus, the top-entry specimen chamber can be used for an exchange of a top-entry specimen holder. The motion of the monitors is bellows-sealed. When the head is at its working position, the airlock space is separated from the specimen chamber by a greaseless O-ring and is evacuated differentially by a turbomolecular pump.

In Fig.2 the geometrical configuration of the head(1), the monitors(2,2') and the specimen(3) is more clearly seen. The vapour streams from the filaments (11,11') separated by a wall(12) reach to the monitors and the substrate through holes of a fixed cylinder(14) and a shutter cylinder(13). The motion of the shutter is bellows-sealed(17)(see Fig.3). A modified top-entry holder(15) and a plate(16) are protectors to prevent a top-entry goniometer and others from being contaminated by evaporated materials. An extra electrode(18) in Fig.3 is for a high voltage power supply which will be used in case of a modified evaporator head of an electron gun type for refractory metal depositions.

Figures 4 and 5 are photographs of the evaporator and that attached to the microscope, respectively. Air cylinders for pneumatic drives are arrowed.

CRYOGENIC SYSTEM: To reduce a local pressure around the specimen a liq.He(or N₂) cooled tip(19) which surrounds the specimen holder(10) in Fig.2 was made. It can be cooled down to 20K and its temperature is monitored by a carbon resistor. The tip is removable and a hole(20) on the left is used for a top-entry holder. In order to reduce the pressure in the top-entry specimen chamber, a liq.He(or N₂) cooled removable plate(21) and a liq.N₂ cooled fixed plate(22) are devised.

SIDE-ENTRY HEATING HOLDER: A single tilt specimen heating holder(<1000°C) has been used. A double tilt specimen heating holder(±30°, <1200°C) will be used.

PERFORMANCE

Vacuum: Evaporants and a substrate crystal can be exchanged independently and the pressure in the specimen chamber recovers to 10⁻⁶ Pa level within ten minutes after the exchange. The use of the cryogenic system reduces the pressure in the specimen chamber to a low level of 10⁻⁶ Pa. Around the specimen much lower pressure is expected to be realized(Liq.He cryogenic tip). No deterioration of the ultimate vacuum was noticed by putting the evaporator in the chamber.

DEPOSITION: Ag and Au were deposited on to air cleaved thin crystals of molybdenite(MoS₂) at 30-350°C. The substrates are cleaned by heating(800-900°C) at the specimen position. The specimen holder is out-gassed by preheating at around 900°C in a separate UHV chamber. Fig.6 shows a sequence of Au growth on MoS₂ at 270°C. Moire fringes(1.7nm) are due to (111) oriented Au and MoS₂ lattices. Growth processes similar to those observed with use of UHV 100kV microscope were observed. So called secondary nucleation is seen at positions indicated by arrows.

RESOLUTION: Figure 7a) shows (111) lattice fringes of a multiply twinned particle of Au "during" deposition at "270°C", and (b) shows (111) lattice fringes of Au platelet grown at a brim(arrowed) of a MoS₂ film and (10,2)_M lattice fringes. (200) lattice fringes of Ag and Au could also be resolved during specimen heating and liq.He flow. When the flow was stopped and the specimen was at room temperature, specimen vibrations due to the flow were reduced and

(220) lattice fringes (0.14nm) of deposited particles could be resolved. **OBSERVATIONS OF CLEAN SURFACES OF DEPOSITED METALS:** Figure 8 shows a diffraction pattern and a dark field image from (111) oriented Au platelets grown on MoS₂. As observed previously with use of the UHV 100kV microscope[7], diffraction spots A, B and C due to the reconstructed structure of the clean Au(111) surfaces and the forbidden (10,0)_G(Au) reflections are seen in (a) together with (10,0)_M(MoS₂) reflections and in (b) 6.3nm spaced fringes (A, B and C) due to the reconstruction are seen. In Fig.9 of (10,2)_{hex} Ag(grown on MoS₂) dark field image, monatomic high terraces bordered by surface steps are seen[8].

IRRADIATION EFFECT: An irradiation of 1MeV electrons causes lattice defects in crystals. Damages in substrates were noted as an increase of nucleation density of deposits in irradiated areas. Damages in the overgrowth were noted during observations of flat surfaces of Ag platelets. Small bright or dark disk images with contrast similar to that of surface terraces in Fig.9 were noted.

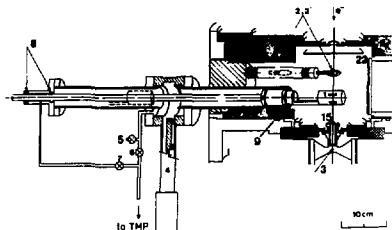
CONCLUSIONS

The in-situ deposition system devised for the UHV LMV HREM have satisfactory performances of vacuum, in-situ deposition and resolution. The system does not disturb other users and does not deteriorate the basic performance of the HREM[9]. The observations of the surfaces in Figs.8 and 9 indicate that the routine surface studies can be done with use of the present system as in the case of the UHV 100kV microscope[4]. An increase of a penetrating power in HVEM does not cause a decrease of image contrast of surface structures. Since the microscope has a point to point resolution around 0.17nm[9], structure imaging of clean and adsorbed surfaces is possible with use of the present system[6]. Fig.9 suggests that clean surfaces without a substrate can be observed and that an edge on observation is also possible.

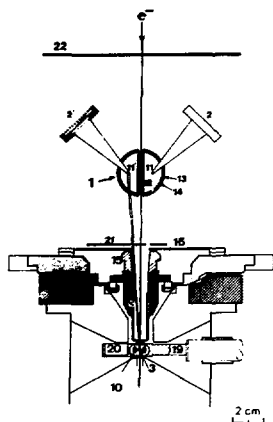
The authors express their sincere thanks to Professor Nagakura for his support of the present work.

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↑ Fig. 1 A vertical cross section of a specimen chamber and the evaporator.

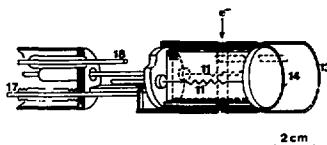
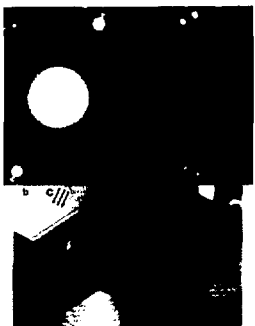


+ Fig. 2 A vertical cross section of a specimen chamber perpendicular to Fig. 1.

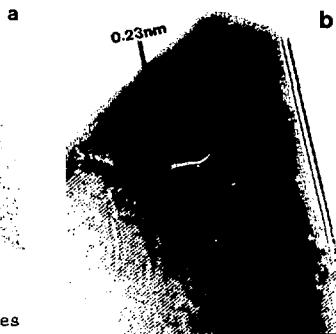
+ Fig. 4 Evaporator.

+ Fig. 5 Evaporator attached to the microscope column.

+ Fig. 6 Growth sequence of Au on MoS_2 at 270°C .



+ Fig. 3 Evaporator head.



+ Fig. 7 (111) lattice fringes of Au taken (a) "during" and (b) "after" deposition on MoS_2 at 270°C

+ Fig. 8 Diffraction pattern (a) and a dark field image (b) of the reconstructed structure of clean Au(111) surface.

+ Fig. 9 Atomic steps on Ag(111) surface.



DYNAMIC RECORDING SYSTEM FOR HVEM IN SITU STUDIES*

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INTRODUCTION

In many high-voltage electron microscope (HVEM) in situ studies, such as those dealing with deformation or gas-solid reactions, the microstructural changes of interest often occur too rapidly to be recorded by the standard plate camera and possibly even to be observed visually. Conventional still photography does not lend itself to represent the dynamic nature of these processes or to document the continuous microstructural evolution involved. A dynamic recording system based on a low-light-level television (LLTV) camera/videotape recorder (VTR) is under development for the ORNL Hitachi HU-1000 HVEM.

SYSTEM DESCRIPTION

A schematic diagram of the dynamic recording system is given in Figure 1. An electrically isolated vacuum chamber was attached to the bottom of the HVEM plate camera. The transmission phosphor screen is located near the bottom of this chamber, which also serves as a deep Faraday cup for beam current measurements. The 15-cm-diam phosphor screen is located ~32 cm below the plate camera giving an additional 1.7 $\times$ magnification and is viewed from below through a viewing port and 45° front surface mirror. The 90° bend in the optical path allows the COHU 7302A isocon LLLTV camera to be placed outside the radiation shielding below the HVEM plate camera chamber. The nonintensified isocon was selected to achieve reasonable low-illumination capability without sacrificing image resolution. The camera can be operated with either of two high-speed close-conjugate lenses, a Cannon 50-mm, f1.4 lens with closeup lens or a CTR Nikkor 55-mm f1.2 lens designed for close-conjugate imaging and high transmission of phosphor images. The LLLTV camera can be replaced by a Cannon 35-mm camera both for still photography and for system resolution testing (including the Cannon lens). The recording system is a Panasonic NV-9600 VTR with a NV-A960 editing controller for slow-speed playback and inspection.

PERFORMANCE TESTS

Initial performance tests on the dynamic recording system indicated that high-quality video images could be obtained at image current densities of $\sim 2 \times 10^7 \text{ e cm}^{-2} \text{ s}^{-1}$ (at the plate camera height). This current density is slightly less than used for typical exposures (5 s) with the plate camera and is 5-20 times lower than required for visual observation from the reflection phosphor screen. Thus, a usable image can be recorded with at least 200 times lower electron dose per frame.

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One of the critical elements in the dynamic recording system is the transmission phosphor screen. Various HVEM investigators have reported using phosphor screens deposited on either thin foil substrates or directly on the viewing window. For the current system, two thin foil screens were made by deposition of P-11 phosphor ($\sim 20 \text{ mg cm}^{-2}$) on substrates of 25- μm -thick aluminum ($\sim 1.7\%$ of the 1 MeV electron range) or 75- μm -thick molybdenum ($\sim 18\%$ of the 1 MeV electron range). Relative screen brightness was estimated by measuring the exposure (optical density) curve as a function of image current for 35-mm photographs of the phosphor screen recorded under standardized conditions. System resolution was measured by a method similar to that used for estimating film resolution by Downing [1]. A 50-mesh grid test object ($\sim 100\%$ contrast) was placed in the normal plate camera position and was imaged on the phosphor screen by simple shadow projection. The resultant images were recorded with the 35-mm camera using Plus X film. Optical diffractograms of the 35-mm negatives were used to estimate the highest spatial frequency multiple of the grid spacing recorded in the negative, from which the number of lines per frame was calculated. Figure 2 gives an example of the grid image and the resultant optical diffractogram which indicates a system resolution of 1300 lines/frame. Initial comparative studies between the aluminum and molybdenum substrate screens indicated similar brightness within the reproducibility of coating thickness. However, the resolution obtained with the molybdenum substrate was 2-3 times poorer than with the aluminum substrate, presumably the result of increased electron scattering. For this reason, all further studies employed phosphor screens on aluminum substrates.

It became evident from the early performance tests that there was a background level of light detected in areas of the phosphor screen where no incident electrons were present. This effect is easily visible in Figure 3 where identical exposures of different-sized selected area apertures were recorded under constant current density (i.e., increasing image current). The amount of light detected from areas of the phosphor screen masked by the aperture increased with total image current. On the basis of the measured optical densities of the negatives and the exposure curves of the film, the amount of light detected in the masked areas of Figure 3(c) was equivalent to that resulting from one-sixth the current density of the central area. This indicates a decreased image contrast from the $\sim 100\%$ level of the electron image to an 84% level of the light image. Possible origins of this background include reflected light or secondary fluorescence of the phosphor screen by scattered electrons or by bremsstrahlung produced by those electrons.

In order to check if reflected light was the origin of the background, the phosphor was completely removed from one area of a transmission screen and the intensity of background light was measured with the image of a small SAD aperture on areas of the screen with and without phosphor. For a screen 2.5 cm above the window, little or no change in background intensity was observed, indicating that reflected light was not the origin of the background.

The dependence of background intensity and system resolution upon the height of phosphor screen above the viewing window was investigated in order to understand the origin and influence of the secondary fluorescence process. Three screen-to-window spacings were used; contact (to simulate a thick substrate screen), 25 and 146 mm. Figure 4 illustrates the effect of screen-to-

window spacing on the image of an SAD aperture (prints were made to preserve relative optical densities of the negative and give similar image sizes). At contact [Fig. 4(a)], the background is quite low, but the edge of the aperture image is slightly blurred. The directionality of the blurring probably arises from a correctable nonparallelism between phosphor screen and camera film plane. At 25 mm spacing [Fig. 4(b)], significant uniform background and edge blurring are observed. At 146 mm spacing [Fig. 4(c)], the background is quite low and the edge sharpness is good. Table 1 gives the measured system resolution as a function of screen height and f-stop of the Cannon lens with a 2-diopter closeup lens. The surprising result is that the system resolution is strongly dependent on the f-stop of the lens and only weakly dependent on screen height. Although the specified performance of the Cannon lens is greater than that observed, the resolution for close-conjugate imaging is apparently degraded. Such an observation is supported by the second measurement of resolution at 146 mm in Table 1, which was performed without the close-up lens. On the basis of system resolution, a spacing of 146 mm is best. However, for such a system, a larger focal length lens (~100 mm) is required to achieve the desired image demagnification for the LLLTV image tube. Such a lens with a large aperture, close-focusing capability, and flat field of focus is probably unobtainable. The next choice appears to be a phosphor screen deposited on the viewing window with a close-conjugate lens. If the localized edge degradation resulting from the secondary fluorescence process is small relative to the screen (frame) diameter, the system resolution will be limited by the LLLTV camera and not by the phosphor screen. Resolution tests of the current system with a lower contrast (~30%) test object (a magnification-calibration grid) indicate system resolution (not including the LLLTV camera) of greater than 600 lines/frame, which exceeds the camera resolution.

- [1] K. H. Downing, Proc. 37th Electron Microscopy Society of America, ed. by G. W. Bailey, Claitor's Publ. Division, Baton Rouge, 1979, pp. 126-27.

Table 1. System Resolution (lines/frame)

f-stop	Screen Height		
	Contact	25 mm	146 mm
1.4	600	600	700 (230)*
4	1100	1000	1000 (700)
11	1100	1000	1300 (1000)

*Values in parentheses for Cannon lens without closeup lens.

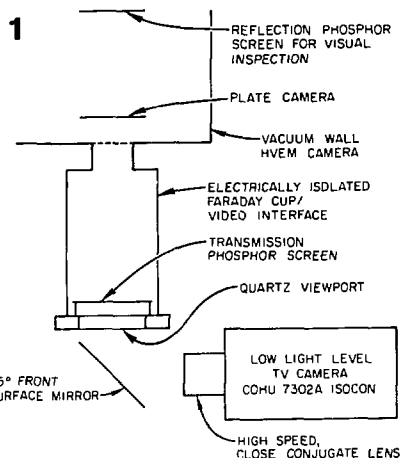


Figure 1. Schematic diagram of LLLTV dynamic recording system for ORNL HVEM.



Figure 2(a). Enlargement (10 $\times$) of 35-mm image of 50-mesh grid projection image on phosphor screen. (b) Optical diffractogram of area of negative showing eight orders of diffraction. System resolution 1300 lines/frame.

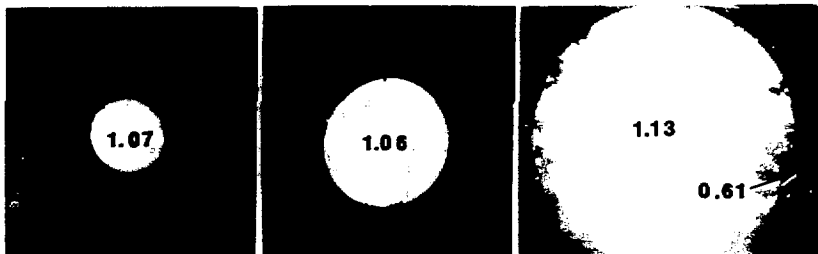


Figure 3. Phosphor screen images of different size SAD apertures recorded at constant current density. Numbers indicate optical density of original negatives at indicated positions. Notice variation in background intensity. (a) 150 μ m, (b) 250 μ m, and (c) 500 μ m diameter apertures.

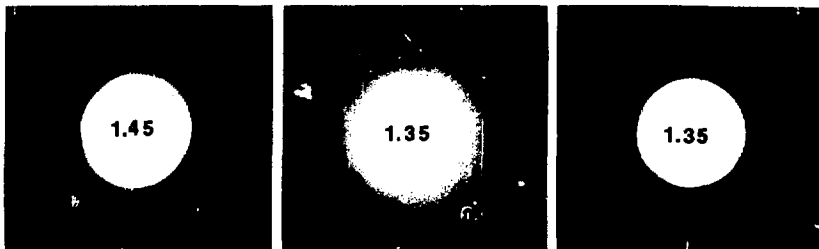


Figure 4. Phosphor screen images of SAD apertures recorded at different screen-to-window spacings. Numbers indicate optical density of original negative at indicated positions. (a) Contact, (b) 25-mm height, and (c) 146-mm height.

A NEW BATTERY SYSTEM FOR FILAMENT EXCITATION IN A HIGH-VOLTAGE ELECTRON MICROSCOPE

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ABSTRACT

A new battery system for exciting the gun filament has been designed and installed in the A.E.I. EM7 High-Voltage Electron Microscope in Albany, N.Y. This battery system features: 1) two independent banks that can be alternately switched in and out of the circuit, 2) diodes in the battery array to prevent cell-to-cell discharge, and 3) a multiplexing circuit to allow the DC voltage on the battery bank to be read simultaneously with charging. The New York State high-voltage electron microscope facility is supported as a National Biotechnology Resource by the Division of Research Resources, Department of Health and Human Services, under grant number RR01219.

The two battery banks are switched by means of a mechanical ratchet-and-cam arrangement which is toggled by the lucite control rod which previously operated the series-parallel switch bank. Momentary activation of this control rod switches to the other battery bank, where it remains latched until the next momentary activation.

The first battery bank consists of 48 NiCd 15 amp-hour cells (Varta SD-15) arranged in 16 branches of 3 cells in series. Diodes were added to provide separate charging and load paths so that no cell-to-cell discharge could occur. We used Motorola Schottky rectifiers IN5823 to minimize junction loss. This bank provides 3.2 volts and 240 A-hr. Resistors are necessary for load balancing in run mode and current regulation in charge mode.

The second battery bank consists of two AgZn wet cells (Yardney LR-660) connected in series and remarkably provides 3 volts at 660 amp-hours.

One can read the voltage on the battery bank with a multiplexing circuit. In the rack-mounted charger-timer unit a large capacitor is placed in series with the transformer secondary to pass the AC power while blocking the DC component from the battery. In the terminal, the primary of the charging transformer is placed in series with the battery bank. The result is that 220 V AC and 3 to 7 V DC appear on the charging telescopes. The large capacitor charges up to the battery voltage while completely passing the AC power. The charging transformer sees only the AC once the capacitor voltage equals the battery voltage.

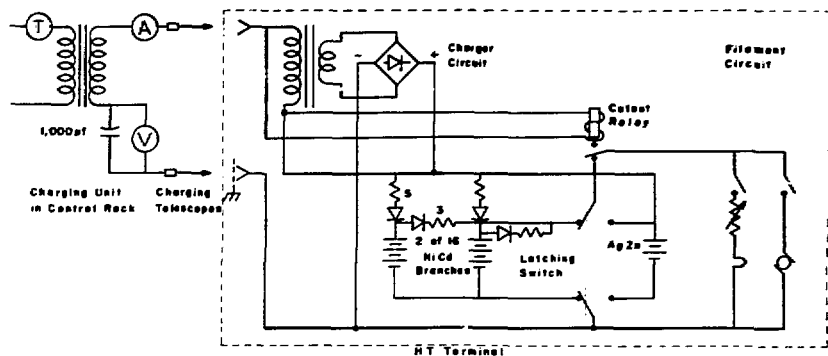


Figure 1. Schematic diagram of the dual battery system for the AEI-EM7.

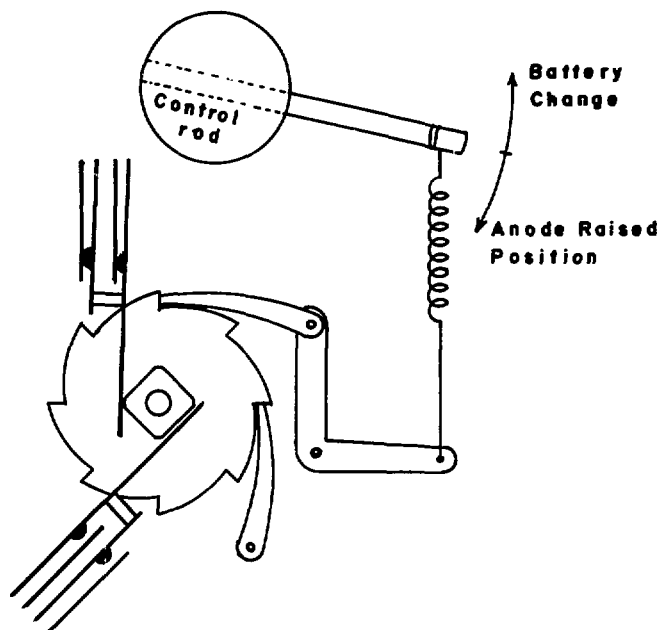


Figure 2. Drawing of the switch for the dual battery system.

A WIRE DETECTOR FOR MeV ELECTRONS

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ABSTRACT

An electron detector consisting of a 10- μ m wire and a 20-stage electron multiplier is described. The thin wire is suitable for analyzing a one-dimensional electron-energy spectrum by interacting with only a 10- μ m portion of the beam. The rest of the beam passes the wire and enters a beam dump a sufficient distance from the detector to minimize noise induced by x rays and back-scattered electrons. This work is supported by the Department of Health and Human Services under grant number 5 R01 GM28614-03.

It is found that the high-energy incident electrons produce enough secondaries to produce a measurably positive current from the wire. The production of a number of low-energy electrons and the amplification of the electron multiplier provide sufficient gain to detect and count individual primary electrons at a rate exceeding 100 kHz.

This arrangement is used as a serial detector in an electron-energy-loss spectrometer for the HVEM. A significant problem arises in scaling up the beam energy from 100 kV. The effectiveness of the usual energy-selecting slit system in removing unwanted spectral electrons from the detector region decreases as energy increases. This shows up as greater transparency at the slit edges and as an increase in Bremsstrahlung produced by the slit material. Both effects produce undesirable noise in a detector system. The thin-wire-electron-multiplier arrangement is a method of bypassing these two noise sources.

In this arrangement the output of the electron multiplier is fed through a discriminator to a multichannel scaler, while a ramp current fed to the analyzing magnet synchronously scans the spectrum.

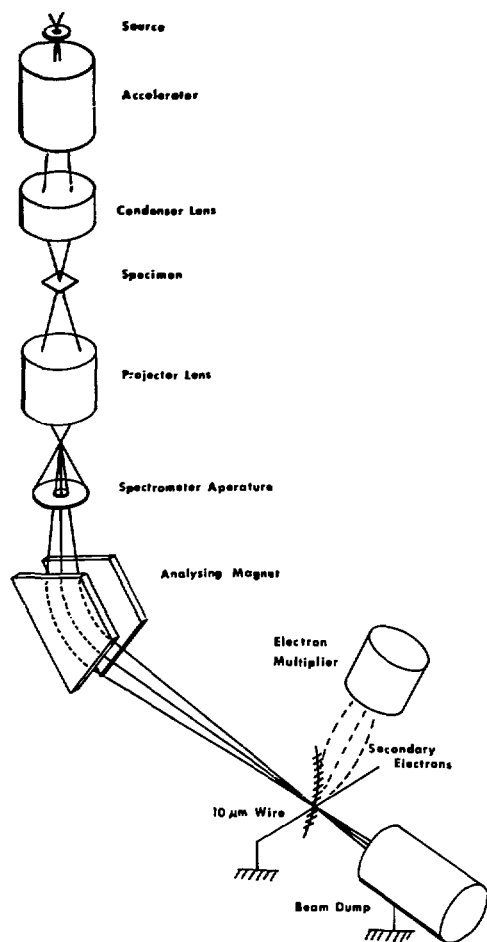


Figure 1. Schematic diagram of electron paths through the high voltage electron microscope and electron energy-loss spectrometer. As the current through the analysing magnet is varied, electrons having various energy loss intercept the wire.

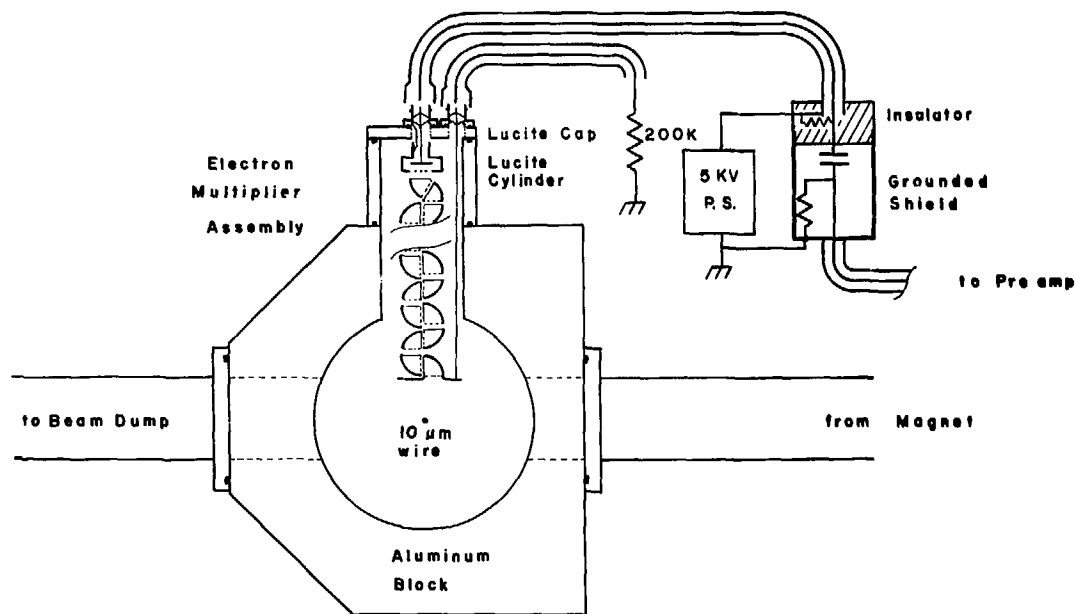


Figure 2. Drawing showing the geometry of the wire detector. The electron beam is in the plane of the drawing.

NOTES

CRYO-HVEM FOR BIOLOGICAL APPLICATIONS

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At the National Facility for HVEM in Boulder we are currently extending the beneficial traits of high-voltage electron microscopy to low temperatures because admittedly the following favorable and unique circumstances become accessible and relevant to biological research: (i) the fixation of cells and tissues by rapid freezing has been shown in recent years not to damage the specimen and thus to represent a favorable alternative to chemical fixation because in many cases it arrests cell movement faster and may eliminate some of the subsequent preparative artifacts, (ii) hydrated specimens, such as whole cells or certain hydrated protein crystals, can be viewed in frozen form or their process of dehydration and attendant alterations followed directly, (iii) thick cryosections are easier to produce, (iv) there is some improvement at low temperatures, even if to an uncertain extent at present, in beam-induced damage as well as in specimen stability (e.g. reduced stain displacement), and (v) the larger space available between the pole pieces can house large and stable cryostats.

Since for our purpose at this point it does not seem essential to reach the lowest possible temperatures or to have a tilting capability and in order to make the above circumstances accessible for direct evaluation, we have developed a relatively simple but high-performance LN₂-cooled cryostage for our top-entry JEM-1000 instrument [1,2,3]. In the adopted geometry the specimen is almost completely surrounded by a cold sink made of OFHC copper and cooled by nitrogen (liquid or gas) circulating in copper tubing wrapped around it; the copper sink also incorporates a heating wire. Adequate insulation is provided by PVC or Roulon ring insulators as adopted in an earlier design [4], but no cooled shielding has been incorporated for simplicity. Only the top cover plate cooled by the return line provides partial radiation shielding toward the specimen chamber. (An improved, He-cooled version with double thermal shield has also been built and is currently being assembled and evaluated.) The coolant is supplied from an external dewar by a high-efficiency, 12 ft.-long transfer line and fed into the microscope column by a permanent feed-through arrangement. The line connection is satisfactorily made inside the specimen chamber by means of two copper-gasket miniconnectors. This cryostage can be interchanged with the normal goniostage in about 15 minutes.

The temperature of the cryostage is stabilized by an automatic controller that regulates the balance between coolant flow and heater current. Depending on the stabilization of the precooled transfer-line sheath, the cryostage can be cooled in 10-20 min. Thermal stabilities of better than $\pm 0.1\text{K}$ over many

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minutes can thus be reached at arbitrary temperatures down to 78 K. Several examples of thermal stabilities are given in Fig. 1. Under these circumstances the standard performance of the instrument is maintained also below room temperature throughout the entire cooling range; several resolution tests with graphitized carbon (0.34 nm) and Sn/Sn Te alloy (0.31 nm) at various temperatures are shown in Fig. 2.

Frozen specimens can be inserted into the column and placed on the cryostage in about 5 min. in a special procedure developed for this purpose that maintains the specimen uninterruptedly immersed in liquid nitrogen, and thus isolated from the atmosphere, until pumping is completed in the air lock.

What can be visualized by cryoHVM in typical biological samples is illustrated in Fig. 3. Whole cells cultured on support grids were fast-frozen in propane, transferred in liquid nitrogen and inserted onto the cryostage cooled at 78 K in the microscope column as described. The cryostage temperature was then raised and maintained at about 180 K for several hours until etching was completed. On this portion of a cultured NRK cell most organelles are normal. The cell edge is unruptured as is also the nuclear envelope. Some of the mitochondria, perhaps because of incomplete dehydration, seem less structured than others in which cristae are clearly visible. The cytoplasmic matrix appears structured and uniformly distributed. Although the last to dehydrate, the nuclear matter also has the expected appearance and two

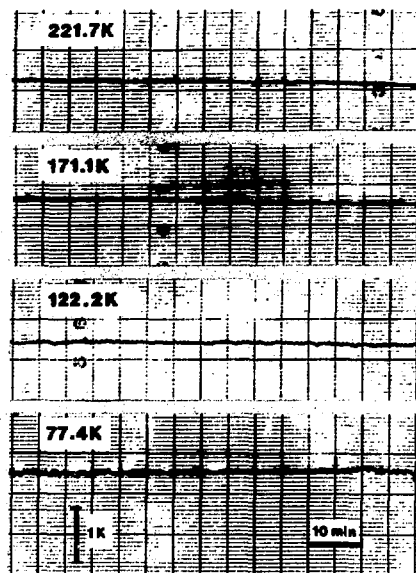
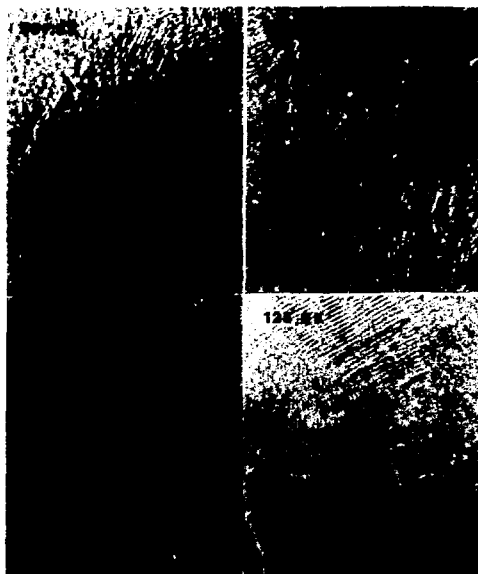


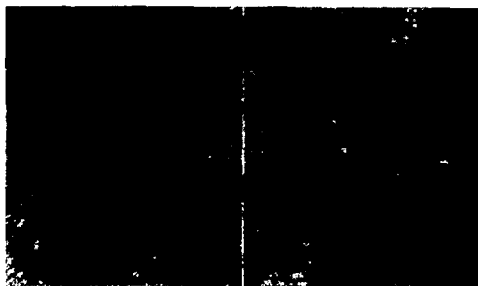
Fig. 1 Thermal stability of the LN_2 -cooled cryostage at various temperatures (0.075K/small division).

nucleoli are clearly distinguishable. The fine structures of the cell visible in this micrograph imply not only good instrumental stability and good resolution, but also good preservation and good contrast in spite of the fact that the cell was neither fixed nor stained as in conventional procedures.

This work was supported in part by NIH Grant No. RR00592 from the Division of Research Resources and by NSF Grant No. PCM-79-05631.



Lattice of Graphitized Carbon (spacing 0.34nm)



Lattice of Sn/SnTe Alloy (spacing 0.31nm)

Fig. 2 Performance of the LN₂-cooled cryostage at various temperatures and 1MV.

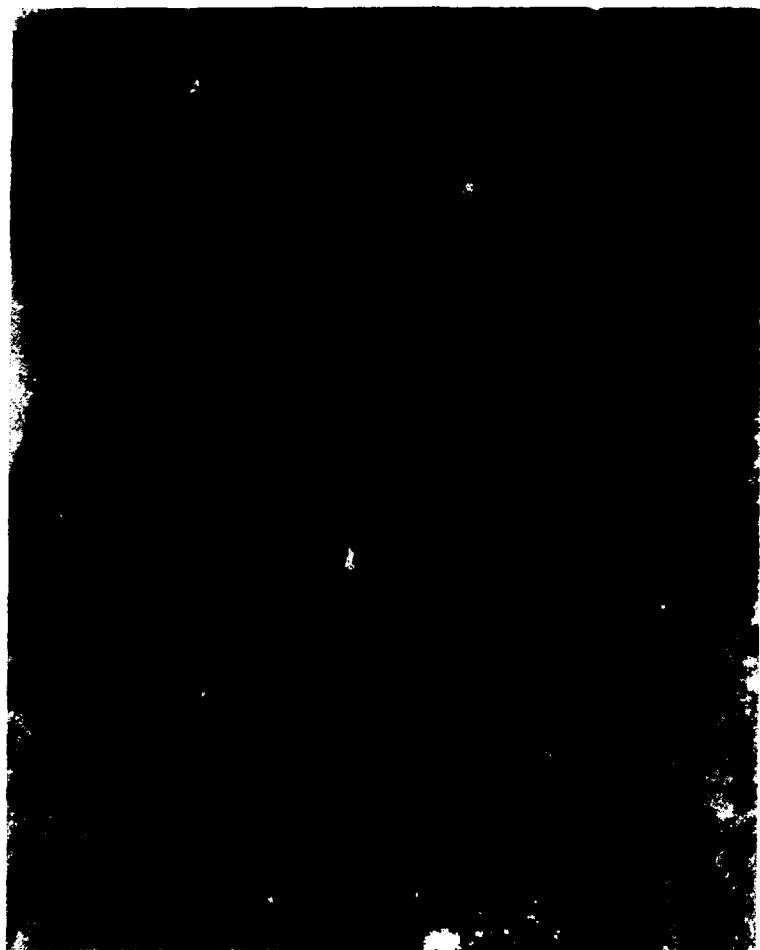


Fig. 3 Portion of a cultured NRK whole cell, unfixed and unstained, fast-frozen in liquid propane, transferred onto the cryostage in liquid nitrogen, and etched in situ and imaged at 188.2K and 1MV.

IMPROVEMENT IN RESOLUTION OF 1 MILLION VOLT ELECTRON MICROSCOPE WITH SIDE ENTRY GONIOMETER

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ABSTRACT

The 1000 kV high voltage electron microscope of Kyushu University was improved for high resolution observation. The main factors considered in the improvements are (1) the aberration coefficients of the objective lens, (2) the electrical and mechanical stabilities and (3) the brightness of electron source. A new objective lens pole-piece was prepared for the side entry goniometer stage. The spherical and chromatic aberration coefficients are 3.9 and 3.7 nm, at 1000 kV, respectively. A ripple of the voltage was reduced to less than 10^{-6} , at 1000 kV. The specimen stage was modified to suppress the thermal drift of the specimen holder. The tungsten filament was replaced by the lanthanum hexaboride cathode to obtain high brightness. The maximum magnification was increased from half million to one million. As a result of these improvements, it is possible to attain routinely the resolutions of 0.14 nm in lattice fringe and 0.20 nm in the image of particles.

INTRODUCTION

The high resolution high voltage electron microscopy has been successfully used for determining order-structures in binary alloys [e.g.1]. Most of the high resolution studies through high voltage electron microscopes have been performed by the use of top entry goniometer stages which hardly suffer from mechanical vibrations and drifts as compared with side entry goniometer stages. The side entry stages, on the other hand, which enable us to select an eucentric specimen position by a z-control, are convenient for the use of various kinds of specimen holders such as heating and cooling holders. We attempted to improve the high voltage electron microscope with the side entry stage in order to obtain high resolution images.

PRACTICAL FACTORS INFLUENCING THE RESOLUTION

The performance of an electron microscope is commonly evaluated in terms of contrast transfer function CTF which is given by $\exp\{-\frac{1}{2}\chi(u)\}$ [2], where $\chi(u)$ is a phase difference due to spherical aberration coefficient C_s and defocus Δf of an objective lens, and u is the spacial frequency. The resolving power depends on C_s through CTF when illumination is fully coherent. The effect of instabilities of high voltage and lens current is related to actual focal spreads, and it is usually described by the envelope function $E(u)$ [3] which results in attenuation of ideal CTF. The mechanical instability of the specimen holder is a serious weak point for side entry stages. The brightness of electron source affects the images through illumination angle which is taken into account in $E(u)$. Keeping in mind the above factors, we improved our instrument as follows: (1) decreasing of the aberration of the objective lens, (2) stabilizing of the high voltage, (3) modification of the specimen holder, (4) increasing of brightness and (5) realizing of high magnification.

NEW OBJECTIVE LENS

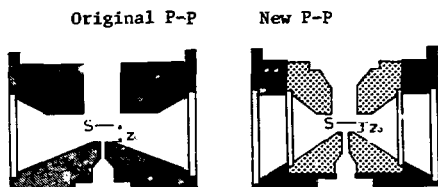


Fig. 1 Section of the objective pole-pieces for the side entry stage.

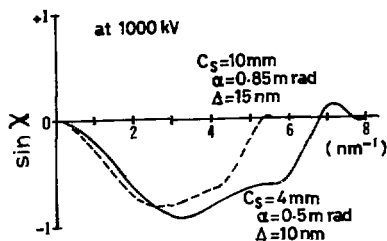


Fig. 3 Contrast transfer function for weak phase objects. Solid line: new pole-piece, $\Delta f^c = 70$ nm, broken line: original pole-piece, $\Delta f^c = 110$ nm.

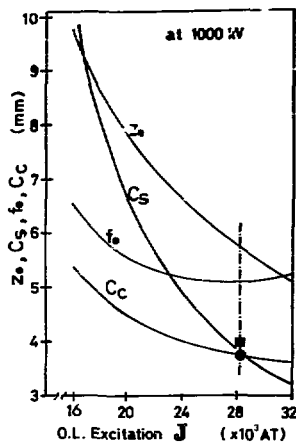


Fig. 2 Characteristics of the new objective lens for various lens excitations. ■: measured C_s , ●: measured C_c .

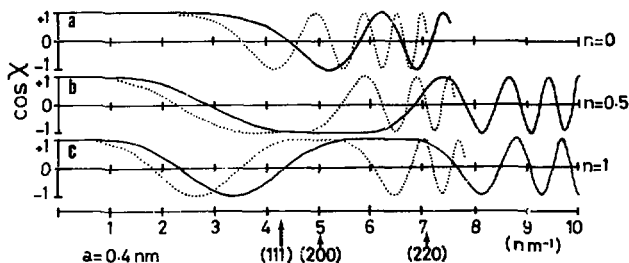


Fig. 4 Contrast transfer function for crystals. Solid line: new pole-piece, broken line: original pole-piece. $\Delta f^c = (4n C_s \lambda)^{1/2}$.

Table 1

The characteristics of the objective lens pole-pieces.

Pole-piece	z_0	C_s	C_c	f_0	J	Effective Scherzer focus and limit	
Original P-P	9.0 mm	10 mm	5.2 mm	6.6 mm	21500 AT	110 nm	0.19 nm
New P-P	3.5	3.9	3.7	5.3	28000 AT	70	0.15

The basic concept for the design of the objective lens and the material of the pole-piece are the same as those for the top entry stage [4]. The schematic drawing of the new lens pole-piece is shown in Fig. 1 together with the one of the original pole-piece. The characteristics, theoretically expected for the new lens, are shown in Fig. 2, where C_c is the chromatic aberration coefficient, and f , the focal length. The measured values of C_s and C_c are also indicated in Fig. 2. The lens parameters of the original and new pole-pieces at the eucentric position of specimens are listed in Table 1.

ELECTRICAL AND MECHANICAL STABILITIES, AND BRIGHTNESS

The drift and ripple of high voltage were reduced to 1×10^{-6} /min and 1 V (peak to peak) at 1000 kV, respectively, by utilizing the stabilizer [4]. The thermal drift of the specimen holder was significantly reduced by the replacement of the material of the specimen stage. However, some vibrations especially perpendicular to the axis of the holder still remain. The maximum magnification was increased from half million to one million. The brightness of electron source was increased by five times or more, by the use of a LaB₆ single crystal cathode, DENKA M-3. The life time of the cathode was about 300 ~ 400 hours without any improvement of the vacuum system.

CONTRAST TRANSFER FUNCTION

When the weak phase object approximation is satisfied, CTF can be represented by $\sin \chi(u)$ for bright field images. The CTF at effective Scherzer focus [5] is shown in Fig. 3 for the original and new pole-pieces. The image resolution of 0.18~0.20 nm is expected by the use of the new pole-piece. Actually 0.20 nm was resolved in the image of carbon particles.

For the crystal specimen, images are formed by strong Bragg reflected beams and CTF is represented by $\cos \chi(u)$ [6]. The CTF for the original and new pole-pieces are shown in Fig. 4 as a function of defocus. It appears from Fig. 4 (c) that the reflected beams between $u = 5$ and 7 nm^{-1} and the transmitted beam are in phase and that the resolution of 0.14 nm may be achieved if multi-beam bright field image is formed with these beams. Fig. 5 shows an example of high resolution images of an Au crystal. An example of structure images for ordered Ag-Mg alloy is shown in Fig. 6 where the specimen is rather thick so that the intensity of the superlattice reflections becomes strong [7]. As a result of the present improvements it is possible to resolve 0.3~0.4 nm directly on the fluorescent screen and to obtain routinely high resolution images of 0.14~0.20 nm.

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Fig. 5 Examples of high resolution images of gold crystal; at 1000 kV, with the side entry stage, axial illumination; direct magnification; 620,000 ~ 870,000.

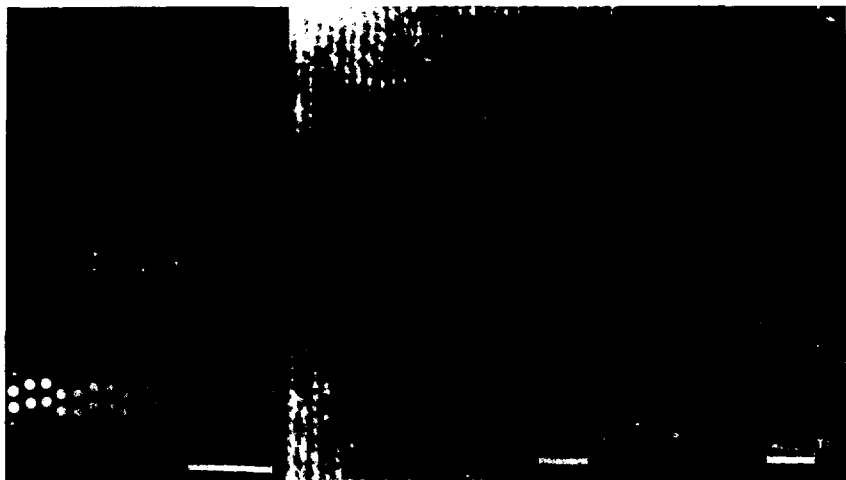


Fig. 6 Multi-beam bright field images of one dimensional long period superstructural alloy of α' Ag-Mg; at 1000 kV with the side entry stage. Black or white dots correspond to the sites of minority Mg atoms.

HIGH TEMPERATURE IN SITU EXPERIMENTATION IN HVEM INSTRUMENTATION AND APPLICATION TO MATERIALS SCIENCE

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ABSTRACT

In situ experimentation on superalloys and ceramics necessitates the design and construction of very high temperature specimen holders. A heat transfer investigation has permitted the realization of a double tilting heating specimen holder (1500 K) and a high temperature double tilting straining holder which combines a high operating temperature (1300 K) with a heavy load on the specimen (several daN). Some applications to materials science will be described in order to illustrate the possibilities of these high performance instruments.

INTRODUCTION

High temperature in situ experiments not only require the use of thick specimens but also very specific equipments which are not commercially available on a conventional HVEM. This equipment includes a high vacuum specimen chamber [1], a low light level high resolution visualization and recording system [2], a reliable and sensitive eucentric goniometer stage and high temperature specimen holders. In each case, the physical phenomena which may limit the capabilities of those systems were evidenced through a physical approach of the problems. The optimization of these physical parameters has then guided the design and construction of these high performance instruments. For instance, a critical analysis of the available goniometer stages and a thorough investigation of the vibrations of the microscope column has permitted the realization of a completely new eucentric stage with elastic connections [3]. Combining specimen movements of a high sensitivity with a good resolution (10 Å), this eucentric stage is perfectly well adapted for the in situ experimentation.

THE DOUBLE TILTING HEATING SPECIMEN HOLDER

This new specimen holder is based on a commercially available Philips furnace (1300 K at an input power of 5 W). This platinum furnace is held into a pivoting bushing which not only ensures the second tilt movement, but also acts as a thermal shield (Fig. 1). With such an optimized construction, a maximum temperature of 1500 K is attained at an input power lower than 7.5 W [4].

THE HIGH TEMPERATURE DOUBLE TILTING STRAINING HOLDER

In this case, the difficulty is to combine the high operating temperature with the heavy load (several daN) which is necessary to deform high strength materials such as ceramics and superalloys. Due to the size of strong elongating jaws, an enormous power will be required to reach a temperature of 1300 K (more than 100 W). This radiant energy would contribute elevating the temperature of the surrounding elements such as the pole pieces and the tip of the specimen holder (thermal drift). The heat transfer investigation is

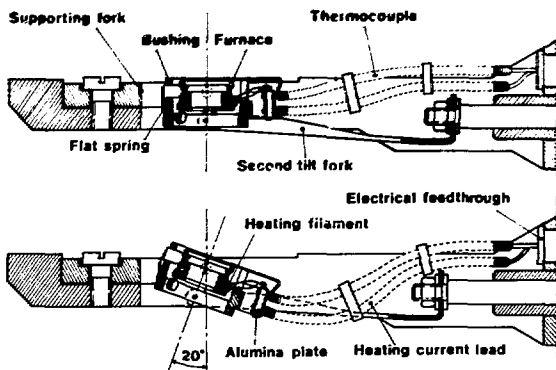


Fig. 1 - The double tilting heating holder (1500 K).

therefore aimed at limiting the input power to the lowest possible value. This result may be attained by optimizing the heating system and reducing the loss of energy. The loss of energy is proportional to the fourth power of absolute temperature in the case of thermal radiation whereas it is proportional to the temperature gradient in the case of heat conduction. Consequently, the high temperature straining holder must be designed in order to reduce the loss of radiant energy.

Design and Construction of the High Temperature Elongating Jaws

The chemical composition and the surface roughness have a great effect on the radiative properties of materials. Moreover, at temperatures as high as 1300 K, refractory jaws are required. Optically smooth tungsten seems to be the most appropriate material since it combines superior mechanical properties at high temperature with a low emissivity : 0.1 at 1300 K, instead of 0.3 in the case of ceramics. However, grain boundary microcracks develop during spark-machining of pure tungsten, sometimes leading to fracture. Consequently, the alloy W - 26% Re was used, the effect of alloying with rhenium being to toughen the grain boundaries. Moreover, this alloy shows a high ductility and overcomes the problem of embrittlement. As regards the thermal properties, the emissivity is approximately equal to that of tungsten.

The double tilting elongating device is designed in order to ensure compatibility between straining and tilting. The first tilt ($\pm 30^\circ$) is provided by the goniometer stage. The second tilt ($\pm 6^\circ$) is assumed by the rotation of a cam acting on a lever (Fig 2). The movable jaw is connected to the straining shaft through a fork-joint and a sector centred on the second tilt axis. With such a connection, straining is possible for any orientation of the specimen. The fixed jaw is held into the tip of the holder by two pivot screws. The linear displacement between the movable jaw and the fixed jaw is provided by two linear ball-bearings directly machined in the jaws.

The Tip of the Specimen Holder

The jaws being radiating within a non-black enclosure, radiant energy will be reflected by the surface of the enclosure i.e. the tip of the specimen holder. Consequently, the material of the tip must be chosen in order to

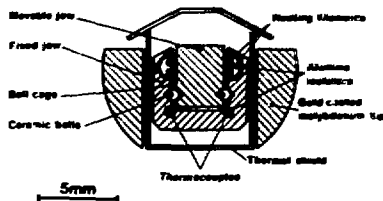
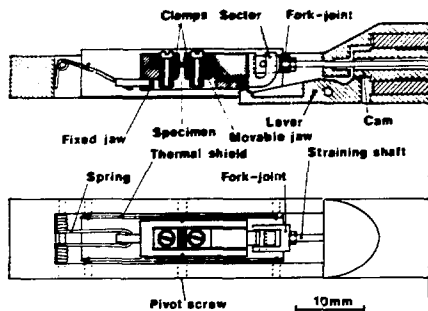


Fig. 3 - The heating system.

Fig. 2 - The high temperature double tilting straining holder.

optimize this reflection phenomenon. At the temperature of the jaws, the wavelength at which the emissive power is a maximum is approximately $2\mu\text{m}$. As regards reflectivity, the most appropriate metal is gold ($r = 0.95$ for $\lambda = 2\mu\text{m}$). However, good mechanical properties being also required, molybdenum was chosen and the tip was electropolished and gold coated.

The Heating System

The problem is to minimize the thermal gradient between the jaws and the heating elements, thereby limiting the temperature of the tungsten heating filament. This is both aimed at preventing the embrittlement of the filament and also at minimizing the loss of energy by conduction through the connecting wires. The heat transfer between the tungsten filament and the jaws may be achieved either by heat conduction or by thermal radiation. Thermal conduction through an isolating cement seems to be the most efficient. However, changing the heating elements necessitates breaking the cement. Moreover, the quality of the thermal contact between the heating elements and the jaws is essential. If there is no contact, the exchange of energy is confined to radiation. Unfortunately, the emissivity of ceramics decreases as the temperature is increased (0.5 at 1000 K and 0.25 at 1500 K); the isolating cement will thus act as a thermal shield. Consequently, a radiation heat transfer seems to be the most appropriate solution. If a concentric cylindrical configuration is assumed, then the net radiant energy from the tungsten heating coils to the jaws is given by the relation :

$$Q_{12} = \sigma S_1 \frac{\epsilon_1 \epsilon_2}{1 - (1 - \epsilon_2)(1 - \frac{S_1}{S_2} \epsilon_1)} (T_1^4 - T_2^4)$$

where ϵ_1 , S_1 , T_1 and ϵ_2 , S_2 , T_2 are the emissivities, the surfaces and the temperatures of the filaments and of the holes. The system will be optimized by maximizing the exchange surface and increasing the emissivities. At high temperature, the emissivity of the as-extruded tungsten wire is nearly that of a blackbody. The two long cylindrical cavities, directly machined in the jaws, have a rough surface and small openings thereby providing a very close approximation to a blackbody (Fig. 3). The tungsten filaments are held in alumina isolators which are machined in such a way that the tungsten filaments directly radiate towards the fixed jaw and the movable jaw (Fig. 3). In order to limit the loss of energy by conduction, the connections are made on isolating alumina pins directly fixed on the jaws. The temperature of the

connections, which directly determine the loss of energy by conduction is thus the temperature of the jaws instead of that of the filaments.

The Radiation Shield

Heat transfer calculations, similar to those already mentioned in this paper, have shown that, if two gray surfaces such as the jaws and the tip of the holder are separated by a radiation shield having a low emissivity on both sides, then the radiant energy may be reduced by a factor of 4. The thermal shield must offer good radiating properties in order to remain flat at high temperature. As regards the emissivity, gold is the most appropriate metal. However, since pure gold does not offer sufficiently good mechanical properties at high temperature, a gold alloy foil must be used. Unfortunately, the emissivity of the alloy is much higher than the emissivity of gold. As regards metal shields, the only possible solution is a tantalum shield ($\epsilon = 0.2$). In fact, the best solution is a golden molybdenum shield. However, due to the high diffusion rate of gold in Mo at high temperature, the temperature of the shield must be lower than approximately 1100 K.

This optimized construction of the double tilting heating holder has permitted to attain a temperature of 1300 K at an input power lower than 30 W.

APPLICATION TO MATERIALS SCIENCE, CONCLUSION

In situ recrystallization, irradiation and thermal cycling tests on superalloys and ceramics have already demonstrated the efficiency and the reliability of the high temperature (1500 K) double tilting holder. Moreover, in situ annealing tests have shown that different recrystallization mechanisms were observed in heavily rolled specimens and in specimens cold-rolled to 40% reduction. The observed mechanisms are thus governed by the prior rolling treatment and not by surface or irradiation effects. These experiments therefore demonstrate that the in situ annealing tests are representative of the bulk material [5].

As regards the high temperature double tilting straining holder, the heat transfer investigation has permitted to combine a very high operating temperature (1300 K) with a heavy load on the specimen. In situ experiments have already been performed on a high strength single crystal superalloy. Dislocation movements and γ' precipitates shearing were observed directly in the microscope at a temperature of 1200 K [6]. These preliminary experiments already demonstrate the feasibility of high temperature in situ experiments on high strength materials and the reliability of the high temperature straining holder.

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PROGRESS IN X-RAY MICROPROBE AND ELECTRON ENERGY-LOSS
SPECTROMETRY ON A HIGH VOLTAGE ELECTRON MICROSCOPE

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ABSTRACT

X-ray microprobe and electron energy-loss spectrometers have been installed on the high voltage electron microscope at Albany, NY. Background problems for x-ray analysis have been solved and probe size measured. Sensitivity measurements are in progress. Background reduction and improvement of electron optics for electron energy-loss spectroscopy are also in progress.

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A Kevex energy-dispersive x-ray detector was specially designed for the AEI EM7 high voltage electron microscope. The detector is mounted on a carriage which provides variable geometry; in the extended position, the detector is 16.8 mm from the sample, giving a solid angle of collection of 0.035 sr, and when fully retracted, the detector is clear of the specimen area so that it does not affect the normal operation of the microscope (see Fig. 1). A modified specimen ring was designed (see Fig. 2) which incorporates a removable lead plug to shield the detector from stray radiation when it is not in use. The detector looks upward at a 15° angle and the specimen can be tilted at various angles to get the optimum signal-to-noise ratio. Fig. 1 is a drawing of the specimen area and Fig. 3 is a drawing of the microscope column showing the location of the x-ray detector and the electron energy-loss spectrometer.

Shielding the x-ray detector against stray radiation has proved to be a formidable task in other installations [1,2]. The two sources of stray radiation are the upper part of the column and scattering within the specimen chamber. At conventional voltages (100 kV or less) contributions from these sources are roughly equal [3].

Shielding was begun from the top down. C1 and C2 apertures were designed which were made of aluminum and which were thick enough to absorb 1.2 MeV electrons. It was hoped that the use of low-Z material would minimize bremsstrahlung x-ray production, and that using apertures which could not be penetrated by the most energetic electrons would reduce stray radiation from electrons which would not be focused into the beam. Neither of these hopes were fulfilled; the background with the new C1, C2 or both was worse than previously measured. From these tests, it was concluded that geometry is more important than material in considerations of the stray radiation produced by apertures.

A series of lead disks was constructed which fit in the upper objective pole piece (see Fig. 1). Holes were drilled in the centers of the disks which

were alternately the size of the hole in the upper objective pole piece, and 1/32" larger. When these were inserted in the pole piece, they provided 7/8" of lead with a crenellated central hole to minimize scattering from the sides of the hole. These disks were found to give excellent shielding at all voltages. The spectra are very clean (see Fig. 4) even though the spectrum taken at 1.2 MeV had 85% dead time and shows evidence of pile-up.

A lead shroud was designed to fit in place of the lead plug. This was intended to reduce counts arising from multiple scattering within the specimen area. However, difficulties arising from space limitations in the specimen area precluded its use. Even without special precautions, there is low background in our microscope arising from the specimen area in contrast to the situation at conventional voltages. This is probably due to the relativistic kinematics of higher energy electrons and the consequent forward peaking of scattering, but the geometry of the specimen area may also play a role, since distances are larger than in a conventional instrument and thus solid angles subtended by possible scattering and fluorescence sources are less.

Note that the ratio of the copper peaks to the aluminum peak decreases with increasing electron energy (except at 1200 kV where there are other problems with the spectrum). The copper signal and the very small sulfur, chlorine, and potassium signals arise from electrons scattered within the specimen area, and the decrease with increasing energy is consistent with the greater forward peaking of scattering at higher energies. This effect is particularly noticeable in the very small peaks which are produced by the delrin clip.

Rough measurements of probe size showed that the electron beam was about 1 μ m in diameter. More accurate measurements were made by taking photographs of the focused beam. The photographs were taken at a series of exposures and magnifications which allow the determination of electron intensity over three or four orders of magnitude. They show very little penumbra. Quantitative evaluation of the beam profile at all voltages from 100 kV to 1200 kV is in progress.

Also in progress are determinations of minimum detectable mass and minimum mass fraction using specimens which have been analysed at conventional voltages.

The electron energy-loss spectroscopy has been installed (see Fig. 3) with a wire detector [4]. A major difficulty has been high background from electrons backscattered from the beam dump. Redesign of the beam dump incorporating a permanent magnet to reduce backscatter has lowered this background, and work is still in progress to reduce it further. A power supply for the P3 lens is being constructed to allow the use of P3 to focus the probe on the spectrometer entrance slit. This will demagnify the probe image and improve both the resolution and positional stability.

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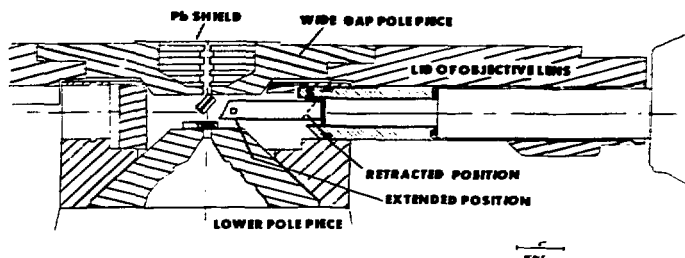


Figure 1. Specimen area of the high voltage electron microscope showing the location of the x-ray detector in the extended and retracted positions and the lead disks in the upper objective pole piece.

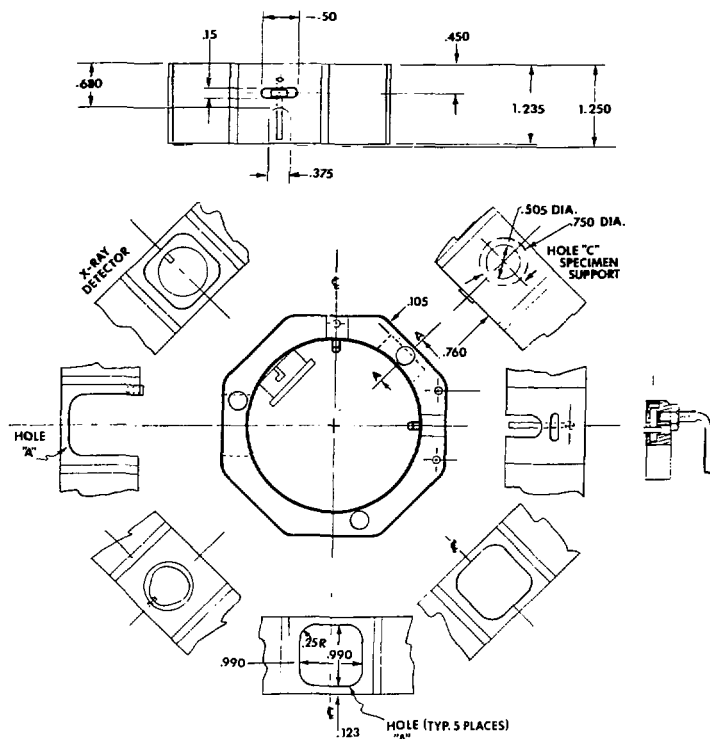


Figure 2. Specimen ring for use with the x-ray detector. Removable lead plug allows the detector to remain in the microscope column during normal operation.

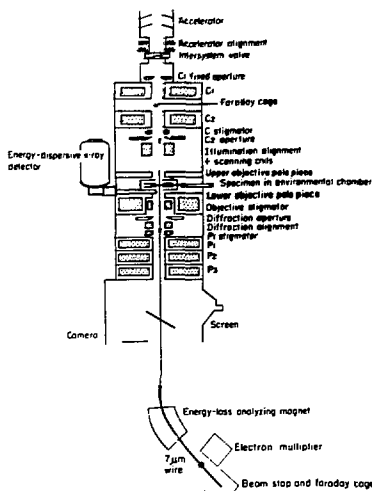


Figure 3. Diagram of the microscope column showing the locations of the x-ray detector and the electron energy-loss spectrometer.

X-RAY SPECTRA OF A 1000 Å THICK ALUMINUM SPECIMEN ON A COPPER GRID WITH DELRIN CLIP

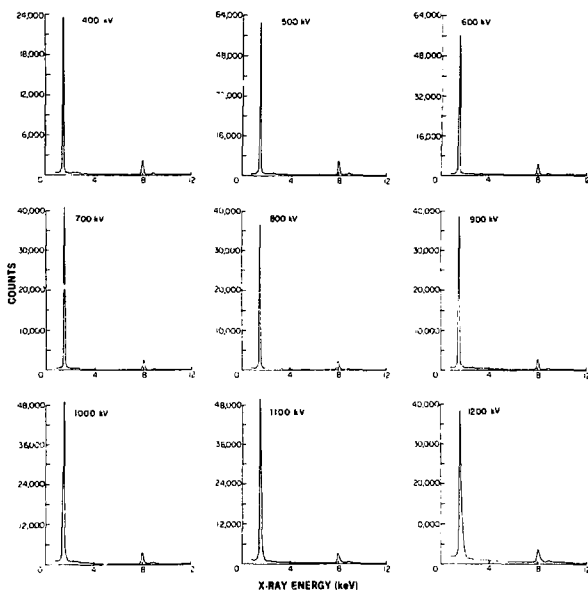


Figure 4. X-ray spectra obtained at voltages between 400 and 1200 kV.

RADIATION EFFECTS



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IN-SITU OBSERVATION OF THE ENERGY DEPENDENCE OF DEFECT
PRODUCTION IN Cu AND Ni*

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ABSTRACT

The damage function, the average number of Frenkel pairs created as a function of lattice atom recoil energy, was investigated in Cu and Ni using in-situ electrical-resistivity damage-rate measurements in the high voltage electron microscope (HVEM) at $T < 10K$. Electron and proton irradiations were performed in-situ on the same polycrystalline specimens using the Argonne National Laboratory HVEM-Ion Beam Interface. Both Ni and Cu exhibit a sharp rise in the damage function above the minimum threshold energy (~ 18 eV for Cu and ~ 20 eV for Ni) as displacements in the low threshold energy regions of the threshold energy surface become possible. A plateau is observed for both materials (0.54 Frenkel pairs for Cu and 0.46 Frenkel pairs for Ni) indicating that no further directions become productive until much higher recoil energies. These damage functions show strong deviations from simple theoretical models, such as the Modified Kinchin-Pease damage function. The results are discussed in terms of the mechanisms of defect production that govern the single displacement regime of the damage function and are compared with results from recent molecular dynamics simulations.

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INTRODUCTION

Analyses of irradiation effects experiments often require knowledge of the number of point defects (Frenkel pairs) produced in a particular irradiation, i.e., the total cross section for Frenkel pair production or displacements per atom (dpa). A fundamental quantity in dpa calculations is the damage function, the average number of stable Frenkel pairs created as a function of lattice atom recoil energy. The damage function is important for

*Work supported by the National Science Foundation and the U.S. Department of Energy.

prediction and correlation of damage production in various irradiation environments, e.g., fission or fusion reactors, yet, in general, the damage function cannot be measured directly by experiment. The total cross section for Frenkel pair production is an experimentally measurable quantity that for electron irradiation is related to the damage function by:

$$\sigma_d(E) = \int_0^{T_m(E)} v(T) \frac{d\sigma}{dT} dT \quad (1)$$

where E is the electron energy, $d\sigma/dT$ is the Mott differential scattering cross section [1], T is the recoil energy, $T_m(E)$ is the maximum recoil energy transferred in a head-on collision, $\sigma_d(E)$ is the total cross section for Frenkel pair production and $v(T)$ is the damage function. In order to determine the damage function from experimental measurements of the total cross section for Frenkel pair production, a deconvolution of Eq. (1) must be performed.

Because there is no comprehensive experimental determination of the damage function for any material, a great deal of emphasis has been placed on the Modified Kinchin-Pease [2] model (MKP) damage function which is given by:

$$v_{MKP}(T) = \begin{cases} 0 & \text{for } T < T_{d,eff} \\ 1 & \text{for } T_{d,eff} < T < 2.5 T_{d,eff} \\ \frac{0.8 \hat{E}}{2T_{d,eff}} & \text{for } T > 2.5 T_{d,eff} \end{cases}$$

where $\hat{E}$ is the corrected mean damage energy [2] and $T_{d,eff}$ is the effective threshold energy. Evidence of the inherent inadequacy of these models has appeared in the literature (e.g. see Ref.3) indicating the need for a detailed experimentally determined damage function. Such a damage function would provide more accurate predictions of defect production than the Modified Kinchin-Pease model. Further, the "real" damage function would also carry information on basic defect production mechanisms.

In the present work, electrical-resistivity damage-rate measurements were carried out in-situ at $T < 10$ K in the HVEM. Polycrystalline samples of Ni and Cu were irradiated with HVEM electrons in the energy range 0.4-1.1 MeV and with protons in the energy range 0.1-1.0 MeV using the HVEM-Ion Beam Interface at Argonne National Laboratory. Using a fitting procedure, Eq. (1) was unfolded to yield damage functions for both Ni and Cu.

BASIC PRINCIPLES

Experimentally we measure the damage rate, $d\Delta\rho/d\phi$, where $\Delta\rho$ is the irradiation induced resistivity change and ϕ is the particle dose. Correction of the measured damage rates for the so-called "saturation" effect yields the damage rate in the undisturbed lattice or the initial damage rate. These initial damage rates are proportional by the Frenkel pair resistivity, ρ_F , to

the total cross section for Frenkel pair production. The Frenkel pair resistivity clearly plays an important role in deconvolution of Eq. (1) to extract the damage function. Because the Frenkel pair resistivity is a scaling factor, unless it is known e.g., from Frenkel pair concentrations determined by diffuse x-ray scattering experiments or from analysis of threshold energy anisotropy experiments, only the quantity $\rho_F v(T)$ can be determined [4]. Since Eq. (1) cannot be unfolded analytically to determine the damage function, a trial and error fitting procedure was employed to obtain an optimum fit of total cross sections calculated from Eq. (1) based on a trial damage function to the total cross sections measured experimentally. Two approaches to the fitting procedure are possible. First, if the Frenkel pair resistivity is known, $v(T)$ is varied to obtain a good fit to the experimental data. Second, if $v(T)$ is known but ρ_F is not, ρ_F can be adjusted to give a good fit. In Cu, the damage function and ρ_F have been determined from threshold energy anisotropy experiments [5,6]. In such experiments, the damage function is less susceptible to systematic errors than ρ_F , therefore, in the present analysis the damage function was fixed and optimization was carried out with respect to ρ_F . In the case of Ni, diffuse x-ray scattering experiments [7] have given the best estimate of ρ_F which was used to derive $v(T)$.

EXPERIMENTAL

The experiments were carried out at the High Voltage Electron Microscope-Tandem Accelerator Facility at Argonne National Laboratory which consists of a 1200 keV KRATOS-AEI EM7 high voltage electron microscope coupled via the Argonne Ion Beam Interface to a 300 keV and a 2.0 MeV ion accelerator. Specimens were located in a side-entry type, helium-temperature specimen stage with the capability of making in-situ electrical resistivity measurements at $T < 10$ K. The Ni and Cu specimens used in the present investigation were polycrystalline thin films ~ 2000 Å thick. The Cu specimens were prepared by vacuum evaporation onto a room temperature NaCl single crystal substrate coated with a thin carbon film. Ni specimens were prepared by electron beam evaporation onto a heated (250 C) single crystal NaCl substrate. All samples were irradiated at ~ 30 degrees tilt with respect to the electron beam where the effect of possible crystal texture on the measured damage rates was confirmed to be negligible. The method of mounting the sample and producing the shape necessary for four-point dc electrical resistivity measurements is described in Ref. 8.

Experimental Procedure

Each specimen was irradiated at 1.1 MeV, the reference energy, with electrons to establish the initial portion of the saturation curve. Following this, damage rates were measured as a function of incident electron energy between 0.4 and 1.1 MeV. Finally, the sample was irradiated at the reference energy to approximately 0.5 of the saturation resistivity which we define as the x-intercept of the linear portion of the damage rate vs. irradiation induced resistivity curve. The experimental data was corrected for the saturation effect and the electrical resistivity size effect as described in Ref. 6 and 8 to obtain the initial damage rate.

RESULTS AND CONCLUSIONS

Figure 1 shows a plot of the total cross section for Frenkel pair production as a function of incident electron beam energy for Cu. The detailed damage function of King et al. [5,6] was used in the energy range < 30 eV and the Frenkel pair resistivity was adjusted to give a good fit to the polycrystalline damage rate data. The procedure resulted in a value of the Frenkel pair resistivity for Cu of $2.6 \times 10^{-4} \Omega\text{-cm}$ [9] in good agreement with that derived in the single crystal

experiments, $2.75^{(+0.6)}_{(-0.2)} \times 10^{-4} \Omega\text{-cm}$ [5,6]. The resultant damage function,

plotted in Fig. 2, exhibits a plateau at 0.54 Frenkel pairs, slightly lower than the single crystal plateau. This damage function exhibits marked deviations from the Modified Kinchin-Pease model. Although both experiment and model show a sharp onset of defect production, the experimental result indicates that a plateau in the damage function exists at a value of $v(T) < 1$. This plateau at 0.54 Frenkel pairs is observed to extend to quite high energies ($\sim 7 T_{d,\min}$) when the high energy electron data of Wurm [10] and Dworschak et al. [11] are included in the analysis [9]. Further experiments in which samples are irradiated with both electrons, protons, and self-ions are required before more firm conclusions can be drawn about the extent of the plateau and the onset of multiple defect production.

The damage function of Fig. 2 and Frenkel pair resistivity, $2.6 \times 10^{-4} \Omega\text{-cm}$, are found to be in good agreement with the results of single crystal irradiations of King et al. [5,6]. The apparent disagreement at $v(T) > 0.5$ (see Fig. 2) arises from the insensitivity of the single crystal experiment to the high threshold energy regions of the threshold energy surface. Therefore, detailed comparisons can only be made below the plateau [9].

Recently, King et al. [5] used molecular dynamics computer simulation to calculate the threshold energy surface and damage function for Cu. Their results also indicate that such a plateau exists in the damage function at ~ 0.5 Frenkel pairs. This plateau was observed to extend to $\sim 5 T_{d,\min}$, which is considered to be in agreement with our analysis. Although the low energy portion of the damage function has been established with relative certainty, the rate at which the onset of multiple defect production occurs is somewhat in question. When results from previous ion and neutron irradiation experiments are used in conjunction with our results (see Ref. 9), multiple defect production is observed to occur quite rapidly compared with, e.g., the damage function determined from molecular dynamics simulation [5]. This is at variance with results from thermal neutron experiments [12] which in the case of Cu give a measure of the damage function over a rather narrow range of recoil energies (1.83 Frenkel pairs at 480 eV median recoil energy [13]). This result is in good agreement with molecular dynamics simulation [5]. Further electron and ion irradiations are required to resolve this difference.

The total cross section for Frenkel pair production in Ni as a function of incident electron beam energy is plotted in Fig. 3. These experimental results are in good agreement with the measurements of Lucasson and Walker [14]. The damage function determined from this data is shown in Fig. 4. As in the case of Cu, Ni also exhibits a sharp onset of defect production which is followed by a plateau at 0.46 Frenkel pairs. The minimum threshold energy

is ~ 20 eV. Preliminary proton irradiation data indicate that the plateau extends to ~ 80 eV before the onset of multiple defect production begins. As in copper, the existence of such a plateau means that $\sim 1/2$ of the threshold energy surface is of low energy, <30 eV (most likely the regions surrounding $\langle 100 \rangle$ and $\langle 110 \rangle$). The remainder of the threshold surface is of much higher threshold energy, >80 eV.

Of course these results are strongly influenced by the value of ρ_v that is chosen. The value that was used for Ni, 7×10^{-4} g/cm, is from the diffuse x-ray scattering work of Bender and Ehrhart [7] assuming a vacancy relaxation volume of -0.22 atomic volumes and is felt to be the best available value.

Clearly the results suggest that the damage mechanisms in copper and nickel are very similar. The threshold energy surfaces have regions surrounding the low index directions $\langle 100 \rangle$ and $\langle 110 \rangle$ that are within ~ 10 eV of the minimum threshold energy. In these directions it is relatively easy to generate a replacement collision chain that will efficiently transport the interstitial out of the recombination volume of the vacancy. On the other hand, the remainder of the threshold energy surface is of much higher threshold energy ($\geq 5-7 T_{d,min}$). The corresponding plateaus in the damage functions at $v(T) \sim 0.5$ are a key feature of this work. Although the exact extent of the plateaus have yet to be established, they extend to at least $5 T_{d,min}$. Further experimentation using proton and self-ion irradiation is expected to elucidate the extent of the plateau and the onset of multiple defect production.

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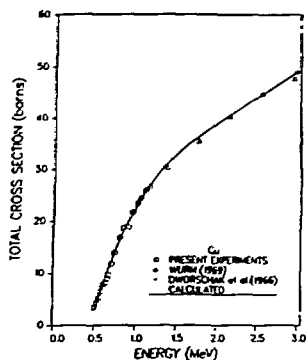


Figure 1. Total cross section for Frenkel pair production as a function of electron energy for Cu. Present experimental results are plotted along with those of Wurm [10] and Dworschak et al. [11]. Calculated curve based on damage function shown in Fig. 2.

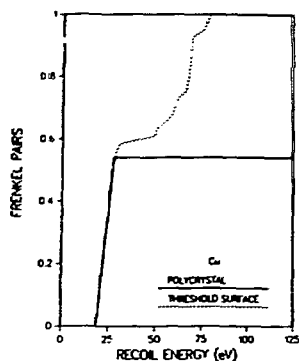


Figure 2. Damage function for Cu determined from the data in Fig. 1 along with the damage function determined from single crystal experiments [5,6].

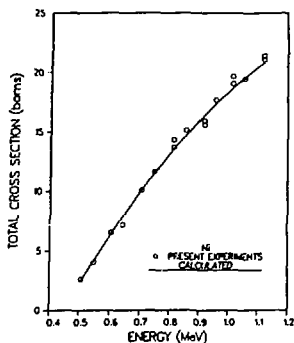


Figure 3. Total cross sections for Frenkel pair production as a function of electron energy for Ni. Calculated curve based on damage function shown in Fig. 4.

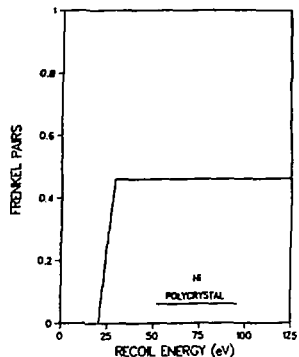


Figure 4. Damage function for Ni determined from the data in Fig. 3.

Duf

IN-SITU STUDIES OF CASCADE DEFECT FORMATION AT $T < 10$ K

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ABSTRACT

Thin films of Ag and Au were ion irradiated at temperature (T) < 10 K and simultaneously observed using the Argonne National Laboratory high voltage electron microscope ion-beam interface system. Displacement cascades were produced by Kr^+ ion bombardment in the energy range 20-140 keV. For Ag, 20% of the 20 keV cascades and 100% of the 100 keV cascades produced observable contrast. Analysis of the observed dynamical black-white (BW)-contrast indicates that the clusters are of vacancy type. Subcascades were observed in the high energy irradiations. The present results demonstrate that during the evolution of displacement cascades in Ag and Au, extensive athermal rearrangement of vacancies occurs which gives rise to clustering and "collapse" to dislocation loops.

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INTRODUCTION

The microstructural and microchemical evolution of materials under heavy ion or fast neutron irradiation depends strongly on the spatial distribution of defects in individual displacement cascades. The classical cascade model is that of a vacancy rich depleted zone surrounded by interstitials [1]. However, evidence exists that this simple picture has to be considerably modified. Previous room temperature transmission electron microscopy (TEM) observations of displacement cascades in Ag, Au and a number of other metals have shown considerable clustering of vacancies and agglomeration to dislocation loops [2,3]. The clustering either occurs during the time evolution of the cascade or is due to thermally stimulated processes. Electrical resistivity measurements at liquid helium temperature suggest a significant amount of athermally stimulated recombination of point defects due to atomic motion during the thermal spike phase of the cascade [4]. The existence of such spike effects was also shown in TEM observation of surface craters in Au bombarded with Bi and Bi₂ ions at room temperature [5]. However, direct TEM observation of cascade formation at low temperature has

not been carried out to confirm the existence of such spike effects.

In the present work, Ag and Au thin films were irradiated in-situ in the Argonne National Laboratory HVEM ion-beam interface system at $T < 10$ K. The existence of athermally stimulated rearrangement and collapse of the vacancy rich core of the cascade was confirmed by direct observation at low temperature.

EXPERIMENTAL

Thin film (~ 1000 Å thick) specimens of Ag and Au were prepared by vacuum evaporation and subsequent annealing. These films were irradiated with Kr^+ ions at $T < 10$ K in the high voltage electron microscope (HVEM) using the ion-beam interface system at Argonne National Laboratory [6] and the single tilt He temperature specimen stage [7]. Ion energies were 20 keV and 100 keV for Ag and 140 keV for Au. The irradiations were interrupted several times and TEM observations were carried out without warming the specimen. The ion dose was measured using a transmission Faraday cup which intercepts an annular fraction of the beam and is positioned at the end of the ion-beam line inside the HVEM column, just above the specimen stage (the ion beam axis was inclined 33° with respect to the electron beam axis). Ion beam rastering in two orthogonal directions perpendicular to the beam axis was employed to ensure that the integrated beam current density was homogeneous over the 3 mm diameter entrance aperture of the cup. The highest electron energy used for TEM observation was 500 keV which is well below the displacement threshold in both Ag and Au. At the electron current densities ($\sim 10^{18}$ e/cm²/sec) used, the specimen temperature rise due to electron beam heating was calculated to be negligible [8]. Micrographs were taken at specimen orientations near [111] (Ag) and [100] (Au) under kinematical bright field conditions and also dynamical bright and dark field conditions. The defect type was determined from the direction of $\hat{\ell}$, the vector from the black lobe to the white lobe of the BW-contrast under dynamical conditions, relative to the diffraction vector $\hat{g}$ [9]. The defect yield, the fraction of displacement cascades which form visible defect clusters, was evaluated by measuring the areal density of defect clusters or subcascade structures on micrographs and comparing it with the measured ion dose. TEM observations of the same areas were also performed after warming the irradiated specimen to room temperature.

RESULTS

Figure 1 shows the BW-contrast of cascade defect clusters in Ag irradiated with 20 keV Kr^+ ions at $T < 10$ K. All the BW-contrasts observed had $\hat{g} \cdot \hat{\ell} > 0$. The calculated mean penetration depth (using the TRIM code [10]) for 20 keV Kr^+ ions in the Ag specimens was 65 Å, well within the first layer of the depth oscillation of BW-contrast (the approximate thickness of the first layer is $0.3 \lambda_g = 164$ Å, when imaged with $\hat{g} = 220$ at electron energy of 400 keV [11]). The clusters were therefore identified as being of vacancy type. Three different $\hat{\ell}$ vectors were found. One was parallel to $\hat{g}$, others were close to the projection of [111], or [1 $\bar{1}$ 1] direction onto the (111) plane. Clusters which have $\hat{\ell}$ parallel to $\hat{g}$ may have a spherically symmetrical strain field and may be small stacking fault tetrahedra [12,13] or uncollapsed vacancy clusters [14]. Other clusters are thought to be Frank dislocation loops with Burgers vector $\vec{b} = \frac{a}{3} \langle 111 \rangle$. Subcascade formation, i.e. the splitting of a cascade into multiple depleted zones, was observed for 100 keV

cascades in Ag (Fig. 2. (a), (b)) and 140 keV cascades in Au (Fig. 3). The yield of visible cascades in Ag was 0.2 for 20 keV irradiation and 1.0 for 100 keV irradiation (closely spaced subcascades were counted as one). The defect density increased linearly with ion dose. Fig. 2 illustrates the development of the defect structure with dose. Subcascade structures during in-situ observation (Fig. 2. (a), (b)) always appeared simultaneously, indicating that they are associated with individual ion impacts. Fig. 4 shows 100 keV cascades in Ag after warming to room temperature. No significant changes in the defect density were observed when warming the specimen to room temperature.

DISCUSSION

The defect yield values can be compared with previous data on self-ion bombardment of Ag at room temperature [14]. For 100 keV both the room temperature and low temperature results indicate a cascade yield of 1. For 20 keV irradiation the present yield (0.2) was slightly lower than that found in room temperature self-ion irradiation (0.35 Ref. [14]). This is probably not due to an ambient temperature effect, since a lower yield is expected due to the lower energy density of Kr^+ ion cascades compared to self-ion cascades. The existence of defects which were out of contrast under kinematical bright field conditions used for defect density measurements [12] could also give lower yield values, although the comparison with micrographs of the same areas taken under dynamical conditions indicated that only a small fraction of the defects was out of contrast.

The present results demonstrate that in Au and Ag vacancies in an individual cascade of high energy density are clustered and collapse into Frank dislocation loops even at low temperature where the thermal migration of point defects is suppressed. A possible explanation for this very effective rearrangement of vacancies is given by thermal spike effects during the evolution of displacement cascades. After the cascade establishes its branching sequence of collisions producing many Frenkel pairs (typical time $\sim 10^{-13}$ s [15]), the kinetic energy of knocked-on atoms dissipates into the surrounding lattice. In the early stages (lifetime $\sim 10^{-12}$ s [15]), most of the energy is shared with the atoms in the immediate vicinity. Therefore the kinetic energy is still contained within a small volume comparable to the volume of damage straggling. During this period the energy density, i.e. average energy per atom in the volume, is so high that rearrangements of interstitial atoms and vacancies can take place by diffusional or quasi-diffusional jumps. Since the lifetime of this excited state is only on the order of a few tens of lattice vibration periods, it seems apparent that this atomic agitation is also accompanied by collective interactions which then lead to the observed extensive clustering of vacancies within the depleted zone and the collapse into a Frank dislocation loop as a stable configuration.

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Fig. 1. Black-white contrast of cascade vacancy clusters in Ag irradiated with 20 keV Kr⁺ ions at T < 10 K, dose = 1.2×10^{11} ions/cm², microscopy at T < 10 K with 400 keV electrons, dynamical dark field, $g = 220$.

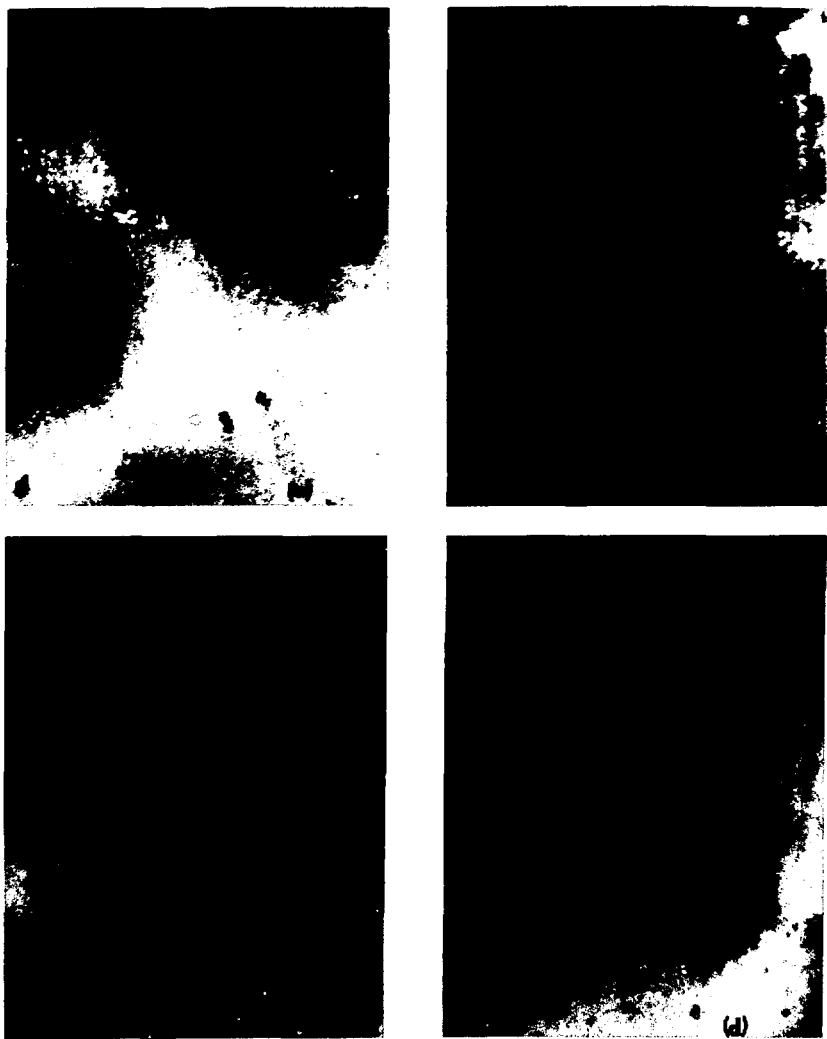


Fig. 2. Cascade vacancy clusters in Ag irradiated with Kr^+ ions at $T < 10$ K, microscopy at $T < 10$ K, kinematical bright field.
 100 keV $\text{Kr}^+ \rightarrow \text{Ag}$: (a) 2.3×10^9 ions/cm², (b) 5.6×10^9 ions/cm²;
 20 keV $\text{Kr}^+ \rightarrow \text{Ag}$: (c) 5.5×10^{10} ions/cm², (d) 1.2×10^{11} ions/cm².



Fig. 3. Cascade defect clusters in Au irradiated with 140 keV Kr^+ ions at $T < 10$ K, microscopy at $T < 10$ K, kinematical bright field.

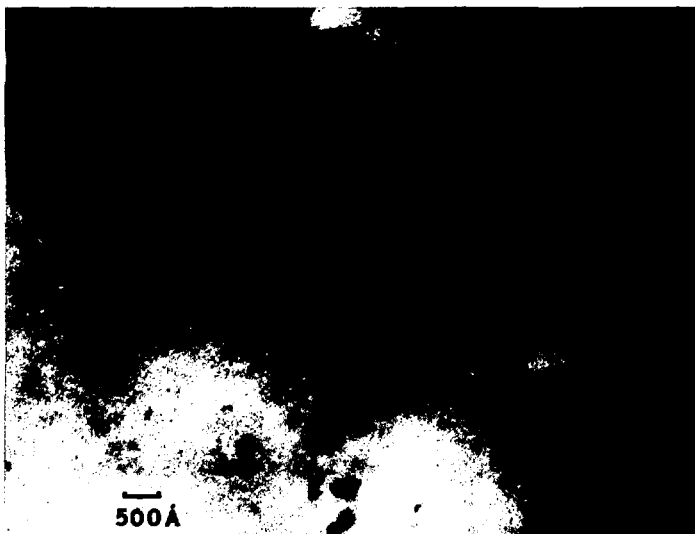


Fig. 4. Cascade vacancy clusters in Ag warmed to room temperature after 100 keV Kr^+ ion irradiation at $T < 10$ K, kinematical bright field, dose = 1.2×10^{10} ions/cm².

ELECTRON DAMAGE IN Zr AND Ti

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ABSTRACT

Specimens of Zr (99.9%) and Ti (99.8%) have been electron irradiated at temperatures up to 873 K using a 1 MV electron microscope. The damage structure has been analysed at room temperature and the results show that in Zr and Ti both vacancy and interstitial loops of $\frac{1}{2}\langle 11\bar{2}0 \rangle$ nucleate and grow. In addition vacancy loops of $\frac{1}{2}[0001]$ and interstitial loops of $\frac{1}{2}\langle 11\bar{2}3 \rangle$ are formed in Zr specimens which have foil normals (N) near $[0001]$ and $\langle 11\bar{2}0 \rangle$ respectively. In the case of Ti, complex loops, which microanalysis shows contain Fe, are observed at higher irradiation temperatures.

In all cases there is a partitioning of loops such that vacancy loops generally tend to have $\frac{1}{2}\langle 11\bar{2}0 \rangle$ as near parallel as possible to N and interstitial loops similarly have $\frac{1}{2}\langle 11\bar{2}3 \rangle$ perpendicular to N . The observations are discussed in terms of the factors which may be responsible for the stability of vacancy loops in Zr and Ti.

INTRODUCTION

The observation [e.g. 1,2] that large vacancy loops are formed during neutron irradiation of Zr and Ti has led to a reassessment of the factors which govern the clustering of point defects during irradiation at temperatures high enough for both vacancies and interstitials to be mobile. High temperature, high dose irradiation gives rise to voids and interstitial dislocation loops in virtually all other metals and alloys, and all theories developed to describe these observations require that vacancy loops are intrinsically unstable over the relevant temperature range. At the lower temperatures interstitials are assumed to be preferentially attracted to dislocations so that any vacancy loops shrink and interstitial loops grow. At higher temperatures any vacancy loops shrink by vacancy emission.

In view of the observations of vacancy loops in neutron irradiated Ti and Zr it has been suggested [3] that vacancy loops nucleate in cascades and that the interstitial bias is far higher in these metals than in others, although the reason for this large bias is not explained. Various suggestions have been made concerning the change of bias with loop size and the role of network dislocations in removing mobile interstitials but the problem with these modifications which have been suggested is that they should be equally applicable to other metals. Recent suggestions have been made involving anisotropic diffusion and anisotropic elasticity effects [4].

In the present work specimens of Ti and Zr have been electron irradiated with 1 MV electrons and the nature of the dislocation loops determined. The observations have shown that the type and nature of loops are influenced by the foil orientations. The significance of these observations is discussed in terms of the various factors which may influence loop nucleation and growth.

EXPERIMENTAL

Specimens for electron irradiation were prepared by electropolishing 3 mm discs of single and polycrystalline Zr and polycrystalline Ti using standard electropolishing conditions. Irradiations were carried out at temperatures up to 873 K using a $\pm 25^\circ$ double tilting heating stage in an EM7 operating at 1 MV. Defect analysis was carried out to a limited extent during irradiation but in the main detailed analysis was carried out on an EM400T which was interfaced with EELS and EDX facilities.

RESULTS

(i) Observations of Loops with $\mathbf{b} = \frac{1}{3}\langle 11\bar{2}0 \rangle$

The series of micrographs shown in Fig. 1 were taken from a Zr specimen with $\mathbf{N}_f$ the foil normal, near $[2314]$ (i.e. away from $[0001]$) which had been irradiated at 715 K to a displacement of about 0.1 d.p.a. Analysis shows that the loops with $\mathbf{b} = \frac{1}{3}\langle 11\bar{2}0 \rangle$ are made up of approximately equal numbers of vacancy and interstitial loops. The size range of the vacancy loops is found to be similar to that of the interstitial loops. Examination of specimens with different foil normals shows that there is a preference for interstitial loops to have $\mathbf{b}$ as close as possible perpendicular to $\mathbf{N}_f$ and vacancy loops to have $\mathbf{b}$ parallel with $\mathbf{N}_f$, i.e. the loops are oriented such as to relieve a tensile stress parallel with the foil surface. For example for a specimen with a foil normal near $[1211]$ the majority of the vacancy loops was found to have $\mathbf{b} = \frac{1}{3}[\bar{1}210]$ and the majority of interstitial loops was found to have either $\mathbf{b} = \frac{1}{3}[2\bar{1}10]$ or $\frac{1}{3}[1120]$.

Fig. 2 shows examples of loops in a sample of Ti with $\mathbf{N} \approx [0111]$ which analysis shows to be made up of interstitial loops of $\mathbf{b} = \frac{1}{3}[2\bar{1}10]$ and vacancy loops of $\mathbf{b} = \frac{1}{3}[1120]$ and $\frac{1}{3}[\bar{1}210]$. As in the case of Zr the interstitial loops were found to have Burgers vectors as close as possible perpendicular to the foil normal and the Burgers vector of vacancy loops as close as possible parallel to $\mathbf{N}$. In Ti samples with $\mathbf{N} \sim [0001]$ the majority of loops which were identified were interstitial but some vacancy loops were identified. In the samples examined in detail the foil normal was typically $10\text{--}15^\circ$ away from $[0001]$ in a sense towards $\langle 1100 \rangle$ about a specific $\langle 1120 \rangle$, and it was found that the interstitial loops tended to have a $\mathbf{b}$ which corresponded to that $\langle 1120 \rangle$.

It should be noted that in both Zr and Ti it is very difficult to obtain meaningful statistics of loop distributions because of the poor contrast observed with one sense of $\mathbf{g}$ with $\pm\mathbf{g}$ pairs [5] but the loop analysis which has been carried out shows that the partitioning of the interstitial and vacancy loops, although very marked, is not total; some vacancy loops are found with $\mathbf{b}$ nearly parallel with the foil surface and vice versa for interstitial loops.

(ii) Observations of $\mathbf{c}$ -component loops

In addition to the loops of $\mathbf{b} = \frac{1}{3}\langle 11\bar{2}0 \rangle$ found in Zr specimens there is a significant number of loops of $\mathbf{b} = \frac{1}{3}\langle 1123 \rangle$ in specimens with $\mathbf{N}$ near to $\langle 1211 \rangle$. Examples of these loops can be seen in Fig. 3 where $\mathbf{g} = 0004$. All such loops were found to be interstitial and again, as with the $\frac{1}{3}\langle 11\bar{2}0 \rangle$ loops, $\mathbf{b}$ tended to be perpendicular to $\mathbf{N}$. Rem bly it is found that irradiation of Zr foils

with N near $[0001]$ leads to the formation of vacancy loops of $b = \frac{1}{2}[000\bar{1}]$. Thus Fig. 4 shows loops, marked A, which are in contrast with $g = 0\bar{1}11$ and out of contrast with $g = 1210$ and which further analysis shows to be vacancy in nature.

In contrast to the case of Zr no loops which can be unambiguously identified as c-component loops have been found in Ti foils but as shown in Fig. 5 some complex loops are observed for which b is certainly not $\frac{1}{2}\langle 1120 \rangle$. It has not proved possible to determine the Burgers vectors of these loops, because only one invisibility can be achieved, and complex contrast is observed under many imaging conditions. The one invisibility which is observed (see Fig. 5) is consistent with the defects being edge loops and imaging in $\pm g$ then leads to the conclusion that the displacement of the loops is vacancy in nature. The long dislocations visible in this figure are formed by glide which takes place to relieve the stress exerted by the oxide formed during high temperature irradiation. In view of the difficulty in analysing the displacement of the loops EDX analysis was carried out to see if any impurity was associated with these defects and significant Fe segregation was detected. Work using proton irradiation of this same purity Ti showed that the only defects visible were heavily decorated with Fe [6]. EDX analysis failed to reveal any evidence for impurity segregation to the loops in Zr.

DISCUSSION

The fact that vacancy loops are found in electron irradiated Ti and Zr shows that cascades are not essential for the nucleation of vacancy loops during irradiation. It is therefore necessary to consider what other factors may be important in leading to vacancy and interstitial loop nucleation and growth.

The supersaturation of interstitials (i.e. the ratio of the radiation-induced to the thermal equilibrium concentrations) which is built up in the early stages of irradiation, is far in excess of the vacancy supersaturation and it therefore follows that nucleation of interstitial loops will take place first and the dynamic concentration of interstitials will drop rapidly. The concentration of irradiation-induced vacancies will then be able to increase and hence the conditions for either vacancy loop or void nucleation will be reached. The basic question which needs to be answered is why vacancy loops form in Zr and Ti whereas voids form in virtually all other metals.

The present results show not only that impurities interact with point defects, perhaps stabilizing vacancy loops in Ti, but also that the balance between the stability of vacancy and interstitial loops can be changed by foil orientation; it appears that this influence of foil normal is associated with the oxide stress. The fact that the oxide-induced stress can influence the loop population so significantly, despite the fact that this stress is a small fraction of the chemical stress exerted during growth by the radiation-induced interstitials and vacancies, suggests that the balance between the stability of vacancy and interstitial loops is very delicate. In fact calculations based on the assumption that the oxide-induced stress is about equal to the yield stress shows that the bias term will be changed by about 1.0%.

In addition to the demonstrated influence of impurities and stress the high solubility of gases in Zr and Ti is another very significant difference in terms of void nucleation between Zr and Ti and other metals. In this context it is of interest that only interstitial <a> type loops have been observed in electron irradiated Ruthenium - a metal with a similar $\frac{c}{a}$ ratio to Zr and Ti, but with a very low solubility for gases [7].

It is not possible at this stage to decide whether several of these factors are relevant in explaining the stability of vacancy loops in Zr and Ti and further work is clearly necessary to clarify the situation. It is of interest to note that recent measurements of the relaxation volume of an interstitial in Zr show that this is very much smaller than in other metals [8]. This is consistent with the fact that a small change in bias (caused by stress) can alter the relative stability of interstitial and vacancy c-component loops.

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Figure 1 Dislocation loops in Zr, following electron irradiation at 715 K to a dose ~ 0.1 d.p.a. $\underline{g}=\bar{1}2\bar{1}2$, $\underline{B}\sim[1213]$, $\underline{N}\sim[2314]$.



Figure 2 Ti electron irradiated at $\sim 400^\circ\text{C}$ (673 K) to ~ 0.3 d.p.a. $\underline{B}\sim \underline{N}\sim[0111]$, $\underline{g}\sim 10\bar{1}1$.



Figure: 3(a and b) Imaging of dislocation loops of $\underline{b} = \frac{1}{3}\langle 11\bar{2}3 \rangle$ in Zr following electron irradiation at 675 K to a dose ~ 0.2 d.p.a. $\underline{B}\sim[0110]$, $\underline{N}\sim[1211]$, a) $\underline{g}=2110$, b) $\underline{g}=0004$.



Figures 4(a and b) Analysis of basal c -component loops in Zr following electron irradiation at 715 K to a dose ~ 0.1 d.p.a. The faulted loops marked A are vacancy in nature having $b = \frac{1}{2}[0001]$ $N \sim [0116]$, a) $g = 1210$, $B \sim [0001]$, b) $g = 0111$, $B \sim [0112]$.



Figures 5(a and b) Ti electron irradiated at $\sim 450^\circ\text{C}$ (723 K) to ~ 0.5 d.p.a. $B \sim [0112]$, diffracting vectors are indicated. Note the characteristic double arc contrast of the complex loops (marked A) with 2110 .

MIGRATION OF INTERSTITIALS IN Nb-Zr ALLOYS DURING ELECTRON IRRADIATION BY USING A HIGH VOLTAGE ELECTRON MICROSCOPE

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ABSTRACT

Through examining the nucleation and growth process of dislocation loops in Nb-3.1 and 10.0wt.%Zr alloys during electron irradiation, apparent migration energies of interstitials have been determined. For these alloys two kinds of interstitials, Nb- and Zr-interstitials, contribute to the formation of loops. In order to understand the kinetic behavior of them simulation was performed by use of rate equations for defects produced under irradiation based on an assumption that three kinds of di-interstitials, Nb-Nb, Nb-Zr and Zr-Zr, act as nuclei of loops. The simulated results showed that each interstitial changes their concentration against irradiation time just like their behavior being in pure metals [1-3]. Based on the idea used for pure metals analytical formulation for loop formation was performed and the factor of controlling migration of interstitials was clarified. Migration of Nb-interstitials exerts an influence on the formation of loops and the apparent migration energy obtained experimentally correspond to that of Nb-interstitials.

INTRODUCTION

In order to understand the behavior of point defects in Nb-Zr alloys under electron irradiation, some *in-situ* experiments with a high voltage electron microscope (HVEM) have been performed [4-7]. The dependence of loop density on irradiation time, irradiation flux and irradiation temperature gives us informations about migration of interstitials and/or vacancies. It has been determined that apparent migration energy of free interstitials and binding energies of N- and O-impurities with interstitials in Nb-3.1wt.%Zr alloy are (0.21 ± 0.03) , (0.45 ± 0.04) and (0.69 ± 0.06) eV, respectively [5-7]. In case of the alloy Nb- and Zr-interstitials would contribute to the formation of loops, and have to be taken into account for understanding the nucleation and growth kinetics of loops. The purpose of the present paper is to understand the intrinsic meaning of the apparent migration energy of interstitials with aid of the pseudo-chemical rate theory.

EXPERIMENTAL PROCEDURE

Ingots of Nb-3.1 and 10.0wt.%Zr alloys were made by using an electron-beam furnace under a vacuum of 10^{-4} Pa. The ingots were rolled into sheets and then thinned into foils by electro-polishing in a solution of 5% H₂SO₄ and 2.5% HF in methanol by volume for transmission electron microscopy.

Electron irradiation was performed at temperatures from 578 to 693 K by use of an HVEM at 1000 kV. The irradiation was done along a direction about 1.3×10^{-2} rad away from $\langle 100 \rangle$ to $\langle 110 \rangle$ for minimizing the electron diffraction channelling. Production rate of Frenkel pairs was estimated from the displacement cross sections given by Oen [8].

EXPERIMENTAL RESULTS

Density and mean size of loops were examined during irradiation under a fixed electron flux of 2.9×10^{23} electrons/m²s. Density of loops in Nb-3.1 and 10.0wt.%Zr alloys, whose Burgers vectors and habit planes are $a/2\langle 111 \rangle$ and $\{110\}$, respectively [5,6], saturates very early in the irradiation as shown in Fig.1 for typical irradiation temperatures. The nucleation of loops is completed in the beginning of irradiation and density of loops remains constant for increasing irradiation time. The size of loops, on the other hand, is proportional to the cube root of irradiation time as shown in Fig.2, following a kinetics expected at temperatures where only interstitials are mobile [1-3].

The saturated density which corresponds to the constant level in Fig.1 is plotted against irradiation flux in Fig.3. From Figs.1, 2 and 3, kinetic behavior of defects under irradiation in Nb-10.0wt.%Zr alloy is analogous to that in Nb-3.1wt.%Zr alloy, that is,

$$D \propto t^{1/3} \text{ and } C_L \propto \phi^{1/2} t^0,$$

where D and C_L are the diameter and the density of loops, respectively, t the irradiation time and ϕ the irradiation flux. Therefore, interstitials are expected to migrate freely from 582 to 693 K in Nb-10.0wt.%Zr alloy and apparent migration energy of interstitials E_M^I is derived from the following relations [1-3] :

$$C_L \propto \phi^{1/2} M_I^{-1/2} t^0 \text{ and } M_I = \nu \exp (-E_M^I/kT),$$

where ν is the vibrational frequency of interstitials, k the Boltzmann constant and T the irradiation temperature. Arrhenius plots of C_L vs. $1/T$ are shown in Fig.4 and give $E_M^I = (0.21 \pm 0.03)$ and (0.25 ± 0.03) eV for Nb-3.1 and 10.0wt.%Zr alloys, respectively. The values of E_M^I show scarcely depends on the alloy composition.

ANALYSIS OF THE EXPERIMENTAL RESULTS

Variation of Concentration of Defects with Irradiation Time

Apparent migration energies of interstitials in the both alloys were determined by utilizing a model presented for pure metals. In this model the following assumptions are made, which should be subjected to criticism based on the experimental results ;

The characteristics of Zr-atoms are identical with those of Nb-atoms, that is, $P_{Nb} = P_{Zr}$ and $M_I^{Nb} = M_I^{Zr}$, where P_j and M_I^j (j stands for Nb or Zr) are the production rate and mobility of j -interstitials. The nucleation process of loops in the case where $P_{Nb} \neq P_{Zr}$ and $M_I^{Nb} \neq M_I^{Zr}$ is considered by use of the pseudo-chemical rate theory based on an assumption that only vacancies are dominant sinks for interstitials through the whole stage of

irradiation. An explicit set of kinetic equations is as follows :

$$dC_I^{Nb}/dt = 0.97P_{Nb}(1-C_V)(1-ZC_V) - 2M_I^{Nb}C_I^{Nb}C_V - 2ZM_I^{Nb}(C_I^{Nb})^2 - Z(M_I^{Nb} + M_I^{Zr})C_I^{Nb}C_I^{Zr} - Z(C_{IL}C_L)^{1/2}M_I^{Nb}C_I^{Nb}, \quad (1)$$

$$dC_I^{Zr}/dt = 0.032P_{Zr}(1-C_V)(1-ZC_V) - 2M_I^{Zr}C_I^{Zr}C_V - 2ZM_I^{Zr}(C_I^{Zr})^2 - Z(M_I^{Nb} + M_I^{Zr})C_I^{Nb}C_I^{Zr} - Z(C_{IL}C_L)^{1/2}M_I^{Zr}C_I^{Zr}, \quad (2)$$

$$dC_V/dt = (0.97P_{Nb} + 0.032P_{Zr})(1-C_V)(1-ZC_V) - 2M_I^{Nb}C_I^{Nb}C_V - 2M_I^{Zr}C_I^{Zr}C_V, \quad (3)$$

$$dC_{IL}/dt = Z(C_{IL}C_L)^{1/2}(M_I^{Nb}C_I^{Nb} + M_I^{Zr}C_I^{Zr}) \quad (4)$$

$$\text{and } dC_L/dt = 2Z(M_I^{Nb}C_I^{Nb})^2 + M_I^{Zr}(C_I^{Zr})^2 + Z(M_I^{Nb} + M_I^{Zr})C_I^{Nb}C_I^{Zr}, \quad (5)$$

where C_I^{Nb} , C_I^{Zr} , C_V , C_{IL} and C_L are the concentration of Nb-, Zr-interstitials, vacancies, interstitials in loops and loops, respectively, and Z the number of combination sites between defects of interstitial-to-vacancy, interstitial-to-interstitial and interstitial-to-loop reaction.

Numerical calculation was first performed to estimate the effect of the cross term, $Z(M_I^{Nb} + M_I^{Zr})C_I^{Nb}C_I^{Zr}$, which is the formation rate of nuclei of loops composed of an Nb- and a Zr-interstitial, on C_L . Accumulation manners of the defects under irradiation are shown in Figs.5(A)-(D), where following values are used for the necessary parameters ; the fixed value of migration energy of Nb-interstitials $E_M^{Nb} = 0.21$ eV, $P_{Nb} = 9.2 \times 10^{-4}$ /s and $P_{Zr} = 9.1 \times 10^{-4}$ /s corresponding to a flux of 2.9×10^{23} electrons/m²s, $v = 10^{13}$ /s and $Z = 10^2$.

The values of C_I^{Nb} and C_I^{Zr} reach maxima and decrease in proportion to $t^{-2/3}$ with increasing t for a long time irradiation. The maximum of C_I^{Zr} , $(C_I^{Zr})_{max}$, and the time for $(C_I^{Zr})_{max}$, t^{Zr} , increase with increasing energy of migration of Zr-interstitials E_M^{Zr} . The value of C_L saturates very early in the irradiation and at the time when C_I^{Nb} and/or C_I^{Zr} reach the maxima.

Analytical Solutions for Loop Nucleation under Irradiation

The change in concentration of defects against t obtained from the numerical calculation suggests that Nb- and Zr-interstitials in the alloy behave almost independently with each other. During a very early stage of the irradiation C_I^{Nb} , C_I^{Zr} and C_V are so small that all point defects introduced by the irradiation will accumulate in proportion to Pt , and

$$C_I^{Nb} = 0.97Pt, \quad C_I^{Zr} = 0.032Pt \quad \text{and} \quad C_V = Pt$$

under $P_{Nb} \approx P_{Zr} = P$. The accumulation rate of Zr-interstitials is very small compared with that of Nb-interstitials because of the alloy being low concentration of Zr. The annihilation of interstitials to vacancies becomes dominant with the increase of C_I^{Nb} , C_I^{Zr} and C_V . Then, concentration of Nb- and Zr-interstitials reaches their maximum values at $t = t^{Nb} = (2M_I^{Nb}P)^{-1/2}$ and $t^{Zr} = (2M_I^{Zr}P)^{-1/2}$, respectively. When di-interstitials are stable nuclei of loops, the integrated density of loops, $(C_L^{Nb})_{max}$ and $(C_L^{Zr})_{max}$, until t^{Nb} and t^{Zr} is respectively given as follows :

$$(C_I^{Nb})_{\max} = 0.56(P/Zr_I^{Nb})^{1/2} \text{ and } (C_I^{Zr})_{\max} = 0.22(P/Zr_I^{Zr})^{1/2}.$$

Density of loops for a long time irradiation can be estimated by these equations, and it depends on M_I^I . Kinetics for loop formation can be classified in terms of the ratio of M_I^{Zr}/M_I^{Nb} as follows.

Case [I] $M_I^{Zr}/M_I^{Nb} \gg 1$

In this case nucleation of loops finishes at t^{Nb} and di-Nb-interstitials would act as dominant nuclei of loops (Figs. 5(A)-(C)). The density of loops is then subjected to the term of $2Zr_I^{Nb}(C_I^{Nb})^2$ in Eqn.(5), and the density of loops for a long time irradiation can be obtained as :

$$C_L \propto (P/M_I^{Nb})^{1/2}. \quad (6)$$

From Eqn.(6) an Arrhenius plot of C_L vs. $1/T$ gives E_M^{Nb} . Therefore, apparent migration energy $E_M^I = 0.21$ eV determined from the Arrhenius plot is expected to be E_M^{Nb} .

Case [II] $M_I^{Zr}/M_I^{Nb} < 1$

Taking into account that concentration of Nb is much higher than that of Zr in the alloy, there exist two cases that di-Nb-interstitials or Nb- and Zr-interstitial compounds act as dominant nuclei of loops, and corresponding to the cases nucleation of loops finishes at t^{Nb} (Case [II-1]) or t^{Zr} (Case [II-2]), which lead analytical solutions for C_L as follows :

$$C_L \propto (P/M_I^{Nb})^{1/2} \text{ for Case [II-1]} \quad (7)$$

$$\text{and } C_L \propto (P/M_I^{Zr})^{1/2} \text{ for Case [II-2]}. \quad (8)$$

In the cases of [II-1] and [II-2] an Arrhenius plot of C_L vs. $1/T$ gives E_I^{Nb} and E_M^{Zr} , respectively, from Eqns.(7) and (8). However, following relations can be brought up from analytical solutions for the both cases as :

$$E_M^{Nb} < E_M^{Zr} \approx 0.21 \text{ eV for Case [II-1]}$$

$$\text{and } E_M^{Zr} > E_M^{Nb} \approx 0.21 \text{ eV for Case [II-2]}.$$

The apparent migration energy E_M^I determined by the Arrhenius plot does not agree with the predicted migration energies, E_M^{Nb} and E_M^{Zr} , in the cases of [II-1] and [II-2], respectively.

DISCUSSION AND CONCLUSION

An approximation of $P_{Nb} = P_{Zr} = P$ on making analytical solutions was confirmed to be fairly good from the displacement cross sections [8]. Analytical solutions based on the approximation were in good agreement with results obtained numerically, and could also apply to kinetic behavior of point defects in Nb-10.0wt.%Zr alloy. The relation $C_L \propto P^{1/2}$ predicted in analytical solution in Case [I] was also confirmed by numerical calculation.

The conclusion is that apparent migration energies of interstitials in Nb-3.1 and 10.0wt.%Zr alloys correspond to E_H^{Nb} intrinsically.

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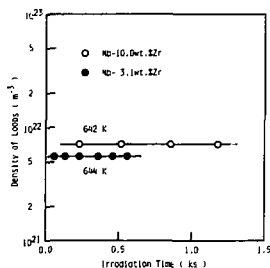


Fig.1 Irradiation time dependence of loop density under a flux of 2.9×10^{23} electrons/m²s.

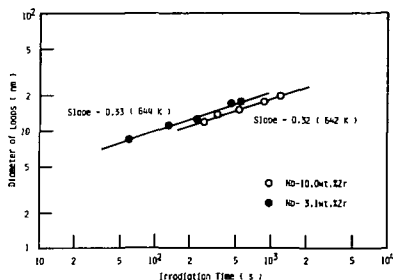


Fig.2 Irradiation time dependence of mean diameter of loops under a flux of 2.9×10^{23} electrons/m²s.

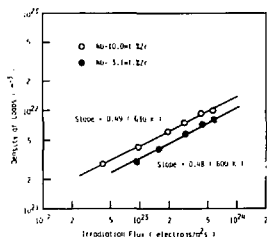


Fig.3 Irradiation flux dependence of loop density.

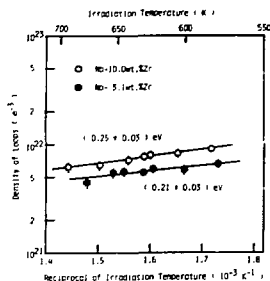


Fig.4 Irradiation temperature dependence of loop density under a flux of 2.9×10^{23} electrons/ m^2s .

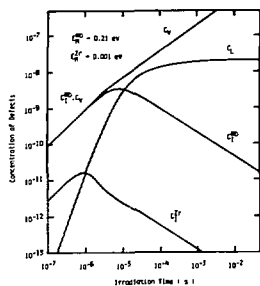


Fig. 5a

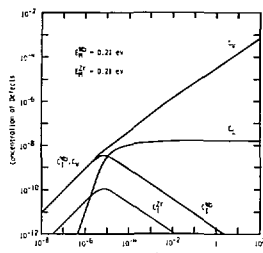


Fig. 5b

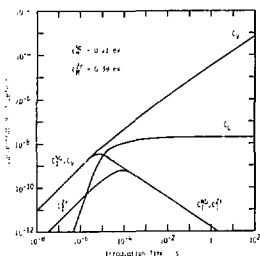


Fig. 5c

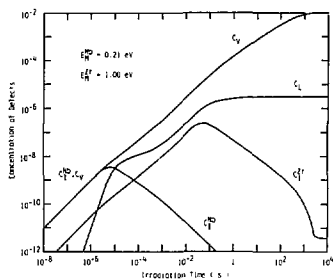


Fig. 5d

Fig. 5. Variation of concentration of each kind of defects with irradiation time under a constant flux of irradiation, which were obtained by numerical calculation. The parameters used are: $P_{Nb} = 9.2 \times 10^{-4}$ /s, $P_{Zr} = 9.1 \times 10^{-4}$ /s, $T = 600$ K, $Z = 100$, $v = 10^{13}$ /s, $E_I^0 = 0.21$ eV and $E_M^0 = 0.001$ (A), 0.21 (b), 0.39 (C) and 1.0 eV (D).

FORMATION OF POINT DEFECT CLUSTERS IN ELECTRON IRRADIATED GERMANIUM

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Abstract

Electron irradiation of germanium below 200°K results in the formation of faulted interstitial loops on {113} planes after fairly long incubation period. The formation is strongly dependent both on crystallographic orientation and electron diffraction condition. After prolonged irradiation, small vacancy type defects (less than 50 Å) of higher density appear in the thinner part of a specimen normally free from interstitial type loops. The intentional contamination of pure specimen by carbon deposition has been found to lead to the formation of vacancy type faulted loops on {113} planes at narrow temperature range around 250°C. The analysis of the shrinkage behaviour of these defect clusters by annealing at above 500°C leads to the conclusion that the self-diffusion in germanium is carried with vacancy type point defects.

1. Introduction

It is well known that high voltage electron microscopy is now serving as a powerful tool to study elementary processes of radiation induced defects i.e. formation and aggregation of point defects in metals.¹⁾ Here in the field of semiconductors, very little is known, at present, on the property of point defects and also point defect clusters despite the past several pioneering efforts.^{2,3)} In this paper, the defect structure development in germanium by electron irradiation will be reported, aiming at the understanding of the nature of point defect clusters.

2. Experimental Techniques

A high voltage electron microscope HU-2000 was used for the introduction of defect clusters and for observations. The microscope was operated at 2000 kV, and the irradiation intensity ranged from 10^{18} up to 1.3×10^{20} electrons/cm². sec. With heating and cooling specimen holders both on a tilting stage, specimens could be cooled down to 100°K and heated up to 600°K. Static and detailed observation of defect clusters introduced by the electron irradiation was carried out with a smaller microscope JEM-200 CX operated at damage sub-threshold energy. Specimens mainly examined were pure germanium single crystals doped slightly with antimony of 10^{13} atoms/cc. A few gallium doped specimens (3×10^{18} atoms/cc) were used for checking impurity effects. Disks of thickness 0.5 mm and diameter 3 mm were cut from the rods by using an ultrasonic cutter. Hollows were digged about 0.15 mm deep and 0.7 mm diameter at the center of both surfaces of each disk by an ultrasonic drill. These disks were chemically polished in a solution of nitric acid (90%) and hydrofluoric acid (10%) to have a small hole around which the crystal was wedge-shaped and suitable for the electron microscope observation.

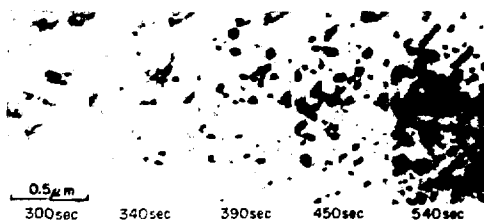


Fig. 1 Formation of dislocation loops at 173°K.
 8×10^{19} e/cm²-s.



Fig. 2 Interstitial type dislocation loops. 1.8×10^{22} e/cm².

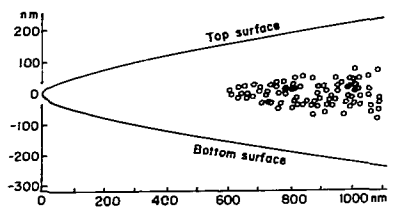


Fig. 3 Distribution of interstitial loops in tapered edge of irradiated specimen foil.

3. Interstitial Type Dislocation Loops

Above 200°K, no defect cluster could be observed in the high voltage microscope even with a prolonged irradiation up to one hour with a strong intensity of 10^{20} e/cm²-sec. Below 200°K, dislocation loops have appeared in the thicker part of a specimen. These defect clusters have been identified to be dislocation loops of interstitial type by using so-called inside-outside contrast technique and widely varied

planes of the loops were all on {113} type.⁴⁾ Dark field images of loops in Fig. 2 show clearly that all the loops contain stacking fault. Parallax analysis of the stereo-pictures leads to the spacial distribution of the loops in a wedge shaped specimen as in Fig. 3, in which the loops are formed only at the central part of the thick part of specimen having defect free zones along to specimen surfaces. As is shown in Fig. 1 and is plotted in Figs. 4 and 5, dislocation loops start their appearance after some time period of irradiation and then increase their number, and decrease later by mutual coalescence. The incubation time is longer and nucleation rate is smaller for higher irradiation temperature, and finally no clustering takes place above 200°K in pure germanium. This limit was found to rise to near room temperature in 3×10^{18} /cc gallium doped one.

Temperature independent constant speed growth of interstitial type dislocation loops in Fig. 5 can be attributed to the growth under the thin foil condition at temperatures high enough for the high speed motion of interstitials and vacancies. Shortly after the start of irradiation, steady concentration level of each type of point defect is established by the balance between the introduction by irradiation and escape to specimen surface. Both of the balanced levels are simply proportional to the production rate of point defects and inversely proportional to the mobility of each defect. Then the diffusion efficiency of each point defect, the product of the concentration and the mobility, becomes simply proportional to the production rate and independent of the mobility --- experimentally independent of irradiation temperature. A loop nucleated under this condition is supplied continuously by a constant rate of interstitial atoms and another constant rate of vacancies, both of which are independent of temperature. Slight difference in the cross-section to absorb interstitials than vacancies makes the loop grow with a constant speed.

The understanding of the existence of the fairly long incubation for the nucleation of interstitial clusters is not so straightforward as that of the growth

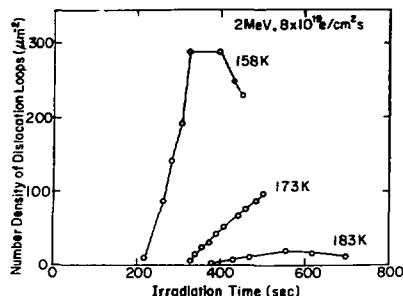


Fig. 4 Nucleation of interstitial clusters at different temperatures.

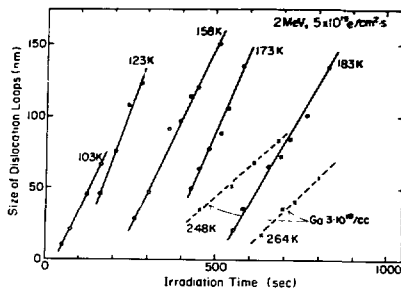


Fig. 5 Growth of interstitial dislocation loops at various temperatures.

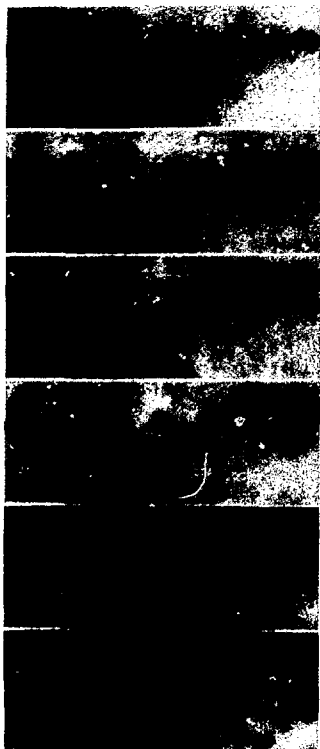


Fig. 6 Development of helical dislocation by electron irradiation. 6.4×10^{19} e/cm²·s at 170°K.

phenomena. This nature of the nucleation is entirely different from these observed in metals in which the nucleation takes place only at the early beginning of irradiation and has been well understood from point defect reactions. The observed long incubation can never be attributed to the waiting time for the establishment of reaction level from any type of conceivable reaction kinetics at present, and even experimentally the start of the development of helical dislocation from a screw dislocation much earlier than the nucleation of interstitial clusters as shown in Fig. 6 tells us the defect reactions has started much earlier than the start of the nucleation.

Formation of interstitial clusters was observed with various electron diffraction conditions in specimen foils with surface normal near $\langle 110 \rangle$ or near $\langle 111 \rangle$, and some representative cases are shown in Fig. 7. Although nothing can be stated on general orientation dependence of radiation damage from these limited data, it can at least be concluded that the damage rate is strongly dependent both on the diffraction condition and crystal orientation. The damage is strongly enhanced when $[220]$ type of reflection is excited with the beam nearly parallel to $\langle 110 \rangle$ direction. This is naturally accepted from crystallographic direction with largest empty channels and also the localization of electrons on the plane of dense atomic packing parallel to this channel.

4. Vacancy Type Fine Clusters

After some development of interstitial clusters by irradiation, smaller defects of higher density appear especially in the thinner area of specimen normally free from interstitial loops.

Stereo observation in Fig. 8 indicates these small defects distributes randomly inside the specimen foil. The technique called 2D⁵⁾ is applied for determining the vacancy or interstitial character of these fine clusters. Figure 9 gives the 2D stereo for under-focused photograph on the left and in-focus photograph on the right with the operating g vector $\langle 220 \rangle$ pointing to the right. The defect clusters which have been mentioned above and already identified to be of interstitial are located on the right half of each photograph and fine clusters are on the left. Illustration of cluster-depth distribution in 2D stereo is given in Fig. 10 which shows clearly the nature of fine clusters to be of vacancy. It should be noted that these fine vacancy clusters can be nucleated up to 100°C and above 100°C no observable defect clusters can be introduced in pure germanium.

5. Vacancy Type Dislocation Loops

Vacancy type dislocation loops which have a trend of growing along $\langle 110 \rangle$ type directions can be nucleated by the irradiation above 150°C only in the specimens coated with carbon film of a few hundred angstrom.⁶⁾

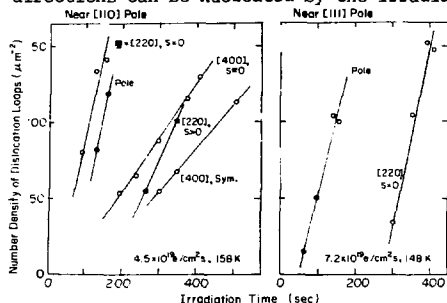


Fig. 7 Orientation and diffraction condition dependence of the nucleation of interstitial clusters.

Above 300°C these loops appear immediately, grow rapidly, and then shrink gradually. No cluster remains after heavy irradiation up to 10^{23} electrons/cm². These clusters are not stable and shrink even by irradiation at 65°C. The nature of these loops was examined with a pair of usual stereographs and a diffraction contrast method, that is, so-called inside-outside technique in JEM-200 CX. Similar to interstitial loops introduced below 200°K, these loops grow on $\{113\}$ type planes but they are identified to be of vacancy type.⁶⁾ Although these loops must be originated in impurity carbon atoms, they must be mainly composed of radiation induced vacancies.

6. Annealing of Point Defect Clusters



Fig. 8 Vacancy clusters in electron irradiated specimen. 5×10^{21} e/cm² at 180°K.



Fig. 9 2D stereo for under-focused photographs(L) and in-focus photograph(R).

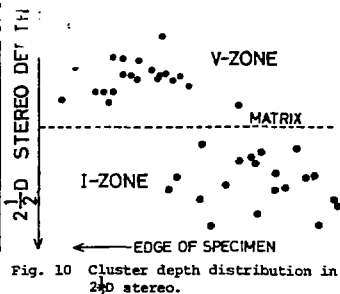


Fig. 10 Cluster depth distribution in 2D stereo.



Fig. 11 Growth of V-type dislocation loops at 250°C by electron irradiation. 1×10^{19} e/cm²·s.

As shown in Fig. 12, experiments on the annealing of vacancy loops have been performed in JEM-200CX. Above 450°C these faulted loops on {113} type planes begin to unfault, shrink their size gradually and change their habit planes by the time the specimen temperature reaches at 600°C, so they can get vacancy type perfect loops on {110} type planes. In order to analyze the shrinkage speed of the perfect vacancy loops, we have to remind the analysis given by Dobson et al.⁷⁾ In the case of vacancy type self-diffusion the shrinkage is controlled by the emission of vacancies and the diffusion of the vacancies from the loop to the specimen surface. The solution of the diffusion equation with a cylindrical boundary condition of radius R is given by

$$-\left(\frac{dr}{dt}\right)_V = \frac{2\pi D}{b \ln(R/b)} \left[\exp\left(\frac{F_C}{kT}\right) - 1 \right] \quad (1)$$

and

$$F_C = [3Gb^2B^2/8\pi] \frac{1}{r} \left[\ln\left(\frac{2\pi r}{b}\right) - 0.37 \right] \quad (2)$$

Here, D is the self-diffusion coefficient, b the Burgers vector and B² is the cross sectional area of a vacancy on the loop plane. In fact the quantity in the bracket of eq.(1) can be approximated to be a/rT , where a is a constant slightly dependent both on r and T. Figure 13 shows us that the rate of shrinkage of a perfect loop is accelerated as it becomes smaller and the shrinkage speed seems to be inversely proportional to the radius. This means that the shrinkage is controlled by the emission of constituent vacancies. These observation and analysis lead us to a greater understanding of the process of self-diffusion. These vacancy loops act as sources to provide the crystal with vacancies, of course, so we have to conclude the self-diffusion in germanium with the mechanism of vacancy type. On the other hand, the annealing



Fig. 12 Thermal shrinkage of vacancy type dislocation loops in irradiated germanium.

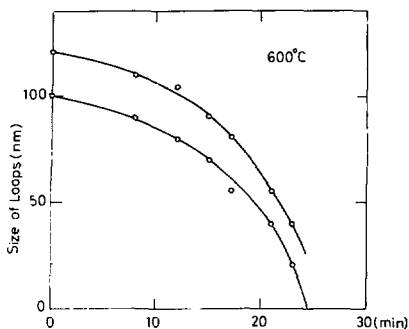


Fig. 13 Shrinkage of typical perfect vacancy loops at 600°C.

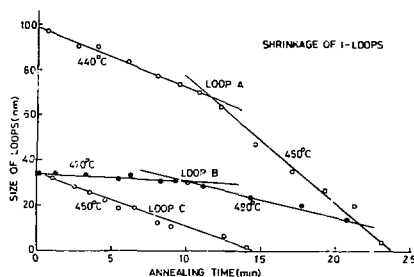


Fig. 14 Shrinkage curves of interstitial type dislocation loops.

of interstitial loops introduced below 200°K was also carried out by means of the similar technique as that of vacancy loops. The shrinkage of the interstitial loops by annealing was found not to accelerate at their smaller size^{1,6)} as shown in Fig. 14, and this observation suggests that the loops shrink by absorbing thermal vacancies, again definitely suggesting the self-diffusion in germanium with vacancies.

Acknowledgements

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RADIATION DAMAGE IN CERAMICS: THE INFLUENCE OF GRAIN BOUNDARIES

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ABSTRACT

Both single crystal and polycrystalline ceramics have been irradiated with neutrons and electrons at high temperatures. Grain boundaries are observed to have an important influence on the microstructure and resulting properties. For example, void and loop alignment leads to anisotropic swelling and cracking along grain boundaries in Al_2O_3 ; denuded zones are observed in $\beta\text{-Si}_3\text{N}_4$; voids are only observed near the grain boundaries in MgAl_2O_4 ; and in YAG the grain boundary phase (Al_2O_3) is damaged much more heavily than the matrix. This research was supported by the DOE, Contract No. DEAC0276ER 02119.

INTRODUCTION

Radiation damage in ceramics has become a subject of increasing interest in the past few years not only because of its fundamental interest but also because of its practical importance with respect to materials behavior in fission and fusion reactors, nuclear waste storage, ion-implantation, etc. Spectroscopy has provided a great deal of information about point defects and small defect clusters and now transmission electron microscopy (TEM) has started to make a significant impact in our understanding of secondary defect formation and growth processes [1]. Both dislocation loops and voids are commonly observed and both electron irradiation (via HVEM) and fast neutron irradiation have been used to produce damage [2]. In many cases the damage is caused by knock-on displacement, as in metals, and we will concentrate on such examples in the present paper (Al_2O_3 , MgAl_2O_4 , YAG, Si_3N_4). In many other cases the principle damage is due to ionization and subsequent radiolysis (displacement) in materials such as alkali halides and quartz.

In the present paper we will concentrate not only on the four ceramics given above, but also on observations in connection with grain boundaries in these materials. It is well known in the case of metals that grain boundaries can have a great deal of influence on the microstructure and the resultant properties of irradiated materials. The materials described below were irradiated in EBR-II at temperatures of 925 and 1000 K to doses of $2 \times 10^{26} \text{ n/m}^2$.

($E > 0.1$ MeV). Details are available elsewhere [3]. Comparisons were made with damage microstructures produced in a Hitachi HU-650B HVE at 650 kV.

Al₂O₃

The microstructure produced in polycrystalline Al₂O₃ by neutron irradiation is quite dramatic (Fig. 1). Void alignment parallel to the c axis is clearly evident; tilting experiments show that there is no void ordering in the basal plane, only perpendicular to it along the c axis. Fig. 1 is a phase contrast image, taken in the underfocussed condition, and so the high dislocation density can only just be made out as a background of dark lines and loops. The dislocations are shown clearly in the weak beam dark-field image of Fig. 2. In fact, the dislocations are produced initially by the formation of faulted $1/3[0001]$ (0001) and $1/3\langle 1010 \rangle \{1010\}$ interstitial loops, as has been shown in HVE irradiation studies [4]. These loops then grow and unfault to give $1/3 \langle 10\bar{1}1 \rangle$ dislocations which interact to give a dislocation network by reactions such as:

$$1/3 [10\bar{1}1] + 1/3 [01\bar{1}1] \rightarrow 1/3 [11\bar{2}0]$$

The network then becomes the biased sink for interstitials which is necessary for vacancy supersaturation and void nucleation. Void alignment is due to an anisotropic elastic interaction between neighboring voids [5].

Also shown in Fig. 1 are grain boundary cracks. The cracking is due to anisotropic swelling which is about four times larger along the c axis than along the a axis of sapphire (Fig. 3). This anisotropic swelling cannot be due to the void alignment but must be due to preferential deposition of interstitials on the basal loops rather than on the prism plane loops so that there is a net growth along the c axis. Presumably the bias of interstitials to the basal loops is due to an anisotropic elastic interaction.

MgAl₂O₄

MgAl₂O₄ spinel damages much less readily than sapphire and a relatively low density of loops is produced for the same irradiation conditions. The loops that do form are observed to be linked together in a rosette pattern. The individual loops are faulted $1/4 \langle 110 \rangle \{110\}$ interstitial dislocations which grow from a central point on all 6 equivalent $\{110\}$ planes, as described before for single crystals [6]. The same rosettes are observed within the grains of polycrystalline spinel, as shown in Fig. 4. The Burgers vectors of the loops is such as to preserve the basic stoichiometry and create a fault only on the cation sublattice, as with Al₂O₃. The relatively low dislocation density in MgAl₂O₄ means that the interstitial sink density is low and the conditions for void formation in the bulk are unfavorable. However, careful phase contrast imaging (Fig. 5) reveals well-defined rows of small voids adjacent to all of the grain boundaries. This may mean that the grain boundaries are biased sinks for interstitials or simply that the interstitial mobility is greater than the vacancy mobility. In the latter case, the denuded zone for interstitials will be wider than that for vacancies so that there will be a region in which the vacancy supersaturation is high enough for void nucleation.

β - Si_3N_4

In β - Si_3N_4 (as in MgAl_2O_4 and YAG), the swelling is relatively low but the damage is extensive and complex. Pre-existing $\{0001\}$ screw dislocations are helicized by the condensation of interstitials and sometimes pinch off to form $\{0001\}$ perfect loops. Faulted loops form on the arms of the helices and also nucleate in great density in dislocation-free regions. Both the helices and faulted loops are shown in Fig. 6. The faulted loops lie accurately on $\{10\bar{1}0\}$ planes but the determinations of their Burgers vector proved troublesome. After extensive $\bar{g}\cdot\bar{b}$ analysis [7], the Burgers vector was concluded to be $1/10\langle 11\bar{2}5 \rangle$, similar to the suggested dissociation for glide dislocations in β - Si_3N_4 [8]. In fact, this partial vector joins $[\text{SiN}_4]$ tetrahedra in the structure and has a magnitude slightly smaller than the c axis vector. Grain boundary effects are demonstrated by the dramatic denuded zones (Fig. 7), presumably due to interstitial/vacancy diffusion distance to the sink. In addition, there is a glassy grain boundary phase which develops voids or bubbles during irradiation. However, no grain boundary cracking is observed.

YAG

Yttrium aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$) reveals remarkably little evidence of irradiation. A very low density of faulted interstitial loops is found on $\{110\}$ planes. This is shown most clearly by lattice imaging (Fig. 8). The loop is clearly interstitial and the lattice appears to be displaced by $1/4\langle 110 \rangle$. It is possible that there is a component of displacement parallel to the beam. However, the vector is apparently different from the $1/4\langle 111 \rangle$ electrostatic fault or the $1/2\langle 100 \rangle$ and $1/2\langle 110 \rangle$ order faults discussed by Rabier et al. [9]. So far as grain boundary behavior is concerned, the most dramatic effect is the damage of Al_2O_3 grain boundary phase which proves of startling contrast to the relative inaction in YAG (Fig. 9). The Al_2O_3 behaves in the same way as the bulk material and is full of dislocations and voids. Its swelling is such as to strain the surrounding YAG, and has the potential to wedge open cracks along the grain boundaries.

DISCUSSION

In general complex ceramics are less sensitive to radiation than simpler ceramics such as Al_2O_3 and MgO [1] because of the difficulty in nucleating secondary defect clusters. For example, stoichiometry and electrical neutrality of interstitial loops in Al_2O_3 are maintained by clustering anti-Schottky quintets. In spinel septets are required, while in YAG an anti-Schottky icoset is needed! However, the present work has shown that this is not the whole story and that grain boundaries can have a potentially dominating effect, as in the following examples:

1. The discontinuous change of orientation in combination with anisotropic swelling can lead to cracking along grain boundaries (α - Al_2O_3).
2. Denuded zones result from the grain boundaries acting as sinks (β - Si_3N_4) and a larger denuded zone for interstitials than for vacancies can give rise to rows of voids (MgAl_2O_4).
3. Grain boundary phases may damage differently and could weaken the boundaries, as in the example of the amorphous g.b. phase in β - Si_3N_4 and the α - Al_2O_3 g.b. phase in YAG.

4. Grain boundaries are also potential sites for the nucleation of new phases during irradiation, but no example has been found in the present study.

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Fig. 1. Phase contrast image of void alignment in three grains of polycrystalline α - Al_2O_3 neutron irradiated at 1100 K (underfocussed condition).

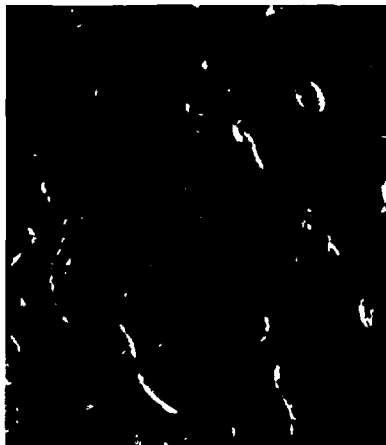


Fig. 2. Weak Beam Dark Field (WBDF) of the high density dislocation network in neutron irradiated α - Al_2O_3 .

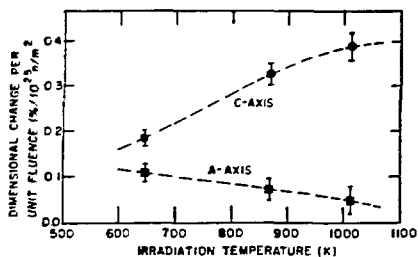


Fig. 3. Anisotropic swelling measured as a function of temperature and neutron fluence [3].



Fig. 4. Weak Beam Dark Field (WBDF) of $1/4 \langle 110 \rangle \{110\}$ faulted, interstitial dislocation loops in polycrystalline MgAl_2O_4 neutron irradiated at 1100 K.



Fig. 5. Voids near grain boundaries in neutron irradiated polycrystalline MgAl_2O_4 (a) general view and (b) a three grain junction with associated voids.



Fig. 6. Weak Beam Dark Field (WBDF) of $\vec{b} = [0001]$ helical dislocations and $\vec{b} \approx 1/10 \langle 11\bar{2}5 \rangle$ loops produced in Si_3N_4 after neutron irradiation at 1100 K.



Fig. 7. Defect-denuded zones near grain boundaries in neutron-irradiated Si_3N_4 . Note voids in the amorphous grains boundary phase.



Fig. 8. High resolution structure image of planar defect in $\text{Y}_3\text{Al}_5\text{O}_{12}$ neutron irradiated at 1100 K.

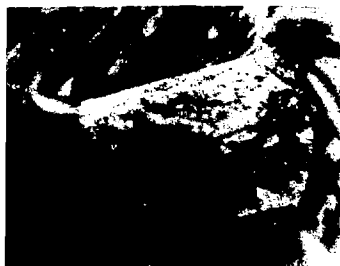


Fig. 9. An included $\alpha\text{-Al}_2\text{O}_3$ grain in a polycrystalline sample of $\text{Y}_3\text{Al}_5\text{O}_{12}$ irradiated at 1100 K, showing the dramatic difference in response to the irradiation.

A STUDY OF RADIATION DAMAGE IN MgO USING HVEM

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ABSTRACT

The nucleation and growth process of dislocation loops in MgO has been examined during irradiation in an HVEM. The nucleation kinetics implies that the loops nucleate with one or two pairs of Mg- and O-interstitial. The growth kinetics at temperatures above $\sim 600^{\circ}\text{C}$ is analyzed with a model based on the steady state of interstitials and vacancies, yielding the migration energy of vacancies 2.0 ± 0.2 eV.

INTRODUCTION

Since high voltage electron microscopy (HVEM) was first used for the *in-situ* observation of the nucleation and growth process of dislocation loops [1], it has been recognized to be useful for understanding not only radiation damage itself but also the kinetic process of point defects in metals [2-4]. There has been also increased activity in recent years to apply the HVEM to ceramics [5,6]. In the present paper, the HVEM is applied to MgO which is a candidate for insulators of fusion reactors. Magnesium oxide is also a wide band gap material that has generally been regarded as a *model* material which could serve as paradigms for other more interesting materials. The purpose is to understand the kinetic behavior of point defects in MgO through a study of the nucleation and growth process of dislocation loops under electron irradiation in an HVEM. The dependence of loop density and loop size on irradiation time, electron flux and irradiation temperature was examined and is analyzed on the basis of nucleation and growth mechanisms for dislocation loops.

EXPERIMENTAL PROCEDURES

Single crystals of MgO were obtained from Norton Co. Thin sections, 3 mm in diameter and 0.1 mm in thickness, were cut and chemically polished to electron transparency by a jet polishing technique in hot orthophosphoric acid ($120 \sim 130^{\circ}\text{C}$). Some thin sections were annealed to reduce carbon contents at 1500°C for 3~5 hours in purified oxygen before the chemical polishing.

Electron irradiation and microscopy were simultaneously performed in the JEM-1000 HVEM of HVEM Laboratory, Kyushu University, operated at 1000 kV. A single tilt, side entry holder was used up to its maximum temperature of 1000°C . The irradiation was always made along a direction about a few degrees away from $\langle 100 \rangle$ to $\langle 010 \rangle$ for minimizing an electron diffraction channelling. Bright-field micrographs were taken during the irradiation at the 800 Bragg position in the 200 systematic condition without strong extra reflections.

EXPERIMENTAL RESULTS

The as-received and purified Norton MgO were irradiated at temperatures from 75 to 1000°C. Figure 1 is a sequence of micrographs showing the nucleation and growth process of circular dislocation loops under irradiation, in marked contrast with elongated dislocation loops in the ORNL MgO [5]. The dislocation loops were found to be perfect interstitial dislocation loops with $1/2 \langle 110 \rangle$ Burgers vectors lying on $\{110\}$ planes. The nucleation of dislocation loops finishes at the beginning of irradiation. The growth rate of loops, on the other hand, is fast in the early stage of irradiation, and it gradually slows down.

The volume density and size of dislocation loops in each MgO were examined as a function of irradiation time, electron flux and irradiation temperature. The volume density is plotted as a function of irradiation time in Fig. 2 for the as-received MgO and in Fig. 3 for the purified MgO, which are examples of the relations at typical temperatures, and it keeps constant for increasing irradiation time. The saturated volume density ρ_L which corresponds to the constant level in Figs. 2 and 3 is plotted against the irradiation temperature. Figure 4 thus obtained shows that the volume density of loops decreases with increasing irradiation temperature with larger rate against the temperature above $\sim 600^\circ\text{C}$ than that below $\sim 600^\circ\text{C}$. The dependence of the saturated volume density on electron flux was examined and is shown in Fig. 5 for the as-received MgO. From Figs. 2, 3 and 5, the volume density of loops ρ_L can be expressed in terms of electron flux ϕ and irradiation time t . The empirical relation is expressed for irradiation below $\sim 600^\circ\text{C}$ as: $\rho_L \propto \phi^{0.5} t^0$ (1) In case of the purified MgO, ρ_L does not depend on ϕ for irradiation at 25°C .

The size of dislocation loops was also traced as a function of irradiation time. On the assumption that the loops grow with a relationship proportional to some power of the irradiation time, the power n was determined for the as-received MgO and is shown as a function of irradiation temperature in Fig. 6. The value of n is $\sim 2/3$ at $\sim 500^\circ\text{C}$ in contrast with that for the Tateho MgO [7], and it increases with increasing temperature and becomes ~ 1 at $\sim 600^\circ\text{C}$. At higher than $\sim 600^\circ\text{C}$ the initial parabolic growth followed by the linear growth. The ORNL MgO was supplementarily used for determining the dependence of the growth rate of loops on electron flux at the higher temperatures by suddenly changing electron flux during the growth of loops. The growth rate is shown as a function of electron flux in Fig. 7, and it is nearly proportional to the square root of electron flux.

The dependence of the growth rate of loops on irradiation temperature was traced for the purified MgO by changing the irradiation temperature stepwisely. The diameter of independent loops is shown in Fig. 8 as a function of irradiation time for the stepwisely changed temperatures. Irradiation at the higher temperatures causes the higher growth rate of loops. The logarithm of the growth rate at each temperature is plotted in Fig. 9 against the reciprocal of temperature. The apparent activation energy for the growth process of each loop was determined from Fig. 9, and it is shown in Fig. 10 as a function of the distance from the each loop position to the specimen surface. The apparent activation energy does not significantly depend on the loop position, and it is 1.0 ± 0.1 eV on an average. If one express the diameter of loops D as a function of ϕ , t and the irradiation temperature T , the empirical relation for irradiation at higher than $\sim 600^\circ\text{C}$ is $D \propto \phi^{1/2} t^{1/2} \exp(-1.0[\text{eV}]/kT)$ (2)

DISCUSSION

The kinetic behavior of interstitial loops should be directly related to

the behavior of interstitials and vacancies. Many theories have been proposed on the kinetic behavior of point defects including the nucleation and growth process of dislocation loops in monoatomic materials such as pure metals under electron irradiation. Characteristics of the kinetics of dislocation loops are classified in terms of the mobility of interstitials and vacancies, foil thickness and nucleation sites of loops. In case that di-interstitials are the stable nuclei of interstitial loops at low temperatures where only interstitials are mobile with their mobility M_I , the density of loops saturates at the beginning of irradiation and is in proportion to the square root of the electron flux, and the loops grow in proportion to the cube root of the irradiation time [3, 4]; that is, $C_L \propto \phi^{1/2} t^{0.5} M_I^{-1/2}$ (3a) and $D \propto \phi^{1/6} t^{1/3} M_I^{1/6}$ (3b). At high temperatures, on the other hand, where vacancies are mobile, interstitials and vacancies establish their mutually balanced steady state just after irradiation, and the diameter of loops is expressed by ϕ , t and the vacancy mobility M_V [4] as $D \propto \phi^{1/2} t^{1/2} M_V^{-1/2}$ (4)

For diatomic oxides, it is seldom the case that displacement rates are identical for both anions and cations. Nor in general will defect mobilities for each ion be the same. Consequently, those circumstances have to be taken into account for understanding the kinetics of defects in MgO. Considering the stoichiometry of the defect aggregates and the electrical neutrality of the matrix, we have proposed a model based on an assumption that a pair of Mg- and O-interstitial acts as the stable nucleus of each loop [8]. The loop kinetics based on the model is analogous to that in metals, or Eqs. (3) and (4). For diatomic oxides, however, M_I in Eqs. (3) and M_V in Eq. (4) should be read respectively as the mobilities of interstitials and vacancies corresponding to the species with the lower value of $C_I M_I$ and $C_V M_V$, C_I and C_V being the concentration of interstitials and vacancies [8]. If each dislocation loop nucleates with two pairs of Mg- and O-interstitial, the power of ϕ in Eq. (3a) and that of t in Eq. (3b) become $1/2$ and $1/2$, respectively [8]. The theory based on one or two pairs of Mg- and O-interstitial as nucleation sites reproduces the experimental results on C_L and D in a satisfactory manner, except that C_L does not depend on ϕ for the purified MgO.

CONCLUSION

Electron irradiation causes the rapid nucleation and growth of interstitial dislocation loops. The kinetic behavior of loops below $\sim 600^\circ\text{C}$, where only both Mg- and O-interstitial are mobile, implies that the loops nucleate with one or two pairs of Mg- and O-interstitial. The growth kinetics of loops above $\sim 600^\circ\text{C}$, where both interstitials and vacancies are mobile, is analyzed with Eq. (4) based on the steady state of interstitials and vacancies, yielding the migration energy of vacancies 2.0 ± 0.2 eV.

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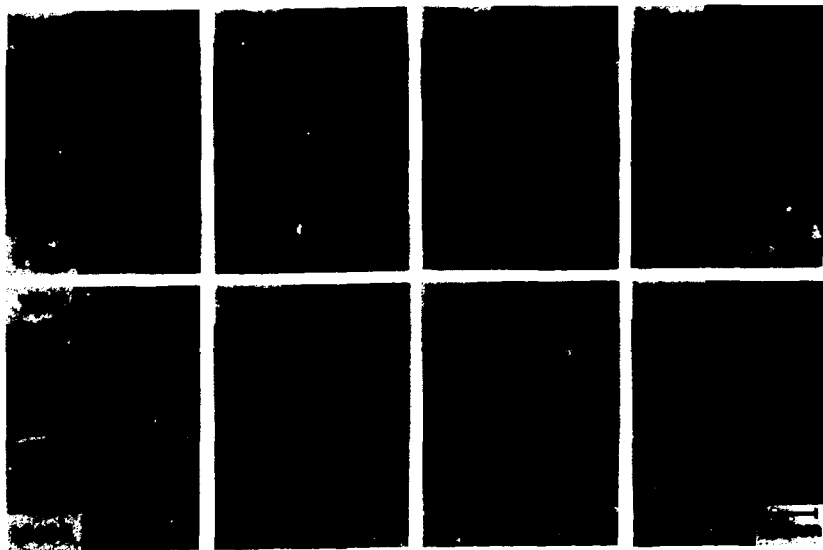


Fig. 1. Formation and/or growth of interstitial dislocation loops in the purified Norton MgO (P-Norton) irradiated at 969 and 1045K with 1 MeV electrons of $1 \times 10^{23}/\text{m}^2.\text{sec}$. The bottom line shows the growth kinetics of loops after irradiation at 969K for 1200 sec and at 1013K for 480 sec.

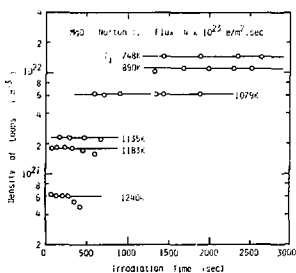


Fig. 2. Time dependence of the loop density during irradiation of the as-received Norton MgO (Norton) with 1 MeV electrons of $4 \times 10^{23} \text{ e/m}^2.\text{sec}$.

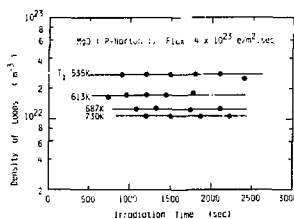


Fig. 3. Same as Fig. 2, but for the purified Norton MgO.

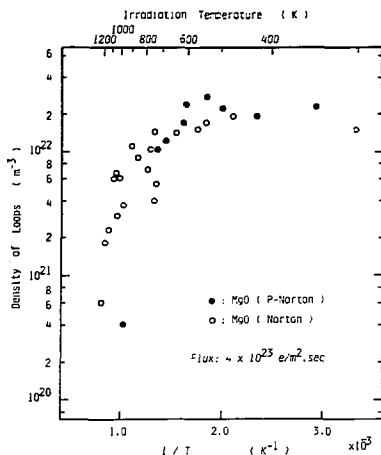


Fig. 4. Temperature dependence of the saturated density of loops in the Norton MgO under irradiation with 1 MeV electrons of $4 \times 10^{23} \text{ e/m}^2 \cdot \text{sec}$.

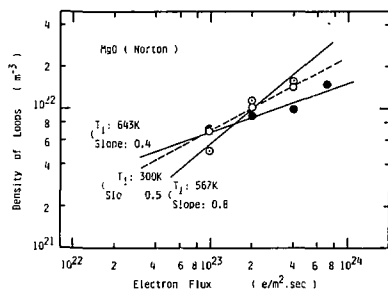


Fig. 5. Electron flux dependence of the saturated loop density at typical irradiation temperatures.

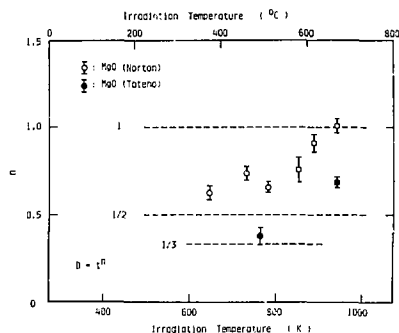


Fig. 6. Temperature dependence of the growth kinetics of loops for the Norton MgO and the Tateho MgO [7]. The value of n was determined on the assumption that the loops grow with the relation, $D \propto t^n$.

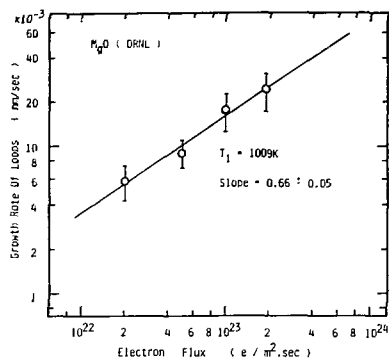


Fig. 7. Dependence of the growth rate of loops on electron flux for the ORNL MgO irradiated at 1009K.

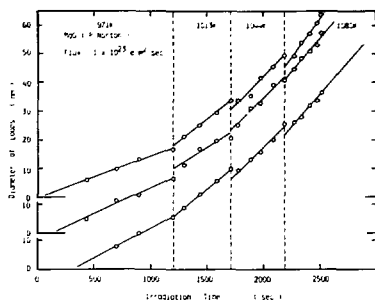


Fig. 8. Time dependence of the diameter of the individual loops in the purified Norton MgO for the step-wise increase of irradiation temperature.

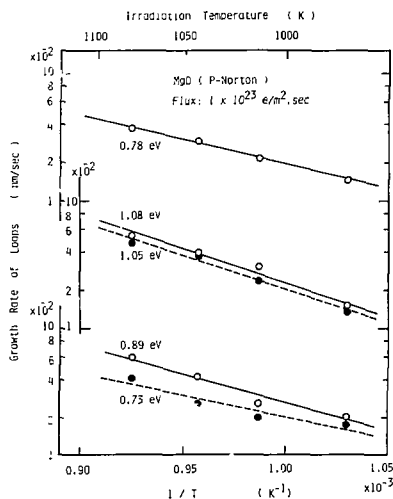


Fig. 9. Temperature dependence of the growth rate of loops in the purified Norton MgO. The apparent activation energy for the growth process of each loop is shown.

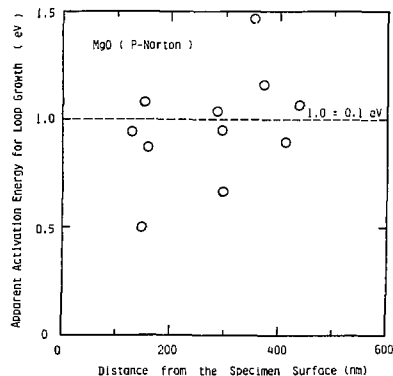


Fig. 10. The relation between the apparent activation energy for the growth process of loops and the loop position for the purified Norton MgO.

IN-SITU HIGH RESOLUTION OBSERVATION OF ELECTRON IRRADIATION DEFECTS IN Si

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ABSTRACT

In-situ high resolution observations of the formation of defects in silicon single crystals during electron irradiation were carried out at room temperature using a 1 MV electron microscope. Interstitial loops lying on {311} planes appear first at the expansion sides of dislocations which are introduced by plastic deformation before the observation. These loops extinct with increasing the irradiation dose. In contrast, a number of loops are formed uniformly in the matrix after an incubation time, and grow up to about 30 nm in length after irradiation of about 3×10^{22} electrons per cm^2 .

INTRODUCTION

Radiation damages in silicon and germanium crystals have been extensively studied by means of conventional transmission electron microscopy. Several investigators[1-4] have observed the formation of dislocation loops lying on {113} planes by electron irradiation at elevated temperatures. Salisbury and Loretto[3] have proposed a structure model of interstitial type of the {113} loops. However, the initial stage of formation of the interstitial loops has not been fully clarified yet.

It is obvious that high voltage electron microscopy is advantageous to investigate in-situ the formation and growth of radiation induced defects in the atomic scale. In this work, many-beam images of silicon crystals were observed to reveal the formation and growth processes of the {113} loops under electron irradiation. For studying the interaction between radiation induced defects and existing lattice imperfections, silicon crystals are deformed plastically at a high temperature before the electron microscopy.

EXPERIMENTALS

The experimental procedures were almost the same as those in our previous work[5,6]. Silicon single crystals grown by floating-zone technique were deformed by either compression of 4% or tension of 30% at 800°C in vacuum. High resolution observations and electron irradiation were carried out at room temperature under the axial illumination along the [110] direction using the Tohoku University 1 MV electron microscope. The flux of electron beam was $3 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$.

RESULTS AND DISCUSSION

In order to reveal the nucleation and growth processes of radiation induced defects in silicon crystals, many-beam images were taken successively at the intervals of one min for the irradiation period of about 15 min. Fig. 1 shows a series of the images with the incident beam parallel to the $[110]$ direction. The two-dimensional fine fringes of 0.31 and 0.27 nm spacings correspond to $\{200\}$ and $\{111\}$ planes, respectively. At the right bottom in each micrograph, one may see an end-on-view of a Z-shape faulted dipole consisting of two dissociated dislocations linked by a ribbon of intrinsic stacking fault [6]. The line orientation of 60° dislocations on the slip planes of $\{111\}$ type is vertical to the foil surface.

Linear defects appearing along the $[\bar{3}32]$ or $[3\bar{3}2]$ direction in the observed images are considered as the dislocation loops lying on the $\{113\}$ planes [1-4], which are parallel to the incident beam. The density of $\{113\}$ loops in the observed images was counted as a function of the irradiation time. As plotted in Fig. 2, the linear density of loops increases suddenly after the irradiation of about 9 min. Consequently the first 9 min may be called an incubation period. In this period, the defects are mostly found in the vicinity of dislocations, particularly in the expansion side of strain field of the partial dislocations, as indicated by arrows in Fig. 1 (a). This is more clearly seen in Fig. 3, which shows an end-on-view of an extended 60° dislocation linked by the stacking fault ab . A $\{113\}$ loop of about 10 nm in length appears in the expansion side, and an extra-half plane is seen in the compression side marked by an arrow. It is evident, therefore, that the loops are an interstitial type.

Small loops with less than 2 nm in length become visible first with slight changes in the image contrast as denoted by arrows in Fig. 1 (c)-(e). After the incubation period, the formation and growth of loops take place randomly over the irradiated area. The linear dimension of the loops along $[\bar{3}32]$ or $[3\bar{3}2]$ directions increases with the irradiation dose and reaches about 30 nm at 2.7×10^{22} electrons/cm². Contrarily, the loops formed initially near the dislocations shrink gradually with the irradiation dose, and finally disappear as seen in Fig. 1 (h).

The large defects as long as 30 nm in length seem to be across the specimen from top to bottom parallel to the incident beam. Some of these defects react each other and are apparently interlocked with kinks as indicated by arrows in Fig. 1 (h). Irregular and dendritic structures for large grown loops of more than 50 nm have been observed in electron irradiated germanium by Ferreira Lima and Howie [2].

While large defects grow up to about 30 nm, new small defects continuously appear during the electron irradiation. Fig. 4 shows a spectrum of the observed number of defects as a function of their linear dimension at the irradiation dose of 2.7×10^{22}



Fig. 1. A series of high resolution images under electron irradiation for 3-15 min with 3×10^{19} electrons/cm²s.



Fig. 1 (Continued)

electrons/cm². This shows that the nucleation and growth of loops proceed simultaneously, because of the relatively low mobility of interstitial atoms at room temperature.

Besides the {113} loops, sometimes rod-shape defects along <112> directions were observed connecting with dislocations or the {113} loops. In Fig. 5, AB is an end-on-view of an extended 60° dislocation and AC is the rod-shape defect along <112>. Some of the defects of this type shrink but some others grow with the increase of irradiation dose. Fig. 6 shows the growth of a <112> defect near the edge of a {113} loop.

We note that the radiation induced defects are distributed uniformly in the observed area in which the thickness is estimated roughly as 15-50 nm, and the denuded zones of defects are not found even in very thin areas near the edge of specimen. This fact suggests that the nucleation of the {113} loops is scarcely affected by the escape of point defects from the specimen surface, but depends on the presence of impurities or contaminations on the surface. It is plausible that impurity atoms knocked into the crystal by the electrons take part in the nucleation and growth of the interstitial {113} loops.

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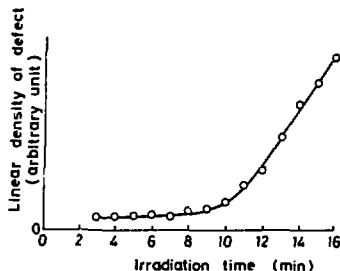


Fig. 2. Linear density of dislocation loops as a function of irradiation time.



Fig. 3. A {113} loop in the expansion side of an extended 60° dislocation. An extra half-plane appears in the compression side marked by an arrow.

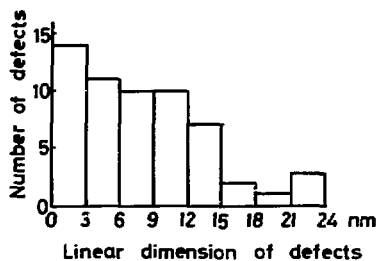


Fig. 4. Size distribution of $\{113\}$ loops at 2.7×10^{22} electrons/cm².



Fig. 5. A high-resolution image of a $\langle 112 \rangle$ defect (AC) connected with an extended 60° dislocation (AB).

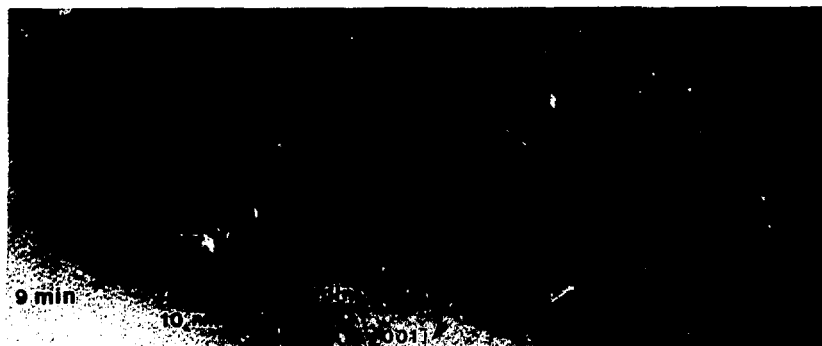


Fig. 6. A series of images showing the nucleation and growth of a $\langle 112 \rangle$ defect near the edge of a $\{113\}$ loop.

**CAVITY GROWTH IN DUAL-ION AND/OR ELECTRON IRRADIATED
TYPE 316 STAINLESS STEEL**

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ABSTRACT

Ir-situ observations of the cavity growth process in dual-ion irradiated or He preinjected samples were performed using HVEMs. The objective of this study is to analyze cavity growth mechanisms as functions of cavity size and of injected He concentration. The materials used were 20% cold-worked (CW) and solution annealed & aged (SAA) type 316 SS. Dual-ion irradiation was carried out at ANL. In-situ observations of damage process were performed in a JEM-1250 or HU-1300 with 1000 KeV electrons.

Dual-ion irradiation of SAA samples produced bimodal cavity size distributions. Dual-ion irradiation of CW samples produced unimodal cavity size distributions with mean size less than 7 nm. Electron irradiation caused rapid growth of cavities larger than the critical size; the critical radius was 4,5 and 7 nm at 400, 500, and 600 C irradiation, respectively. The average sizes of cavities smaller than the critical size were not changed by electron irradiation followed to dual-ion irradiation. Electron irradiation of He preinjected samples produced bimodal cavity size distributions. Without He preinjection, electron irradiation produced unimodal cavity size distributions with most cavities larger than the critical size. These results provide clear evidence of bias-driven and pressure-driven cavity growth mechanism.

I. INTRODUCTION

Radiation induced microstructural evolutions in metals and alloys are not only interesting in material evaluation for structural use in nuclear reactors, but also important for fundamental understandings of primary and secondary defect behaviors. Neutron and charged particle irradiation experiments are effectively performed for the former subject, but these methods are very hard to observe direct process of microstructural evolution under irradiation. On the other hand, in-situ observation of damage process by means of high voltage electron microscopy has an advantage to see structural changes simultaneously with electron damage but has a disadvantage of simple Frenkel defect production as a simulation of fusion neutron damage.(1-3)

Therefore, a correlation study of charged particle irradiation and electron irradiation, including helium effect is expected to be effective for getting fundamental understandings of microstructure change in MFR environment.

The helium produced in materials during irradiation in reactors is known to have an important influence on void nucleation and growth. From neutron and

charged particle irradiation results, bimodal cavity size distribution is found to be a characteristic feature of heavily radiation damaged materials in nuclear reactors. The theoretical models and the analyses of experimental results have led us to the understanding that there are two kinds of cavity growth mechanisms, one is gas pressure assisted pressure-driven growth and the other is bias-driven growth which is resulted from the presence of biased sinks for point defects. But clear evidences of the growth mechanisms have not been provided.

In this investigation, in-situ observations of the cavity growth process in dual-ion irradiated or helium preinjected samples were performed using HVEMs. The objective of this study is to analyze cavity growth mechanisms as functions of cavity size and of injected helium concentration. And the final goal is to get the clear evidence of cavity growth mechanisms, which will make it possible to establish accurate model of microstructural evolution in MFR environments.

II. EXPERIMENTAL PROCEDURE

The material for this study was 316 stainless steel from the MFE heat (15893); the composition is shown in ref.(4). Irradiations were performed on samples with two prior thermomechanical treatments: SAA (50% cold work followed by 0.5 h at 1050 C, 10 h at 800 C) and CW (20% cold-worked). The dual-ion irradiations to 6, 12 or 25 displacement per atom (dpa) were carried out at Argonne National Laboratory using 3 MeV Ni-ions and degraded 0.83 MeV He-ions at 625 C.(5) The 25 dpa dual-ion irradiated sample with 15 appmHe/dpa and the 5 dpa single-ion and followed by 20 dpa dual-ion irradiated sample with average 15 appmHe/dpa are denoted as 25D and 25SD, respectively.(6) Helium was preinjected to 30appm using a 400 KeV Cockcroft-Walton type ion accelerator at the University of Tokyo by 100,200 and 300 KeV multi-energy helium-ions. In-situ observations of the electron damage process were performed in a JEM-1250 at the University of Tokyo and HU-1300 at the Hokkaido University with the accelerating voltage of 1000 KV. Electron irradiations for SAA and CW specimen followed to dual-ion irradiation were performed at 400, 500 and 600 C. The displacement rates adopted for dual-ion irradiation and electron irradiation were 3×10^{-3} and 2×10^{-3} dpa/sec., respectively. The quantitative analysis of TEM photographs was done using the micro-computer system with digitizer data-input.(7)

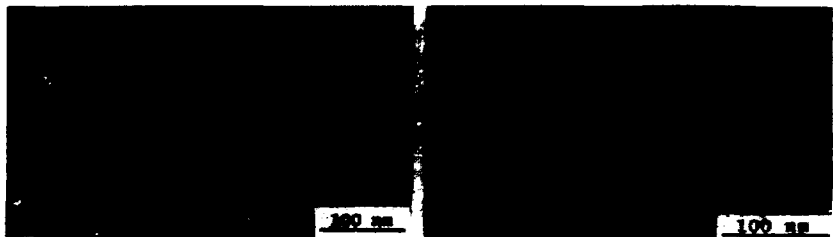
III. EXPERIMENTAL RESULTS

Dual-Ion Irradiation

Dual-ion irradiation to SAA sample produced cavities with bimodal cavity size distribution and the critical cavity diameter for the transition from small cavity to large cavity, which is called the transition from pressure-driven to bias-driven cavity growth(8), was estimated to be about 7 nm.(6) Whereas dual-ion irradiation of CW samples produced unimodal cavity size distributions with mean cavity diameter less than 7 nm. And average cavity sizes for the small cavities were almost identical to be 3 nm in diameter for SAA and CW samples. That is, in the CW samples, cavities seem to be dominantly stabilized by gas pressure. Typical microstructures of the SAA and CW samples are shown in Photo.1 (see ref.(6) for detailed description).

Electron Irradiation To Dual-Ion Irradiated Samples

Although there were a slight rearrangements of microstructures which were



(a) SAA

(b) CW

Photo.1: Microstructures of dual-ion irradiated 316 SS
(25 dpa, 15 appmHe/dpa at 625 C)

caused mainly by irradiation temperature changes, cavity microstructures formed by dual-ion irradiation were stable under electron irradiation in HVEM. Photo.2 shows a typical microstructure of electron irradiated 316 SS samples followed to dual-ion irradiation. In-situ observations in HVEM were performed at thicker foil thickness region, as thick as about 500 nm, than that in the observation region for CTEM, about 200 nm. This difference in foil thickness resulted in the different visibility limit values for small cavities. As shown in Fig.1, cavity number density for the small cavities was nearly dose independent and the slight drop in the density by the initial electron irradiation to several dpa would be come from the thickness difference in TEM observed areas. Figure 1 also shows that there was a rapid increase of large cavity number density by electron irradiation to about 5 dpa electron dose and then there came a saturation of large cavity number density. The increment in large cavity number density by electron irradiation followed to dual-ion irradiation was the largest for 400 C irradiation and was the smallest and nearly null for 600 C irradiation. These increments seem to be come from the temperature dependent critical size for bias-driven cavity growth. Electron dose dependences of average cavity size were very close to those of dual-ion irradiated samples, as shown in Fig.2. Large cavities grew as increasing electron dose, whereas average cavity radius of small cavities was electron dose independent. Although there was a slight increase in the average cavity size of small cavity by electron irradiation followed to dual-ion irradiation, this could be also understood by the difference in foil thickness of TEM observed area. Microstructural changes in CW specimens, dual-ion irradiated and electron irradiated, were significant in cavity size distribution, that is, unimodal cavity size distributions produced by dual-ion irradiation were changed to bimodal cavity size distributions. These microstructural evolutions can be understood by temperature dependent change of critical size for bias-driven cavity growth. Fig.3 is showing swelling behaviors of SAA sample, electron irradiated at 500 C for 10 dpa, SAA and CW samples with 400 and 500 C electron followed to dual-ion irradiations. In SAA samples, swelling by diation at 625 C for 6 dpa.

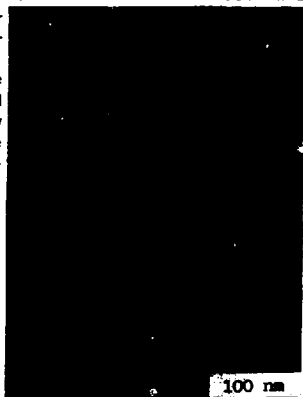


Photo.2: Microstructure of SAA sample, electron irradiated at 500 C for 10 dpa, SAA and CW samples with 400 and 500 C electron followed to dual-ion irradiations. In SAA samples, swelling by diation at 625 C for 6 dpa.

electron irradiation was mainly introduced from bias driven cavity growth of pre-existing large cavities. Therefore, steady state swelling rates were larger at higher temperature. On the contrary, in CW samples, the steady state swelling rates were lower at higher temperature.

Electron Irradiation To He Preinjected Sample

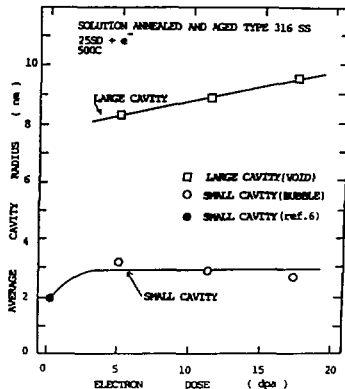
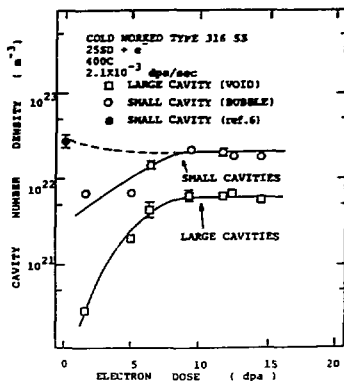
SAA samples with the same thermal history as dual-ion irradiation to 25 dpa (controlled samples) were 30 appmHe preinjected and then electron irradiated in JEM-1250 or HU-1300, the latter has a sophisticated high vacuum system for beam column and sample stage, but there were no significant difference in microstructure developments nor difference in swelling, at least below 500 C. By the helium preinjection at room temperature, no visible defect clusters were found, but by the following Fig.1: Dose dependence of cavity electron irradiation, rapid dislocation number density in 20% cold worked succeeding cavity 316 SS, electron irradiated at formation took place faster than in the 400 C followed to 25 dpa dual-ion samples without helium preinjection. The irradiation at 625 C.

cavity growth behaviors by electron irradiation in He preinjected samples were basically the same as those in the dual-ion irradiated samples. The average cavity size for the small cavities was dose independent and the cavity number density for the small cavities was dose independent. The latter dose independency could be attributed to helium preinjection which suppressed simultaneous cavity formation (gas pressure assisted) during electron irradiation as a synergistic effect. The large cavities were steadily increasing and as the result, swelling showed a linear after transition growth scheme.

IV. DISCUSSIONS

Temperature Dependence Of The Critical Size For Bias-Driven Cavity Growth

From the separation of the bimodal cavity size distribution into two cavity size distributions, the critical size for the transition from one to the other, which called the critical size for bias-driven growth, was experimentally obtained. Figure 4 summarizes the temperature dependence of the critical radius obtained. In SAA samples, the critical size increased as increasing irradiation temperature with the steep increase above 500 C. There were little differences in the critical radius



among dual-ion irradiated or helium pre-injected, and electron irradiated samples. The results of CW samples were very close to those of SAA samples. These temperature dependences were directly obtained by "in-situ" observation and were the first direct data of the temperature dependence of the critical radius. These data coincided qualitatively well with the dual-ion results by S.Wood et al.(8) and the theoretical prediction by A.Hishinuma et al..(9)

Swelling Rate Dependences On Irradiation Temperature, Irradiation History And Prior Thermomechanical Treatment

Steady state swelling rates obtained are summarized in Table 1. From dual-ion and following electron irradiated SAA sample results, temperature dependence of swelling rate, the major part of which came from bias-driven cavity growth, were obtained. In SAA and CW samples of 316 SS The swelling rate became larger in the order from 400 to 600 C and the different rate (filled mark) and at 500 C (open values in the 6D (6 dpa dual-ion irradiated) mark) followed to dual-ion irradiated) samples could be attributed to the difference of large cavity number density; in 6D samples, large cavities were less than those in 25SD and as the result, swelling rate at 500 C in 6D became smaller than that in 25SD. The reverse temperature dependence in dual-ion and following electron irradiated CW samples came from the unimodal cavity size distribution produced by the initial dual-ion irradiation; those samples had only small pre-existing cavities by dual-ion irradiation and following electron irradiations resulted in rapid cavity growth of cavities a little larger than the critical size for bias-driven growth. In this experimental condition, number of cavities larger than the critical size was larger at 400 C than at 500 C. This difference in the number of bias-driven cavities seemed to overcome the difference of the cavity growth rates at 400 C and 500 C (the latter is the larger) and finally led to the higher swelling rate at 400 C than at 500 C. In 30 appmHe preinjected and electron irradiated samples, the swelling rate at 400 C was a little higher than that at 500 C. This was caused by the difference in large cavity number density which could also be understood by temperature dependence of the critical radius for bias-driven growth. The dominant difference in cavity microstructure

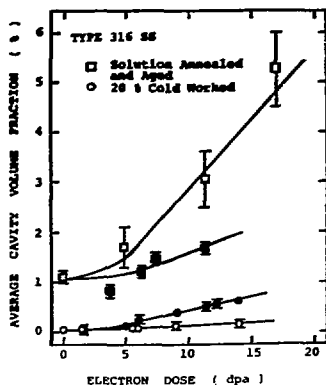


Fig.3: Dose dependence of swelling in SAA and CW samples of 316 SS electron irradiated at 400 C from 400 to 600 C and the different rate (filled mark) and at 500 C (open values in the 6D (6 dpa dual-ion irradiated) mark) followed to dual-ion irradiated) samples could be attributed to the

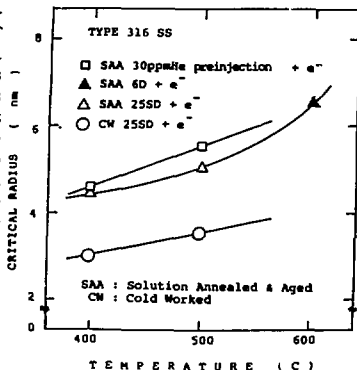


Fig.4: Temperature dependence of the critical size for bias-driven cavity growth.

Table 1: Summary of Cavity Swelling Rate in 316 Stainless Steel

IRRADIATIONS	IRRAD. TEMP.	TREATMENT	SWELLING RATE
Dual-Ion	625 C	SAA	0.067 %/dpa (*)
Dual-Ion	625	CW	0.003 (*)
Dual-Ion(25SD)+electron	400	SAA	0.1
Dual-Ion(25SD)+electron	500	SAA	0.27
Dual-Ion(6D) +electron	500	SAA	0.12
Dual-Ion(6D) +electron	600	SAA	0.17
Dual-Ion(25SD)+electron	400	CW	0.05
Dual-Ion(25SD)+electron	500	CW	0.009
He preinject. +electron	400	SAA	0.15
He preinject. +electron	500	SAA	0.11
electron	500	ST	0.22 (**)

(*): ref.6 , (**): ref.10 , ST: Solution Treatment

irradiation was lower cavity number density of small cavities in the latter than that in the former. The mutual relations of the swelling rate obtained could be understood qualitatively by the above mentioned two cavity growth mechanisms. The detailed explanations of the correlations among heavy-ions and electrons will be appeared in the next paper. Table 1 possibly enables us to estimate swelling value of steady state swelling scheme for dual-ions and/or electron irradiation experiments. To get more precise understanding of intercorrelations, further analyses of microstructure development including microchemical effects would be required.

ACKNOWLEDGEMENTS

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INFLUENCE OF NITROGEN AND CARBON ON VOID SWELLING IN 316 STAINLESS STEEL IN-SITU OBSERVED BY A HVEM

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ABSTRACT

Effects of nitrogen and carbon on void swelling in 316 austenitic stainless steel were investigated by in-situ observation using a HVEM. Specimens were solution treated or 20% cold worked. Electron irradiation was carried out at 600C. In each specimen swelling increased linearly with dose after incubation period. In solution treated specimens, swelling decreased with nitrogen and carbon concentration. This decrease is attributed to the decrease of swelling rate. Incubation dose slightly decreased with nitrogen and carbon concentration but this decrease had little contribution to the observed variation of swelling. Void number density first decreased, and then increased with nitrogen and carbon concentration. While, the tendency was reverse for mean void diameter, so that it first increased and then decreased. In cold worked specimens the swelling rates were nearly the same as those of solution treated specimens for the equal concentration of nitrogen and carbon, but with shorter incubation doses. Void number density increased and mean void diameter decreased with nitrogen and carbon concentration. The behaviors of nitrogen and carbon in irradiated stainless steel is discussed.

INTRODUCTION

Void swelling of 316 stainless steel is an important problem for both breeder and fusion reactors. It is well known that the swelling behavior of 316 steel is very sensitive to the microstructure and especially to compositional variation. Among the additional elements, effects of nitrogen and carbon are important, because those elements are inevitable through steel fabrication processes.

In the first stage of irradiation, solute interstitial atoms such as nitrogen and carbon, or their small precipitates are considered to have effects on swelling behavior mainly through void nucleation. Leitnaker et al. have observed that for relatively high pure material the solute interstitial elements reduced both number and size of voids (1). As for carbon addition in 316 stainless steel, Makin et al. have reported that void swelling decreased and void number density increased (2). As for nitrogen addition in 316

stainless steel, the effect has not been clarified yet.

The objective of this study is to investigate the effects of nitrogen and carbon on the swelling behaviors in both solution treated and cold worked 316 stainless steels.

By means of high voltage electron microscopy, it is advantageous to carry out radiation damage experiments by observing in-situ the whole process up to about 20 dpa with relatively larger displacement rate.

EXPERIMENTAL PROCEDURE

The materials used were vacuum melted 316 austenitic stainless steels. The chemical compositions of these steels are shown in Table 1. The steels were thinned to 0.5mm thick sheets by alternate cold rolling and vacuum annealing. These were solution heat treated in air at 1100C for 30 min and water quenched. To prevent samples from oxidation during the solution treatment, they were wrapped in thin stainless foils. Cold work was introduced by cold rolling with 20% reduction. After mechanical polishing to about 100 μ m thick, specimens were finally prepared for HVEM observation by twin jet electropolishing technique.

The electron irradiation was performed using a JEM 1250 with an accelerating voltage of 1000KV. The incident electron beam direction was parallel to $\langle 110 \rangle$. The beam current density was 3.1×10^{19} e/cm².sec. Assuming the displacement energy of 24 eV (3),⁻³ this beam produces atomic displacements in steel at a rate of 1.3×10^{-3} dpa/sec. The irradiation temperature was 600C.

Determination of void parameters was performed according to the ASTM methods(4). Measurements of dislocation density were carried out the intersection technique at the same area as that of void measurements. Foil thickness of specimen was determined stereographically.

EXPERIMENTAL RESULTS

Before irradiation dislocation densities were less than 1×10^8 cm⁻² in solution treated specimens. In the initial stage of irradiation process, Frank loops were formed and then dislocation loop-loop interaction took place. As a result, dislocation density increased and reached steady state density around 10^{10} cm⁻² within about 5 dpa as shown in Fig.1 and Fig.2. In 20% cold worked specimens dislocation densities were about 5×10^{10} cm⁻², but during irradiation it decreased to certain steady state values. The steady state dislocation density was the same in both solution treated and cold worked specimen within experimental error. The dislocation density reached to the steady state value earlier in the case of lower concentration of nitrogen and carbon than that of higher concentration in comparison of Fig.1 with Fig.2. It was also observed that the addition of nitrogen and carbon increased the steady state dislocation density as shown in Fig.3.

Fig.4 and Fig.5 show the dose dependences of void number densities for low and high nitrogen and carbon specimens respectively. The saturation of void number density always occurred after establishment of steady state dislocation density. In Fig.4 it is shown that the saturated void number density was not significantly different between solution treated and cold worked specimens. But as shown in Fig.5, the saturated void number densities of 20% cold worked

specimens were higher than those of solution treated specimens in the case of higher concentration of nitrogen and carbon. Fig.6 shows the relation between the saturated void number density and the concentration of nitrogen and carbon. Fig.7 shows the dose dependence of mean void diameter, plotted as the function of after-incubation dose (dose- T_s), where T_s is the incubation dose which is defined as the cross point of the extrapolated linear swelling line and the dose axis in the swelling-dose diagram (e.g. Fig.8). It was observed that the increase of mean void diameter became proportional to (dose- T_s)^{1/5} after the saturation of void number density.

As shown in Figs.8 (a) and (b) void swelling decreased with nitrogen and carbon concentration through the decrease of swelling rate for solution treated specimens. In Fig.9, it is shown that swelling rate was suppressed by the addition of nitrogen and carbon similarly as solution treated specimens. As for cold worked specimens the incubation doses became smaller but the swelling rates were nearly the same as those of solution treated specimens as shown in Fig.10.

DISCUSSION

As shown in the previous paper (5), the incubation dose for swelling was closely related to the dose when dislocation density became the steady state value and also to the dose when the void number density saturated. In solution treated specimen the incubation dose for dislocation density settlement was larger than that in cold worked specimen. This corresponds to that the incubation dose for swelling was also larger in solution treated specimen.

In both solution treated and cold worked specimens, the saturated dislocation densities were higher in specimens including more nitrogen and carbon. This must be due to the decrease of recovery rate of dislocations in higher concentration of nitrogen and carbon.

In Fig.6 it is shown that void number density increased simply with nitrogen and carbon concentration in cold worked specimen but it once decreased and then increased with nitrogen and carbon concentration in solution treated specimen. Although the steady state dislocation densities were the same between solution treated and cold worked specimen, the void number densities were different between them. In cold worked specimen, it is considered that the nitrogen and carbon formed their precipitates as results of enhancement by high dislocation density and heavy irradiation. Therefore, the solute nitrogen and carbon atoms would be scavenged and then void number density would become larger with steady state dislocation density which increased with nitrogen and carbon concentration through dislocation bias sink. To the contrary, in solution treated specimen, void number density did not seem to be simply related with the steady state dislocation density. It decreased with nitrogen and carbon concentration possibly because those atoms segregated to dislocation as solute atoms and suppressed the role of dislocation as bias sink. Therefore, void number density decreased with nitrogen and carbon concentration. Further increase of void number density could be understood by the agglomeration of nitrogen and carbon atoms. Such agglomeration would decrease the solute atoms along dislocation lines, and this effect would recover the sink strength of dislocations.

The dependence of the growth rate of void on nitrogen and carbon concentration was opposite to that of void number density as shown in Fig.7, but the difference of the growth rates was not so large. As the result, the

swelling rate decreased with nitrogen and carbon concentration in both solution treated and cold worked specimens. In solution treated specimen, below 0.5 atomic percent nitrogen and carbon concentration, void number density decreased and swelling also decreased with their concentration. This is considered to be due to the decrease of the total sink sites of dislocations by the segregation of solute nitrogen and carbon atoms.

SUMMARY

1. Swelling increased linear with irradiation dose after incubation dose.
2. The incubation dose for swelling was closely related to the dose when dislocation density became steady state and to the dose when void number density became saturated.
3. In solution treated specimens, void number density once decreased and then increased with nitrogen and carbon concentration but the growth rate of the void showed the reverse relation. Swelling rate became smaller as nitrogen and carbon concentration increased. This behavior can be understood by the solute segregation to dislocation line and the decrease of sink strength of dislocations.
4. In cold worked specimens, void number density increased with nitrogen and carbon concentration and growth rate of void decreased and then swelling also decreased with their concentration. This behavior can be understood by cold work enhanced precipitation and resultant scavenging effect for nitrogen and carbon atoms.

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TABLE AND FIGURES

Table 1 Chemical compositions of 316 stainless steels used. (wt%)

	C	N	Ni	Cr	Mo	Si	Mn	P	S
316 L	0.003	0.006	15.87	14.35	2.52	0.47	0.1	0.005	0.004
316 C	0.054	0.007	15.96	14.59	2.54	0.50	0.1	0.003	0.007
316 C,N1	0.060	0.054	15.89	14.77	2.55	0.50	0.1	0.007	0.005
316 C,N2	0.061	0.076	15.99	14.86	2.54	0.50	0.1	0.004	0.004
316 C,N3	0.050	0.094	16.11	14.98	2.56	0.51	0.05	0.001	0.004

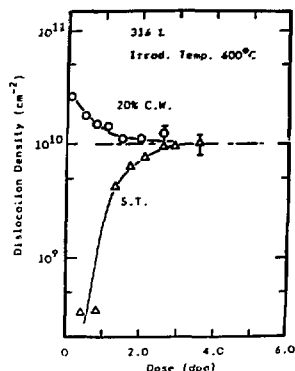


Fig.1 Dose dependence of dislocation density in 316L.

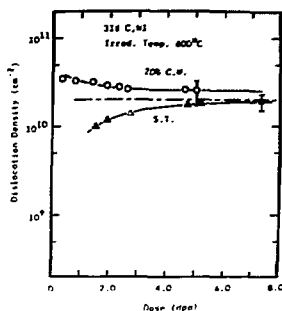


Fig.2 Dose dependence of dislocation density in 316C,N1.

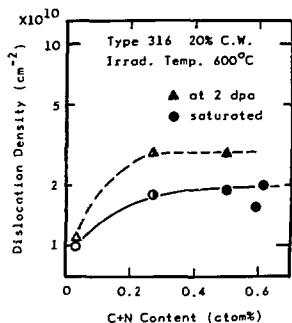


Fig.3 Relation between the saturated dislocation density and nitrogen plus carbon concentration.

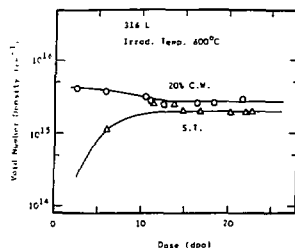


Fig.4 Dose dependence of void number density in 316L.

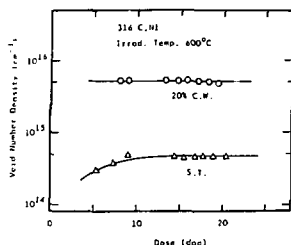


Fig.5 Dose dependence of void number density in 316C,N1.

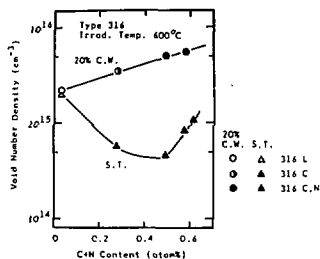


Fig.6 Relation between the saturated void number density and nitrogen plus carbon concentration.

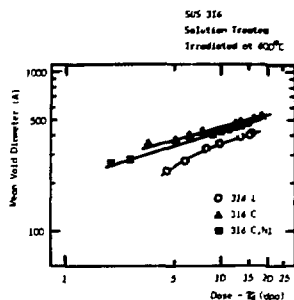


Fig.7 Relation between mean void diameter and after-incubation dose.

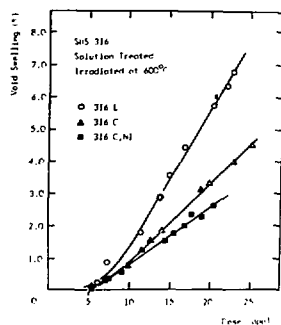


Fig.8(a) Dose dependence of void swelling in 316L, 316C and 316C,N1.

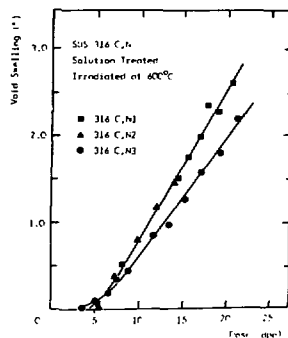


Fig.8(b) Dose dependence of void swelling in 316C,N1, 316C,N2 and 316C,N3.

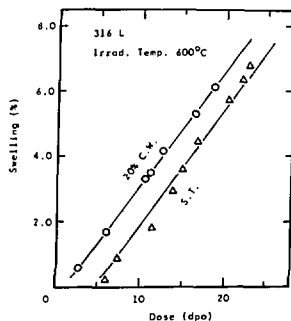


Fig.9 Effect of pre-irradiation treatment on dose dependence of void swelling in 316L.

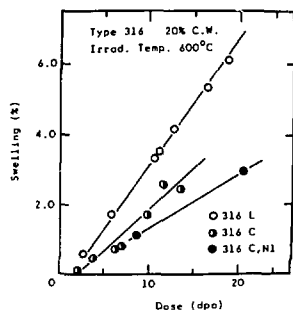


Fig.10 Dose dependence of void swelling in cold worked 316L, 316C and 316C,N1.

ELECTRON RADIATION DAMAGE IN SILICATE GLASSES

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ABSTRACT

Electron radiation damage in silicate glasses has been studied in-situ using HVEM. The damage is evident from the formation of oxygen bubbles and as an amorphous phase decomposition. The bubble formation is consistent with a mechanism involving the fragmentation of oxide bonds and subsequent oxygen stabilization by a cation migration process. The bond fragmentation mechanism appears to be predominantly from ionization.

Bubble regression in the presence of phase separation has been observed and is consistent with enhanced oxygen diffusivity through the high silica phase.

Support for this work has been provided by the Department of Energy under contract no. DOE-AT03-79ER-10467.

Electron irradiation of silicate glasses can cause a dramatic alteration of the original microstructure. Two major effects that have been observed are the formation of small gas-filled bubbles and the decomposition of the glass into two amorphous phases [1]. The behavior of these defects and their interactions have been used to develop a comprehensive model to describe their respective formation mechanisms.

Irradiations were performed in-situ at the Berkeley National Center for Electron Microscopy using accelerating potentials between 500 and 1500 kV. Irradiations were performed under relatively high fluxes using a strongly excited first condenser lens but the second condenser aperture was not removed so as to minimize extraneous beam heating effects.

The glass investigated was similar in composition to those proposed for nuclear waste containment in the United States and is a sodium borosilicate glass with a 33 weight percent addition of heavy metal oxides.

The formation of bubbles in these glasses by irradiation occurs at intermediate temperatures (figure 1) and is induced quite rapidly by the electron beam (figure 2). Analysis of bubble growth reveals that initially a parabolic behavior of the bubble radius with time is observed which levels off and actually decreases with extended irradiation. The bubble regression is illustrated in figure 2. These latter stages occur in conjunction with the development of phase separated microstructures also apparent in this sequence. X-ray dispersive analysis has shown that this phase separation represents the partitioning of the metals to one phase at the expense of the other [1], consistent with the observed variation in mass-thickness contrast.

The formation of bubbles in electron irradiated silicate glass has been observed in a variety of different systems [1,2,3] and that the gas within the bubbles is oxygen can be assumed with some certainty [4,5]. The mechanism commonly evoked to describe the formation of these bubbles is based upon the radiation-induced fragmentation of oxide bonds and the subsequent precipitation of the free oxygen as bubbles through a process of bulk diffusion. It was originally noted by Laval and Westmacott [6] that the rapid kinetics associated with bubble growth is inconsistent with the low diffusivity of oxygen observed in silicate glasses and consistent with our own observations.

We propose that the kinetics of bubble growth reflects the mobility of non-network cations rather than oxygen. A mechanism of this sort can account for the anomalous growth kinetics, since the mobilities of cations in silicate glass are of the correct magnitude and the oxygen pressures within the bubbles are observed to be particularly large.

The initial step in the proposed bubble formation mechanism requires only the radiation-induced fragmentation of the oxide bonds other than the silicon-oxygens, creating separate oxygen and metal cation species. The presence of a charge transfer mechanism could allow the subsequent conversion of these ions to their neutral states or increase the likelihood of the process, but in any event the nucleation step is perceived to occur upon coincidence of a number of neutral oxygen atoms, which are converted into the molecular state, forming a bubble nucleus. The mechanism for the subsequent growth of the bubble is based on the preferential depletion of cations near the bubble surface, adding oxygen to the bubble and accommodating its growth. In this process the cations serve as the charge balancing species in the formation of molecular oxygen.

There are two principal factors which tend to stabilize the bubbles against recombination reactions. The first is the conversion of oxygen to the molecular state which will introduce an activation energy into a recombination reaction and the second is the biased migration of neutrals which would introduce a substantial separation between the fragmentation products thus reducing the likelihood of their recombination.

The absence of the need for long-range oxygen diffusion can be demonstrated by an examination of the local oxygen density before and after the formation of a bubble by irradiation. Assuming steady state conditions [7] and van der Waals behavior, the number of oxygen molecules within a bubble of radius 100 Å is approximately 5.7×10^4 . In comparison, twice the number of oxygen atoms in the undamaged matrix not associated with the silica network occupy a sphere of 86 Å radius. Thus, local cation depletion and subsequent oxygen coalescence can adequately account for bubble formation from the oxygen associated with the metal cations.

The association of the damage with the non-network components comes from a comparison of the radiation responses of the glass and vitreous silica. Electron irradiation of vitreous silica does not lead to bubble formation, even after total doses two orders of magnitude greater than those necessary to form bubbles in the waste glass. This is consistent with the observations of Todd et al., [4] that oxygen evolution in electron irradiated vitreous silica was virtually absent.

The proposed model is consistent with the observed temperature sensitivity of bubble formation [8], which exhibits a peak in the formation rate centered at about 250°C and bounded by room temperature and 400°C (figure 1). The low temperature constraint is likely due to limited cation mobility causing the recombination reactions to dominate. This behavior is also consistent with Primak's observation that significant ionic transport begins at about 150°-300°C [9]. The high temperature limit is believed to reflect the temperature at which oxygen mobility is high enough to allow migration to surface sinks, preventing its stabilization in the form of bubbles.

The formation of the gas bubbles necessitates a bond fragmentation mechanism. This could conceivably occur through either a direct displacement or ionization mechanism, since high voltage electrons are capable of producing either event. Indeed, both processes have been proposed as the cause of the bubbles [2,6].

A common means of identifying the operative mechanism is through the energy dependence of damage. While the interaction cross-sections decrease with increasing energy for both events, the rates of decrease differ, providing a theoretical means of determining the dominant mechanism. The amount of scatter in the data, however, was too large to allow this kind of analysis. Instead, the observed bubble growth kinetics were used to assess the relative magnitudes of the displacement and ionization cross-sections that would be necessary to account for the damage.

By assuming that all the gas within a bubble originated from a process with a characteristic section, σ , an expression can be derived for this cross-section,

$$\sigma = \frac{2 n_g c}{F_1 n_0 V D}$$

where n_g = number of oxygen molecules in the bubble; n_0 = number density of lattice oxygen atoms in the glass; c = electron charge; D = dose to form a bubble (Coulombs per unit area); V = irradiated volume; F_1 = efficiency factor to account for recombination. The bubble content can be estimated by combining a van der Waals approximation with the equilibrium bubble condition,

$$\left(p + \frac{n_g^2 a}{V^2}\right) (V - n_g B) = n_g RT$$

$$p = \frac{2\gamma}{r}$$

where a and B are the van der Waals coefficients; p = pressure; V = volume; n_g = number of moles of gas; R = gas constant; T = absolute temperature; r = bubble radius (assumed spherical bubble); γ = glass surface energy. Using a surface energy of 2.0 J-m⁻² and a temperature of 250°C, we find that for a bubble of radius 100 Å, $n_g = 5.7 \times 10^4$ molecules O₂. Using this and the observed formation dose of 200 C-cm⁻², and assuming an irradiated volume comparable with the bubble volume, we have for an one percent efficiency

$$\sigma \approx 9 \times 10^{-24} \text{ m}^2$$

For comparison, the displacement cross sections tabulated by Oen [10] are on the order of 10^{-26} m^2 even for low displacement thresholds [1] which need not necessarily be encountered [7], and it seems very unlikely therefore that displacement damage is responsible.

The estimation of the cross-section for ionization damage events from electron irradiation begins with an estimation of the radiolytic yield, G ,

$$G = \frac{200 n_e c}{F_2 DV(dE/dx)}$$

where dE/dx is the electron energy loss rate through the foil; F_2 is an efficiency factor, and the remaining terms were previously defined. Again using an one percent efficiency, we find

$$G \approx 0.1$$

Using survival theory with single-hit interaction [12], we can relate this to the ionization cross-section,

$$\sigma = \frac{G}{100 n_o} \frac{dE}{dx} \approx 10^{-23} \text{ m}^2$$

This is not an unreasonable value for an ionization cross-section and suggests that bubble formation is derived from the radiolytic decomposition of the oxide bonds not associated with the silica network.

The phase decomposition which can also result from the electron irradiation of the glass is generally observed during the latter stages of bubble growth after extensive irradiation. The two processes are probably related, the phase separation arising from the high concentration of cations produced by growth of the bubbles. The likely cause of the bubble regression illustrated in figure 3 is an increase in oxygen diffusivity in the high silica phase which forms from the segregation of the cations. This could provide a connected pathway of high mobility for the trapped gas [13], which would diffuse out to the foil surface. The substantial difference between the kinetics of bubble growth and of their subsequent regression lends further credence to a growth mechanism based upon cation diffusion.

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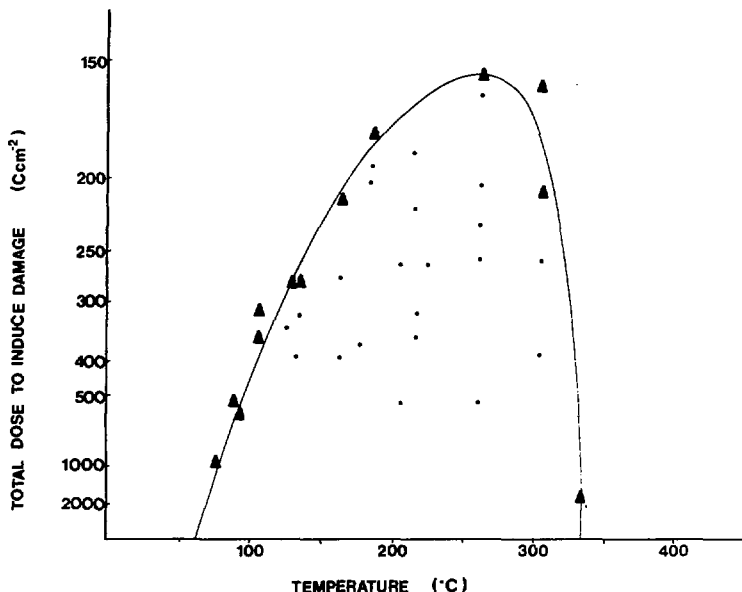


Figure 1 The temperature dependence of bubble formation at constant flux.

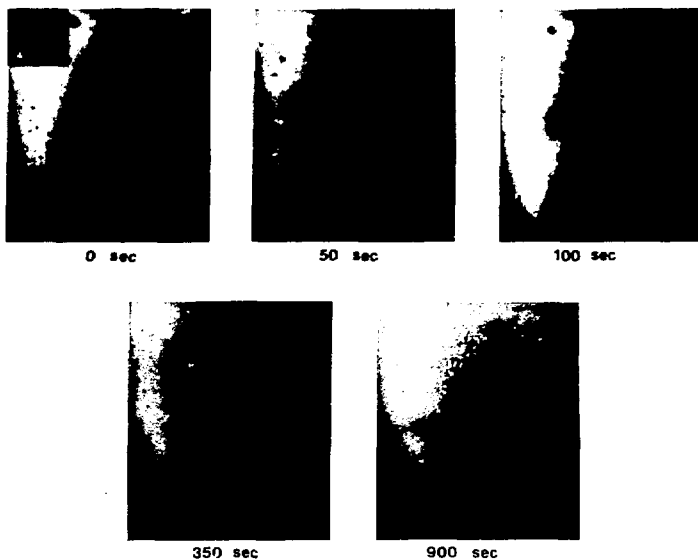


Figure 2 A time sequence of bubble growth in electron irradiated glass

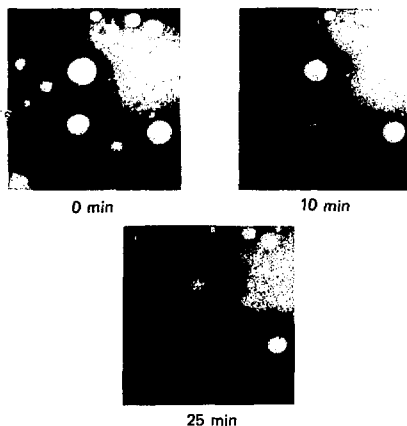


Figure 3 The regression of previously formed bubbles during coarsening phase separation.

IN-SITU AND PHASE TRANSFORMATIONS



IN SITU DEFORMATION AND FRACTURE STUDIES ON PRECIPITATION-HARDENED ALUMINUM ALLOYS*

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ABSTRACT

In situ deformation studies have been undertaken in order to understand the deformation processes that operate in precipitation-hardened alloys and their role in the pronounced embrittlement and tendency toward strain localization that cause premature failure in the hardened condition. The role of precipitate-free zones (PFZ) at grain boundaries on strain localization and failure mode has been investigated in aluminum-based alloys (Al-Zn-Mg and Al-Li).

INTRODUCTION

Precipitation-hardened alloys frequently exhibit PFZs at grain boundaries formed by vacancy or solute depletion to the boundaries. Often these same alloys exhibit strain localization in either the hardened matrix or the soft PFZ and as a result exhibit pronounced embrittlement. Work-softening of the matrix by precipitate shear promotes strain localization in intense slip bands and possibly transgranular failure. The origin of such transgranular cracks is not understood. A second intergranular failure mode is observed where strain localization occurs in the PFZ. Two basic mechanisms have been proposed for the intergranular failure process. The first mechanism suggests that the majority of the deformation occurs in the softened PFZ, while the second suggests that pronounced slip bands form in the matrix and produce stress concentrations at intersections with grain boundaries, which nucleate grain boundary cracks. The current investigation involves in situ deformation of two aluminum alloys in an attempt to study the operative mechanism(s) of strain localization and fracture. The binary Al-Li alloy provides a system where the majority of the matrix hardening results from the ordered nature of the coherent δ' (Al₃Li) phase, whereas for the Al-Zn-Mg alloy coherency strain and/or precipitate misfit play a significant role.

EXPERIMENTAL

Table 1 gives the nominal composition and heat treatments of the three aluminum alloys. The Al-Li A and Al-Zn-Mg were conventionally cast alloys, while Al-Li B was a consolidated powder metallurgy (P/M) alloy. After heat treatment, microtensile specimen blanks (3 × 7 mm) were electrodischarge machined from sheet stock and mechanically thinned to 0.05–0.1 mm thickness.

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Table 1. Alloy Composition and Heat Treatment

Nominal Composition (wt %)		Heat Treatment
Al-Li A	Al-2.3 Li	1 h 538°C; 4 h 200°C
Al-Li B (P/M)	Al-3 Cu-1.5 Li-1 Mg-0.2 Zr	1 h 538°C; 2% stretch; 6 h 190°C
Al-Zn-Mg	Al-6.1 Zn-3.1 Mg	1 h 450°C, range - 0-8 h 180°C

Specimens were jet electropolished in a 1:2 nitric acid:methanol solution at -20°C.

In situ deformation studies were performed both in the Hitachi HU-1000 HVEM at 1 MV using a Gatan straining stage and in a Philips EM400T at 120 kV using a straining stage designed and built by Dr. J. A. Horton (ORNL). The majority of studies were performed prior to dynamic recording systems being available on either microscope, and as such standard plate micrographs were used to record microstructural evolution. This required the deformation to be stopped or significantly slowed.

OBSERVATIONS AND DISCUSSIONS

Aged Microstructures

Alloy Al-Li A was recrystallized with a grain size of ~100- μ m-diameter, with wide (~180 nm) PFZs evident. Matrix precipitation was δ' (Al₃Li), while grain boundary precipitation was the equilibrium δ (Al-Li) phase. Alloy Al-Li B was not recrystallized due to the presence of coherent Al₃Zr precipitates. Intergranular T₁(Al₂CuLi) and S'(Al₂CuMg), and intragranular T₂(Al₆CuLi₃) and S (Al₂CuMg) were present. Grain size was ~4 μ m, and no PFZ was evident. Alloy Al-Zn-Mg was recrystallized with a grain size of ~200 μ m, with varying PFZ width, depending on aging treatment. Both η and η_1 (MgZn₂) phase precipitates are observed in the matrix. Grain boundary precipitates presumed to be T(Al,Zn)₄₈Mg₃₂) phase were observed.

In Situ Deformation

Both the Al-Li A and Al-Zn-Mg exhibited pronounced matrix strain localization by the formation of intense shear bands even in the peak-hardness condition. Figure 1 illustrates the deformation behavior of the Al-Li A alloy in the vicinity of the grain boundaries with associated PFZs. Dislocations from the slip bands entered the PFZ and tended to channel (cross slip) along the unhardened, denuded zone. These dislocations often left segments pinned on the precipitates at the PFZ-matrix interface [Fig. 1(a)]. Gradually a dislocation wall is formed at this interface, resulting in a significant misorientation (>5°) between the matrix and the adjacent PFZ, which can be observed in Fig. 1(a) as a shift in the bend contour. Similar dislocation wall structure and misorientation were observed in bulk-deformed specimens. Figure 1(b) shows a shear crack in the Al-Li A alloy, propagating through a PFZ by void nucleation ahead of the crack and ligament failure. However, this observation was made in a thin area (~0.3 μ m thickness) and has not yet been observed in thicker foils.

Figure 2 illustrates several other observations made on the deformation of the PFZs. At point A in Fig. 2(a), the plastic zone ahead of a shear crack, which nucleated at the foil edge, is present in grain 1. At point B, an unidentified inclusion is present in the PFZ of grain 2. The grain boundary is oriented at $\sim 25^\circ$ to the tensile stress axis and therefore a large component of the deformation should be PFZ sliding parallel to the grain boundary. Figure 2(b) illustrates the microstructure after the shear crack had advanced and significant deformation had occurred in both PFZs. Dislocations in grain 1 were observed to move along the shear bands, pass through the PFZ, and enter the grain boundary. Long-range motion of dislocations in both directions parallel to the grain boundary occurred in the PFZ of grain 2. A large jog was produced in the grain boundary and a significant widening of the PFZ in grain 2 occurred as a result of the absorption and emission of these dislocations. Dislocation emission at this grain boundary jog into grain 2 is illustrated in Fig. 2(c and d). The formation of a dense dislocation tangle by dislocations moving in the PFZ was observed at the interface of the PFZ and the matrix in grain 2. In addition, the dislocations channeling in the PFZ of grain 2 resulted in the decohesion of the inclusion-matrix interface of the previously mentioned particle marked B [Fig. 2(e)]. The resulting void was sheared by additional dislocations.

The strong influence of microstructure on the mechanical performance of such precipitation-hardened aluminum alloys is illustrated in Fig. 3 from the in situ deformation of the Al-Li B alloy. Microstructurally, this alloy is significantly different from alloy Al-Li A; the grain size (and slip distance) is ~ 25 times smaller; the easily sheared δ' precipitates have been replaced by T_1 and S' ; and the PFZs have been eliminated or significantly reduced in width. On the basis of mechanical properties, alloy B is far superior to alloy A, with roughly three times the yield strength (555 MPa versus 195 MPa) and a slight increase in elongation to fracture (8.0% versus 6.6%). Figure 3(a) shows two stages in the propagation of a shear crack through this alloy. Thinning ahead of the crack occurs by homogeneous deformation. There was no indication of matrix slip localization which was apparent in the other two alloys. The crack was primarily transgranular in nature with voids forming predominantly at grain boundaries and linking to the crack as deformation proceeded (see area indicated in Fig. 3).

A question remains as to the influence of the foil thickness on the observed deformation behavior of alloys which exhibit a tendency toward strain localization. Clearly, in such thin sections, there is a minimal constraint imposed on plastic deformation by neighboring grains. Although this may not have an effect on precipitate-dislocation interactions, it may promote slip localization within weak zones that extend through the entire foil thickness. The formation of the dislocation wall at the PFZ-matrix interface appears similar for in situ and bulk testing. Further comparison of microstructure in bulk-deformed versus in situ-deformed materials will be aimed at resolving the foil thickness question, as will in situ deformation studies of bulk-prestrained materials.

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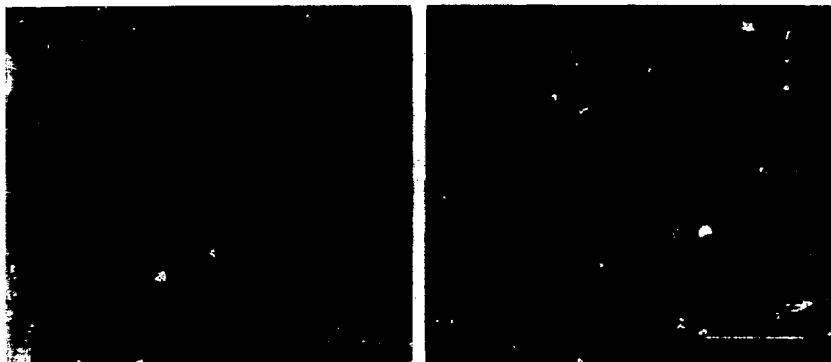


Fig. 1. In situ deformation of Al-Li A alloy. (a) Intersection of intense shear bands with grain boundary PFZ. Note dense dislocation tangles at PFZ-matrix interface and shift of bend contour between PFZ and matrix; (b) propagation of shear crack through PFZ by void nucleation and ligament failure.

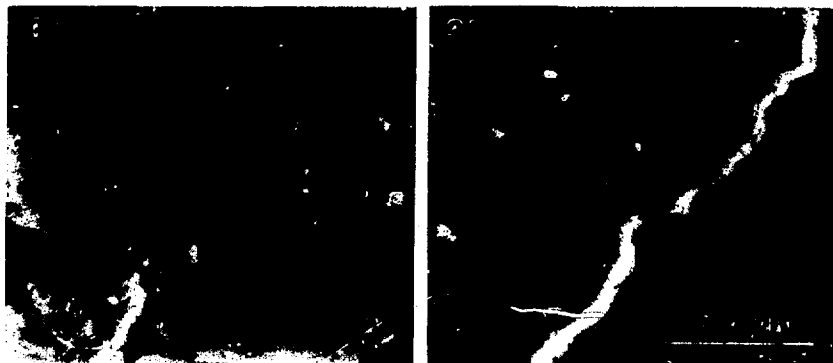


Fig. 3. Propagation of shear crack in Al-Li C alloy. (a) Transgranular crack and localized deformation (thinning) zone ahead on crack; (b) crack after further deformation. Deformation homogeneous, no shears observed. Void at B nucleated at grain boundary triple point (edge).

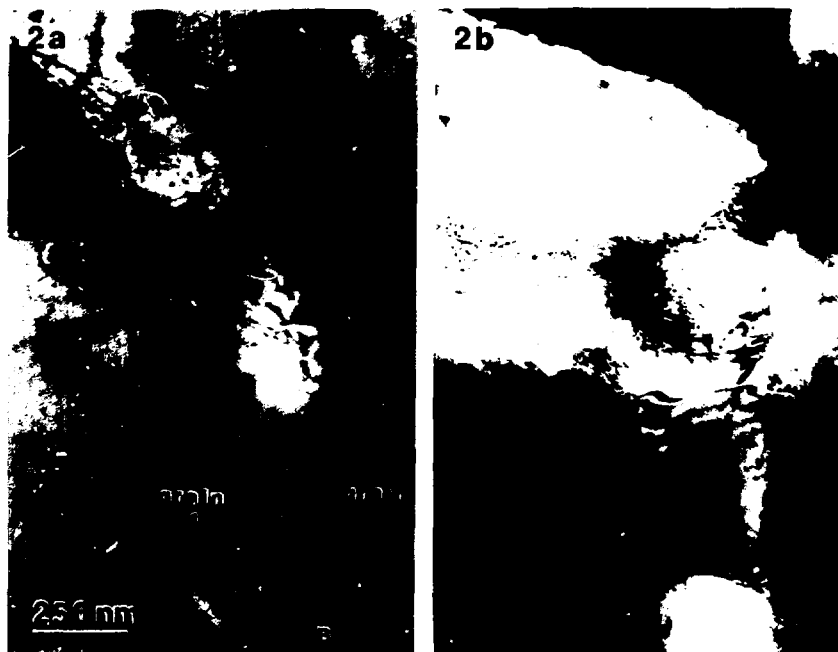


Fig. 2. PFZ deformation of Al-Li A alloys. (a) Intersection of plastic zone A ahead of advancing shear crack with grain boundary PFZ, inclusion B in PFZ grain 2; (b) same area as in (a) after significant deformation. Note large jog in grain boundary and widening of PFZ in grain 2; (c),(d) emission of dislocations from grain boundary jog; (e) formation of void by inclusion-matrix interface decohesion and shearing by channeling dislocations.

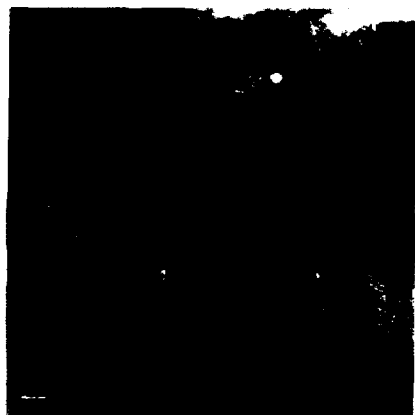


Fig. 2. (continued).

AN IN SITU STUDY OF THE CREEP MECHANISMS OF ALUMINIUM AT INTERMEDIATE TEMPERATURES

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ABSTRACT

Quantitative parameters involved in the constitutive equation of a material can be readily measured during in situ deformation experiments. Some of them are not accessible from macroscopic tests. The method used is described and applied to the observation of the creep mechanisms of Aluminium at intermediate temperatures. It is shown that the total strain is connected to two different processes :

- subboundary migration which occurs by glide of the constitutive segments and accounts for less than 1/4 of the elongation
- glide of individual dislocations which proceed quickly through the subgrains and wait at the subboundaries for periods of time which depend on the rate of straining. They finally cut through the boundaries and a process is involved which is not fully understood but for which cross slip does take place.

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INTRODUCTION

Dorn experiments [1] have shown that the activation energy of creep exhibits a plateau at intermediate temperatures. Its value is higher than in the low temperature regime (intersection mechanism) and lower than at high temperatures where dislocation climb through self diffusion is operating. Conflicting arguments have been proposed for its interpretation : it has been claimed successively that climb by pipe diffusion was the rate controlling process [2] [3], but also cross slip [1][4][5], jog formation during subboundary destruction [6], and at last recombination of junction reactions [7][8]. Here, part of a study is reported which has been undertaken to determine from in situ experiments, what is the rate controlling process of creep under such conditions [9].

EXPERIMENTAL PROCEDURE

- Polycrystalline sheets of Aluminium are predeformed on a creep machine so as to develop the microstructure characteristic of stage II of creep.
- The substructure evolution under stress is studied in situ, the thin

sample being prepared with the same tensile axis direction as the macroscopic one and strained at the same temperature. Under such conditions, only a few additional percent strain can be achieved in the microscope because substructure evolves slowly towards a state which is characteristic of the thin foil.

- With respect to surface effects, it is accepted that these are not too strong as long as the characteristic substructure dimension is smaller than the foil thickness [10]. For creep at intermediate temperatures, this condition is satisfactorily fulfilled since the subgrain size, the Frank network link and the subboundary meshsize are respectively of the order, smaller and much smaller than the foil thickness.

- For Burgers vector determination of moving dislocations, standard tests cannot be used, but it can be determined from the slip traces of the corresponding defect (Fig. 1). During glide, they are straight and parallel and indices of the slip plane can be unambiguously determined. If cross slip occurs, the traces are usually of the form shown in Fig. 1a) and 1b). They are separated by a translation vector $\vec{B}$ parallel to the Burgers vector. If cross slip is very frequent, they can look like Fig. 1c) and 1d), where the $\vec{B}$ vector can also be determined. If the dislocation is climbing, both traces are wavy again but cannot be connected by a translation. On Fig. 1e), a dislocation with Burgers vector parallel to $\vec{B}$ is gliding upwards with slip traces h and b and cross slips from a {111} plane on to another one and then climbs (traces h' and b').

- Quantitative measurements related to the in situ creep tests can be performed as follows. The stresses or strain rates applied to the sample are not significant because of its complicated shape. But local measurements can be done very successfully and a local creep curve can be established. For small strains and strain rates, the number of dislocations gliding across a given subgrain can be counted as a function of time and the resulting shear strain ϵ can be derived from the corresponding swept area : $\epsilon = Nb/2L$, where N = number of traces (corresponding to N/2 glide planes) and L = subgrain size.

The local creep curve of Fig. 2 has been obtained in this way. In abscissa, the time has been plotted as well as the elongation ΔL imposed to the sample. On the Y axis, the local strain ϵ (or the number of glide events) is reported for two slip systems which were visible here for two different diffraction conditions ($\epsilon = \epsilon_1 + \epsilon_2$). The strain is proportional to the elongation ΔL but their ratio is found to be different in various experiments. In addition, the strain rates agree in order of magnitude with that of the macroscopic tests [9]. For larger strains and strain rates, slip traces cannot be unambiguously counted but the local strain can be estimated from the distance between characteristic points of the sample (small loops, dipoles, etc.). A local deformation map can therefore be established in this way.

The local effective stress can be estimated as well, from the radius of curvature R of the dislocations : $\sigma = \tau/R$ where τ is the line tension.

The dislocation plane and direction as well as its Burgers vector, have to be known since τ strongly depends on the dislocation character and are not. It is however rather easy to measure a relative stress variation since one usually has : $\Delta\sigma/\sigma = \Delta R/R$, where R is the radius of curvature of the projected dislocation image.^P

Strain rate jumps can be performed in situ and, by comparing the resulting $\Delta\sigma/\sigma$ and $\Delta\epsilon/\epsilon$, the strain rate dependance on strain can be derived [11][12].

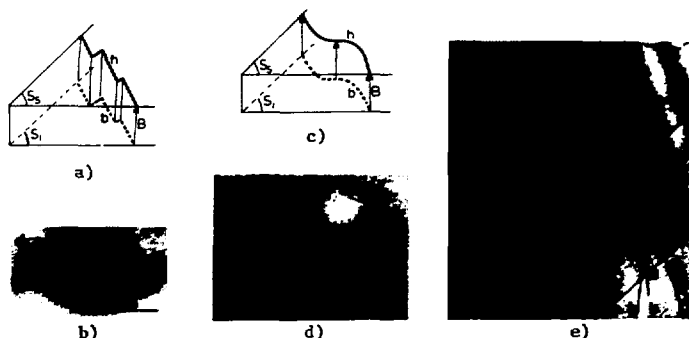


Fig. 1. Dislocation traces in Aluminium (1 MeV). h and b : traces on foil surfaces S_g and S_i . a) and b): cross slip - c): frequent cross slip. B is parallel to the Burgers vector of the moving dislocation - e): dislocation glide and cross slip (h, b) and climb (h', b').

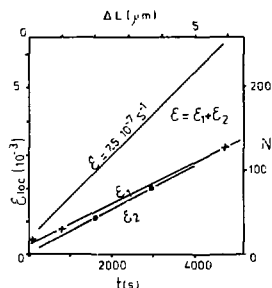


Fig. 2. Local creep curve relative to one subgrain (200°C). ΔL : elongation of the microsample (proportional to time). ϵ_{loc} : local shear strain (see text).

RESULTS

The total strain of the sample has two components bound to subboundary migration [13] and movement of individual dislocations.

Subboundary migration

An example is given on Fig. 3. Subboundaries slowly move as a function of time and it is quite clear from the scheme of Fig. 3d) that they drag along their triple junctions. It has been shown [9] that this occurs by glide of their dislocation segments, that the locus of the subboundary nodes are along $\langle 110 \rangle$ directions and that the constitutive dislocations move along the boundary plane. As an example, dislocations of subboundary B are transferred to E and F while those of A are transferred to G and B. This phenomenon has several important consequences :

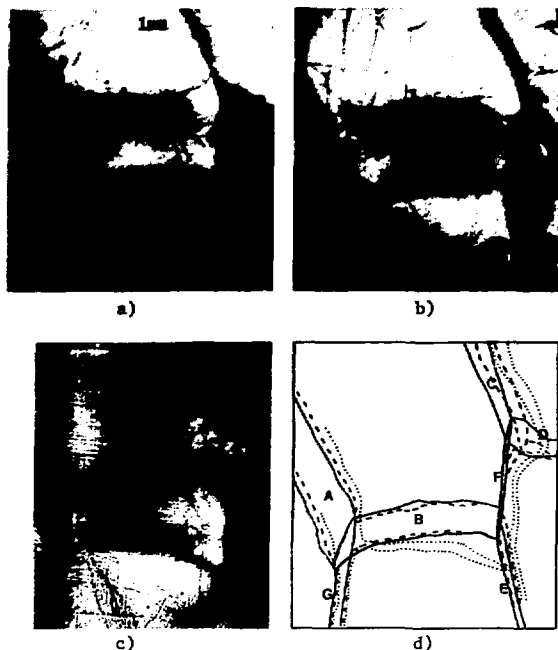


Fig. 3. Sequence of subboundary migration at 200°C (1 MeV). The pictures are separated by about 55 mn, and the successive positions of the subboundaries are reported on the scheme.

- Triple junctions are not strong anchoring points for subboundaries and therefore the unbulging of the latter during unloading is probably not sufficient to account for the large associated anelastic strains [14].

- The transfer of subboundary dislocations through the triple junctions during migration concentrate the stress at irregular points of the network on the one hand. This may be very helpful in the process of cutting through subboundaries by individual dislocations for which high local stresses are necessary [9]. On the other hand, since dislocations redistribute themselves continuously along the neighbouring subboundaries, irregular points in the network disappear and very periodic ones are rebuilt. If not, subboundaries would be destroyed after a large number of mobile dislocations have cut through them. Fig. 4 shows that the amount of subboundary migration is proportional to the total local strain, measured as on Fig. 2. In the case of Fig. 3, the strain due to subboundary migration can be computed. It is found to be of the order of 25% of the total strain for this example. It is often smaller, in agreement with [13]. Therefore the largest amount of strain is due to individual dislocations.

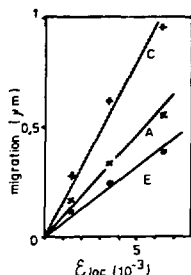


Fig. 4. Distance of migration of subboundaries A, C, and E of Fig. 3, as a function of the total local shear strain. The distance of migration is proportional to strain and time.

Movements of individual dislocations

Dislocation sources have been recorded during in situ creep testing [9] and they are observed inside the subgrains and in some of them only. This implies that, to ensure a homogeneous deformation, dislocations have to travel over distances which are large as compared to the subgrain size. They are observed to do so with a flight time through the subgrain which is negligible with respect to the waiting time at the subboundaries. The latter are the obstacles to dislocation glide and the rate controlling process is the cutting through mechanism of individual dislocations through boundaries. The detailed understanding of this process is not complete, because of the small size of the meshes (some 100 Å) inside which dislocation interactions take place. Nevertheless, information can be obtained again from the dislocation slip traces through the subgrain and near the boundaries. The example of Fig. 5 is quite common. Dislocation d has escaped from subboundary 1, has crossed the subgrain with straight and parallel slip traces which are indication of glide. As it reaches subboundary 2, one of the traces is bent, which is here indication of cross slip (the Burgers vector b of d can be readily determined from such tra-

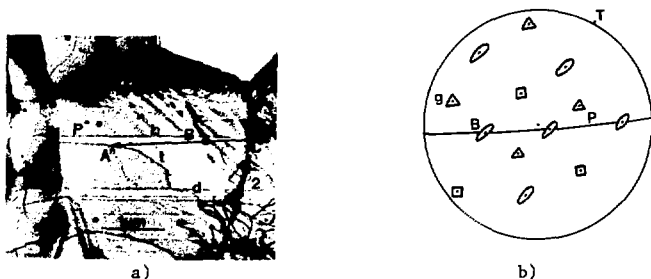


Fig. 5. Insertion of dislocation d into subboundary B (200°C, 1 MeV). Bottom trace b is rectilinear and top trace t becomes curved in A'', with $A''C = B$ parallel to the Burgers vector of the dislocation (see stereogram). This is characteristic of glide in plane P, and cross slip and glide during insertion.

ces). This is an example of insertion of d into subboundary, and traces bound to dislocation extraction are quite similar.

To conclude, quantitative measurements can be achieved during in situ straining experiments in the high voltage electron microscope. In the case of intermediate temperature creep, they have provided valuable information about the rate controlling process which does involve cross slip.

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IN SITU OBSERVATION OF PILE-UP MOTION
UNDER LOAD IN A CONCENTRATED f.c.c. Ni-Cr ALLOY
- DETERMINATION OF THE FRICTION FORCES INVOLVED -

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INTRODUCTION

Previous results of mechanical tests [1,2,3] on flow stress values and activation parameters of pure Nickel and f.c.c. Ni-Cr alloys as a function of temperature, strain rate and concentration between 77 K and 700 K, have shown that :

- The stress strain curves exhibit an inflexion point between two regions of low and high hardening rates respectively as strain increases. This behavior is usually interpreted as a glide softening process occurring at low strains.
- For concentrated alloys (i.e. $15 < C < 37$ weight % Cr), the σ over T dependence satisfies an empirical law [3].

$$(\sigma - \sigma_{\mu})^2 / 3 = (\sigma_{OK} - \sigma_{\mu})^2 / 3 - BT^2 / 3$$

Among the $\sigma(T)$ relationships which were established for other materials [4], this equation has been quoted once already, in the case of neutron irradiated Copper [5].

- The apparent activation volume as measured from relaxation tests is rather strain independent for a given stress strain curve and of the order of some $100 b^3$ depending on temperature and concentration.
- As the strain rate decreases, or the temperature increases and reaches the athermal plateau region, static ageing effects are observed, followed by dynamic ageing effects.

These various features of the mechanical behaviour of the concentrated alloys are quite different from the corresponding ones for pure Nickel and dilute alloys. In the latter case an intersection mechanism operates in the low temperature range investigated here [2]. For concentrated alloys, known dislocation models of solid solution hardening do not fit as well [6,7].

Instead, the influence of short range order was questioned [2][8]. Indeed, neutron diffraction experiments performed with a Ni-30 wt % Cr alloy (33 at %) have revealed [9][10]:

- a practically disordered state after 4 h at 1100°C followed by quenching
- a long range ordered state after 6 h at 530°C
- a state for which short range order is maximum after 250 h at 600°C.

It is also well known that the more concentrated the alloy, the more heterogeneous the deformation [11].

To get a better understanding of the mechanical behavior of Ni-Cr alloys in connection with the dynamic properties of dislocation pile-ups, the following in situ tests were undertaken on single and polycrystals of 30 wt % Cr alloys : deformation at a constant strain rate, load relaxation experiments, static ageing experiments [3]. Some of them are reported below.

EXPERIMENTAL APPROACH

After thermal treatments producing disordered and short range ordered samples, these were predeformed up to 3 to 12 % to avoid the microplastic stage during observations and to increase the probability of defect intersection which is characteristic of stage II. In situ deformation was performed at a rate of about 10^{-6} s^{-1} , at room temperature or $0.19 T_M$ (T_M being the absolute melting point). By using an image intensifier and an accelerating voltage set at 800 kV, radiation damage was reduced as much as possible. The straining stage used [12] was compatible with rectangular microsamples ($3 \times 1 \text{ mm}^2$).

Such observations provide direct information about the interaction of dislocations with various obstacles with a good resolution and particularly mobile dislocation densities and velocities can be measured. In addition, the dislocation configurations being observed under load, the measurement of defect distances along a pile-up can lead to a reasonable quantitative estimation of the local stresses and in particular of the friction stress.

OBSERVATIONS

General aspect of deformation

The montage of fig. 1 shows a typical glide sequence in the alloy being deformed, through successive straining and relaxation periods. An undeformed area is shown on fig. 1a, while on fig. 1b, it has been sheared by numerous active glide planes a little later. The chronology of the different glide events is indicated on the photograph : as an example, slip plane 1 has appeared first and has stopped during a relaxation sequence (relaxation time of the order of 20 s), in spite of any apparent obstacle. As straining is resumed, the deformation proceeds through the rapid multiplication and propagation of dislocations in new glide planes numbered 2, 3, 4, 5 On the contrary, after shorter relaxation times, (of the order of 5 s), the same pile up can be reactivated.

In E, the head of a newly created pile-up (no. 7) has stopped, at the intersection with pile-up no. 2. The problems connected to pile-up interactions are discussed below.

The observation of several deformation sequences such as that of fig. 1 indicates that two defect populations have to be considered separately :

- isolated dislocations : these grown in defects are usually situated outside the glide planes and appear to be strongly pinned by arrangements of solute atoms. They usually remain immobile or move slowly (v of the order of $25 \text{ \AA s}^{-1}$) in areas of high stress concentration, i. e. in the vicinity of stressed pile-ups. Therefore, they do not contribute significantly to the deformation, at least at room temperature.

- dislocations in the pile-ups : video-tape recordings provide useful information about the way dislocations propagate through the planes. At the deformation rate used ($\sim 10^{-6} \text{ s}^{-1}$), newly created pile-ups propagate at first very quickly ($v \gg 40 \mu\text{m s}^{-1}$). Such high velocities are not compatible with thermally activated obstacles. Because of the heterogeneity of deformation, sources are difficult to observe in such experiments : they often operate in thick parts of the crystal, probably in areas of high stress concentration or of weaker friction forces. When a slip plane is active, neighbouring parallel ones are also observed indicating that sources are activated in the high stress regions near the dislocation groups of the former.

During further activity of the same source, small moving groups of dislocations (8 to 10) propagate as waves along the slip plane with a velocity in the $3 \mu\text{m s}^{-1}$ to $20 \mu\text{m s}^{-1}$ range. This indicates that the lead dislocations of the pile up and the following ones propagate through different fields of obstacles.

Resistance to pile-up propagation

Severe friction forces resist pile-up propagation. A method has been proposed to derive them from the actual dislocation distances measured in the loaded foil [3]. An elastic interaction stress σ_{pu} is directly obtained from these distances, at each dislocation of the group and is shown on fig. 2 for a given pile-up. Since long range elastic interaction stresses can be neglected in a foil as a rule (short defect segments instead of infinite ones) [3], σ_{pu} is only balanced by the friction stress σ_f and the applied resolved shear stress σ which is constant all through the foil at a given time. The evaluation of a large number of pile-ups shows that the friction stress is always much higher than the applied stress at the level of several of the lead dislocations and decreases as one moves towards the source (see an example on fig. 2b). This effect is still more pronounced in the short range ordered alloy and the following orders of magnitude have been estimated :

disordered alloy : friction stress at pile-up head = 1.6 CRSS
short range ordered alloy : = 2.7 CRSS.

Intersecting dislocations are quite frequent and alter the regularity of the defect sequence along the active plane as seen on fig. 3. Multipoles are also frequently observed in the alloy. As they are glissile configurations, they are swept away by moving pile-ups as shown in D on fig. 1a and 1b, for example.

Stronger obstacles can resist pile-up propagation such as certain types of grain and twin boundaries. In this case, as an incident plane reaches the boundary, severe local stresses are built up at their intersection, which activate new dislocation sources in the adjacent crystal on one or two plane families. Alternately, soft boundaries are also observed through which the slip plane direction changes without any evidence of stress concentration.

Pile-up intersection seems to be another severe obstacle to glide propagation through the crystal as illustrated on fig. 4. This micrograph corresponds to stage II of the deformation curve. This is a double glide region where pile-ups no. 1 are first activated. They stop when they are intersected and sheared by pile-ups no. 2. The following explanation can be proposed in terms of a glide softening mechanism. The friction force results reported above can be interpreted in that way : the lead dislocations have to propagate

through the microdomains of short range order and destroy them partially, and the following ones glide more easily in a softened plane. On fig. 4, when pile-up no. 1 is sheared, a step in the corresponding glide plane is created at the intersection. For further activation of source no. 1, new lead dislocations have to propagate through the unsoftened alloy, starting from that step, the stress being less concentrated through a shorter pile-up than before intersection. This seems to be very difficult to achieve since no corresponding traces are observed. As a consequence, simultaneous activation of intersecting planes does not seem to be possible and deformation proceeds through activation of pile-ups no. 2.

Stresses necessary for glide intersection can be evaluated using the same method than for measuring friction forces [3]. An example is shown on fig. 5, in a short range ordered alloy. It appears that the stresses necessary for intersection are smaller or of the same order of magnitude than the friction in the undeformed material.

DISCUSSION AND CONCLUSION

The presence of short range order which is evidenced by neutron diffraction techniques strongly influences the mechanical behaviour of concentrated Ni-Cr alloys, as compared to more dilute ones, in the following way. Isolated dislocations are strongly pinned and glide can only proceed through pile-up propagation which concentrates the stress sufficiently. The friction force measured along moving groups is stronger near the head, with higher values in the short range ordered alloys. This has been interpreted as a glide softening process, the lead dislocations of the group destroying the microdomains of short range order. To do so, they have to proceed at relatively high velocities through the alloy and this mechanism is thought to be contributing to the athermal component of the stress. The stress having relaxed at the source, the following dislocations move more slowly, encounter a lower friction due to remaining arrangements of solute atoms, which is thermally activated. This interpretation is in agreement with the inflexion point in the low strain parts of the stress strain curves, with the orders of magnitude of the activation volume values which are about the same in the softened alloy and in the unsoftened one (high strain and low strain portions of the stress strain curve respectively).

This example illustrates how microscopic in situ deformation observations and macroscopic mechanical testing data can be confronted to determine the rate controlling mechanism of concentrated Ni-Cr alloys.

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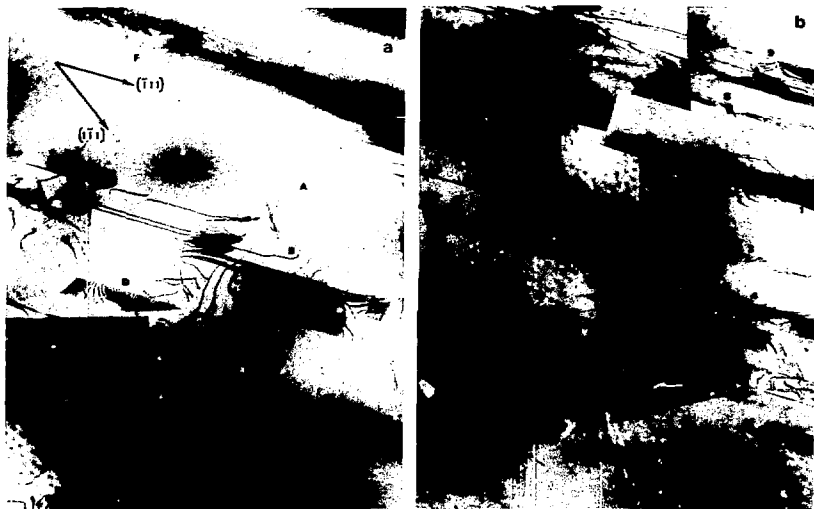


Fig. 1 - In situ dynamic sequence. Ni 30% Cr, disordered state $T = 300$ K - a) an area before straining; b) same area after successive straining-relaxation sequences.

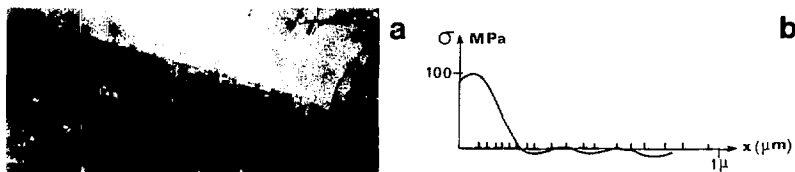


Fig. 2 - Ni 30% Cr, disordered state - a) pile-up created during in situ straining; b) corresponding variation of the elastic interaction stress.

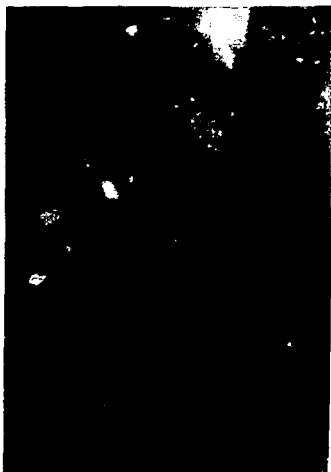


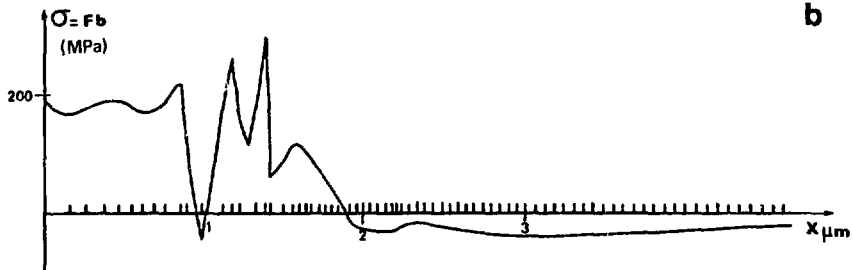
Fig. 3 - Pile up propagation through pre-existing dislocations.



Fig. 4 - Sequence of pile up propagation in a prestrained sample (12%) double glide region.



a



b

Fig. 5 - Analysis of pile-up intersection. Ni 30% Cr, short range ordered, pre-deformed 12% - a) the moving pile up intersects other slip planes; b) corresponding variation of the elastic interaction stress.

IN SITU TRANSFORMATIONS IN STAINLESS STEELS

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ABSTRACT

Samples of 10 Cr/16 Ni stainless steel have been either deformed or cooled in situ in an HVEM and the nucleation and growth of martensite observed. The transformation of austenite to α martensite has been shown to follow a different path from that observed in the lower stacking fault energy 16 Cr/12 Ni steel. Twinning rather than transformation to h.c.p. martensite appears to precede the formation of α martensite in the 10/16 steel.

Introduction

In situ observations made either on cooling or on deformation of a 16Cr/12 Ni stainless steel have shown that the transformation of f.c.c. austenite to b.c.c. martensite occurs firstly by transforming to h.c.p. martensite [1]. Because the observations were made using double tilting stages it was possible to analyse, in some detail, the manner in which the transformation occurred. Stacking faults were generated, either from grain boundaries or from dislocations, and these faults were shown to have a supplementary displacement normal to the $\{111\}$ plane, such that the spacing of the planes which were stacked ABAB., was close to the (0001) spacing of the h.c.p. martensite. When a sufficient number of faults overlapped h.c.p. diffraction spots could be detected. Continued cooling or deformation then could be seen to result in rapid transformation of this region of ϵ -martensite to a martensite and in rapid growth of α into the austenite matrix. Figure 1 illustrates these points.

The stacking fault energy of the 16/12 steel is about 22 mJ/m^2 and it is reasonable to assume that the mechanism observed in this alloy is typical of low stacking fault energy steels. The aim of the present work is to extend the in situ observations to stainless steels of higher fault energy and to relate the in situ observations to recent work where the transformation in bulk samples is studied [e.g. 2].

Experimental

The various composition stainless steels were made up in 100 g batches by melting appropriate amounts of Fe, Cr and Ni in an R.F. vacuum furnace. The small ingots were rolled and homogenised for 96 hrs at 1200°C . For in situ cooling experiments 3 mm discs were prepared using standard electropolishing

techniques. The in situ tensile specimens were made either by the technique described in [1] or simply by polishing a hole in the centre of a 7 mm long, 3 mm wide strip. The 7 mm strip could be mounted directly on the tensile stage [3] and because only very narrow strips are left either side of the polished hole, straining is confined to these regions when the sample is stressed in situ. Deformation was carried out at various strain rates using manual, mechanical or piezo electric straining [3].

Results

Preliminary observations on various stainless steels were made simply by deforming or cooling bulk samples and testing for ferromagnetism. If room temperature deformation or cooling to -130°C (the lowest temperature of the cooling stage) was not able to induce ferromagnetism the steel was not investigated further. Virtually all the present in situ work has been done on two steels, 10 Cr/16 Ni and 11 Cr/16 Ni whose fault energies are about 43 and 39 mJ/m² respectively.

The sequence of events in these steels is somewhat more difficult to observe than was the case for the 16/12 steels. Very commonly regions of α were formed either during specimen preparation or α propagated into the field of view and no useful observations could then be made on the events leading to the formation of α -martensite. Occasionally, however, intense slip, involving both perfect and imperfect dislocations occurred prior to the transformation. The subsequent transformation to α then takes place in at least two different ways. In one case, illustrated in Fig. 2 slip in the grains at the top of the figure has given rise to the complex region, marked T, in the lower grain. Analysis shows that regions similar to this are twinned with respect to the f.c.c. matrix, and it is this regions which acts as a nucleus for the α . In the second case α can be seen to grow into a heavily faulted region as straining is continued, as shown in Fig. 3.

Once nucleated these regions of α propagate slowly through the austenite and a large number of dislocations is generated as the α/γ interface propagates through the γ as illustrated in Fig. 4. Propagation takes place laterally as well and again prolific dislocation generation occurs. The individual α regions continue growing to produce α -regions many microns in width and length generated from each nucleus.

In situ cooling results in the propagation of pre-existing α and no evidence for fault formation has been obtained. The propagation of α appears to occur in a manner which is indistinguishable from the propagation during deformation.

Analysis of the orientation of the α and γ shows the same relationship as observed in bulk transformation.

Discussion

The preliminary observations carried out on the 10 Cr/16Ni stainless steel show that it is possible to observe the martensitic transformation in some detail in this relatively high stacking fault energy steel. It should be noted

that no h.c.p. ϵ martensite is observed when the steel is transformed in the bulk and thinned and this is consistent with the observation that the faulted regions generated by in situ observation appear to be twinned rather than transformed to ϵ . As yet no measurements have been made of any supplementary displacements associated with the faulted region in the steel.

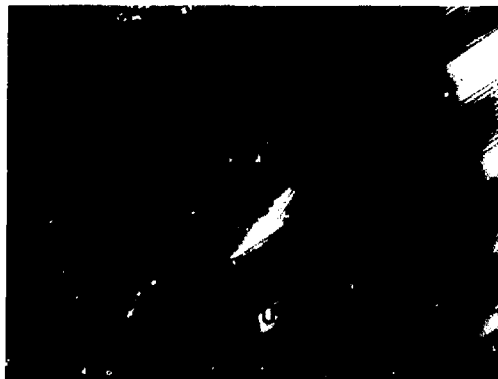
Further in situ work is underway on these stainless steels in which both the nucleation and growth of α martensite will be investigated. Extension to higher fault energy steels is also planned and will be reported.

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Fig. 1 Bright field HVEM (400 kV) micrographs of faults formed during in situ cooling of 16Cr/12 Ni steel. There are five and four overlapping faults at A and B respectively. (a) $\mathbf{g} = [011]$. (b) Strong residual contrast from A and B when $\mathbf{g} \cdot \mathbf{R} = \text{integer}$. $\mathbf{g} = [031]$.



(c) Bright field HVEM micrographs (400 kV) of region of α martensite which was seen to nucleate in a heavily faulted region of ϵ -martensite. Imaged with $\mathbf{g} = [130]$ and $\mathbf{g} = 002$.

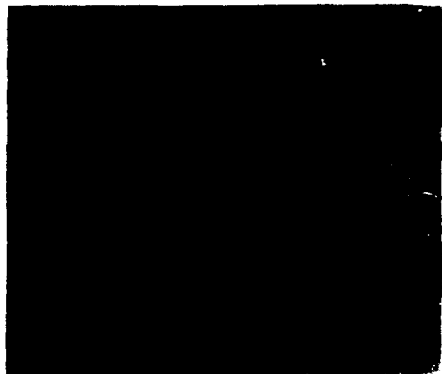


Figure 2 Bright field HVEM (400 kV) micrograph of 10 Cr/16 Ni deformed in situ showing slip bands in grains at top of figure which give rise to region marked T, which is apparently twinned. Many beam imaging conditions.



Figure 3 Bright field HVEM (500 kV) micrograph of 10 Cr/16 Ni deformed in situ showing growth of α , marked A, into faulted region. Imaging conditions, $g = [011]$, $g = 111$.



Figure 4 Bright field HVEM (500 kV) micrograph of 10 Cr/16 Ni deformed in situ showing dislocation generation associated with propagation of α martensite. Imaging conditions, $g = [011]$, $g = 111$.

UHV-HR-1 MV ELECTRON MICROSCOPE OBSERVATION OF MODULATED STRUCTURE AND PRECIPITATED CARBIDE IN TEMPERED IRON-CARBON MARTENSITE

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ABSTRACT

Atomic level observations by using the Ultra-High-Vacuum High-Resolution 1 MV Electron Microscope have shown that the modulated structure is of the displacement type and iron atoms are displaced considerably in the cluster regions. When the modulated structure is destroyed by heating or irradiation, the embryos of η -Fe₂C are formed from the cluster regions. At the first stage of tempering, such embryos grow to η -Fe₂C particles, while the matrix α' transforms to the low carbon martensite α'' . Throughout the structural transition from the modulated structure to the η -Fe₂C formation, the atom rows in the $[101]_{\alpha'}$ direction hold their linearity fairly well but those in the $[101]_{\alpha''}$ direction are displaced considerably so as to produce the atomic arrangement in the η -Fe₂C structure. Such an anisotropic displacement of atoms characterizes the transition from the modulated structure to the structure at the first stage of tempering.

INTRODUCTION

A structural modulation takes place in iron-carbon martensite (α' , bct) at temperatures between 270 K and 370 K [1], prior to the first stage of tempering taking place at around 390 K, where the martensite transforms to the low carbon martensite (α'' , bct, axial ratio $c/a = 1.01$) and η -carbide (η -Fe₂C, orthorhombic, $a = 0.470$, $b = 0.432$, $c = 0.283$ nm) [2]. The modulated structure is characterized by the appearance of satellite spots around every fundamental spot. In a previous study [3], the modulated structure was analysed by measuring the satellite spot intensity in electron diffraction patterns, and a cluster model was presented, where the satellite spot intensity is contributed mainly by the displacements of iron atoms from their average positions caused by the invasion of carbon atoms to the octahedral interstices.

In the present study, direct observations of the modulated structure were made in the atomic level with the aid of the Ultra-High-Vacuum High-Resolution 1 MV Electron Microscope (UHV-HR-1 MV EM) [4,5] recently installed at Tokyo Institute of Technology. The transition of modulated structure to the structure at the first stage of tempering was also investigated. These are described in this paper.

EXPERIMENTAL

Specimen martensite containing 1.5 wt%C (7 at%C, $a = 0.285$, $c = 0.305$ nm, $c/a = 1.07$) was prepared by quenching a carburized pure iron plate and electropolished at 340 K for 30 min. This electropolishing serves also as the tempering for the modulated structure formation. For precipitating η -Fe₂C, the tempering was made at 420 K for 1 day.

Structure images were taken from specimen foils with thickness of about 30 nm under the axial illumination of 1 MV electrons along $[010]_{\alpha'}$, by using an objective aperture with diameter 70 μm , which makes the $101_{\alpha'}$, $200_{\alpha'}$, and $002_{\alpha'}$ types of spots and their satellites contribute to the image formation. In order to minimize the radiation effects, the incident beam was weakened and the magnification was limited to 2.5×10^5 in most cases.

RESULTS

Fig. 1 reproduces an electron diffraction pattern taken with the beam incidence along $[010]_{\alpha'}$, where the satellite spots are observed around every fundamental spot approximately in the $\langle 102 \rangle_{\alpha'}$ direction. The circle indicated corresponds to the objective aperture size used for imaging.

Fig. 2 is an electron micrograph of low magnification showing the modulated structure, where the fringes with spacing of about 1 nm are observed to run in the two directions corresponding to the satellite spot positions in Fig. 1.

Fig. 3(a) is a structure image. The dark dots are the images of iron atom rows in the $[010]_{\alpha'}$ direction. The dark bands running along about $[201]_{\alpha'}$ direction indicate that structural modulation takes place only in one direction in a limited area [3]. They consist of dark patches, each of which is the image of interstitial carbon atom cluster. The cluster size is about 0.5 nm. Fig. 3(b) is an optically transformed pattern of the recorded image from an area corresponding to 25 nm in diameter and covering the area of Fig. 3(a). From this pattern, we can say that the $101_{\alpha'}$, $200_{\alpha'}$, and $002_{\alpha'}$ types of spots and their satellites contribute to the structure image of Fig. 3(a).

The axial ratio c/a measured directly in the inter-cluster regions of Fig. 3(a) is 1.07. This coincides with the values measured from the selected area diffraction pattern and from the optically transformed pattern. This shows that the tetragonality of martensite is held in the inter-cluster region, where the carbon content is considered to be lower than the average.

A close inspection of Fig. 3(a) finds that the atom rows along the $[101]_{\alpha'}$ direction is fairly straight but those along $[010]_{\alpha'}$ bend when they cross the cluster regions. This causes a local symmetry change of martensite from tetragonal to monoclinic.

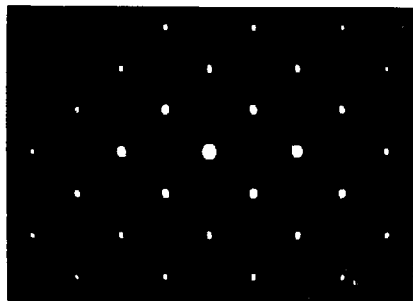


Fig. 1. Electron diffraction pattern of 1.5 wt% C martensite subjected to the structural modulation. Beam // $[010]_{\alpha'}$.

When the tempering temperature is around 370 K or the electron irradiation is strong, the satellite spots become weak and diffuse. Fig. 4(a) is a structure image taken after a strong electron irradiation.

The arrangement of atom rows is straight along the $[101]_{\alpha'}$ direction but irregular along the $[101]_{\alpha''}$ direction. A careful observation finds that in the encircled area the arrangement of atoms is different from the arrangement in the martensite but close to that in $\eta\text{-Fe}_2\text{C}$ projected along the $[001]_{\eta}$ direction. In accordance with this, the optically transformed pattern of Fig. 4(a) produces diffraction spots corresponding to the $2\bar{1}0_{\eta}$ and 210_{η} spots at the positions as indicated by the arrows in Fig. 4(b). The axial ratio of martensite matrix is 1.05, indicating that the specimen tempering is not at the first stage of martensite tempering.

Fig. 5(a) is a structure image of a specimen subjected to the tempering corresponding to the first stage, and composed of the images of $\eta\text{-Fe}_2\text{C}$ and the low carbon martensite α'' with axial ratio 1.005. Moiré images are frequently observed. They are due to the double diffraction between the $(200)_{\eta}$ and $(\bar{1}01)_{\alpha''}$ planes. The $\eta\text{-Fe}_2\text{C}$ particles have a size of about 5 nm and formed coherently with the matrix α'' without any preferential site. It is noticed that the atom rows in $[101]_{\alpha''}$ direction are connected smoothly with the atom rows in $[100]_{\eta}$ direction but the atom rows in the $[101]_{\alpha''}$ direction are not so with those in the $[010]_{\eta}$ direction. This feature is schematically illustrated in Fig. 5(b).

Fig. 5(c) is an optically transformed pattern of Fig. 5(a). It can be seen that only one of the possible orientations between the $\eta\text{-Fe}_2\text{C}$ and the matrix α'' appears in a limited area.

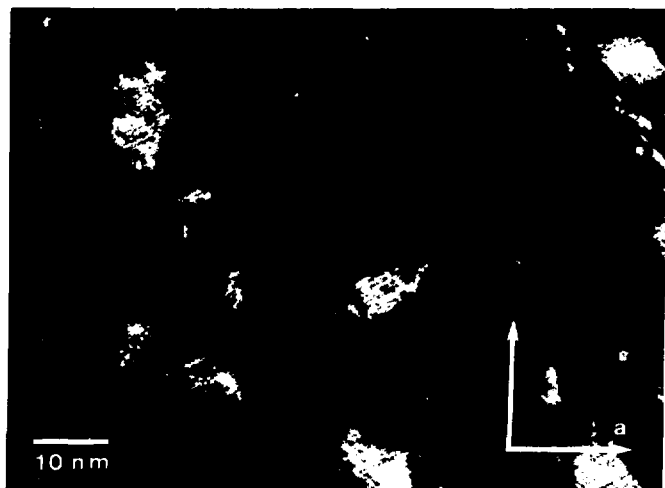


Fig. 2. Electron micrograph showing the structural modulation.

DISCUSSION

In the present study, we made high resolution electron microscopic observations of iron-carbon martensite by using the UHV-HR-1 MV EM and succeeded in observing the modulated structure and its transition to η -Fe₂C and low carbon martensite in the atomic level.

The modulated structure is of the displacement type. This is in accordance with the result of the previous electron diffraction structure analysis [3]. The cluster region, where the carbon concentration is considered to be high, is distorted heavily in such a way that the iron atom displacement is large in the $[101]_{\alpha}$ direction but small in $[\bar{1}01]_{\alpha}$. Such an anisotropic distortion is considered to be due to the anisotropic distortion caused by the invasion of carbon atom to the octahedral interstice.

In the structure of martensite, if iron atoms in every two $(101)_{\alpha}$ plane are displaced in the $[\bar{1}01]_{\alpha}$ direction by one-third of the $(101)_{\alpha}$ interplanar spacing, the produced structure becomes very close to the structure of η -Fe₂C. The images in the encircled area of Fig. 4(a) correspond well to the structure formed by the above procedure. This structural transition may take place in the cluster region most easily, since iron atoms in the cluster are displaced considerably in the $[\bar{1}01]_{\alpha}$ direction. Accordingly, we may say that the cluster changes to the embryo of η -Fe₂C, when the modulated structure is destroyed by heating or electron irradiation.

With increasing temperature the embryo of η -Fe₂C grows to a η -Fe₂C particle by absorbing carbon atoms in the matrix α' , while the matrix α' transforms to the low carbon martensite α'' . Throughout the transition from the modulated structure to the η -carbide formation, the atom rows in the $[\bar{1}01]_{\alpha}$ direction hold their linearity fairly well. On the contrary, for the atom rows in the $[101]_{\alpha}$ atoms are displaced considerably in the $[\bar{1}01]_{\alpha}$ direction so as to produce the atomic arrangement in η -Fe₂C. Such an anisotropic displacement of iron atoms can be said to characterize the structural transition taking place at the low temperature tempering of iron-carbon martensite.

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Fig. 3. (a) Structure image of modulated structure. (b) Optically transformed pattern.

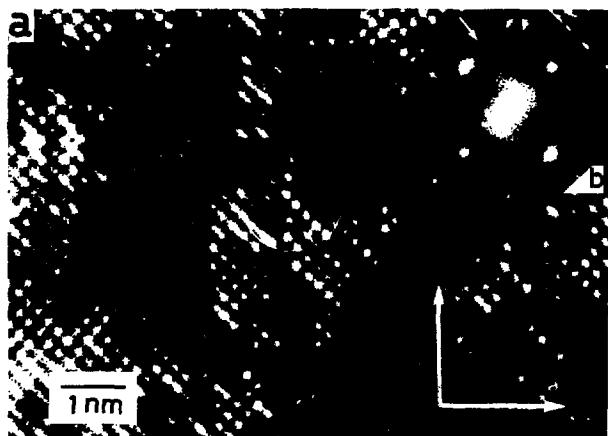


Fig. 4. (a) Structure image of modulated structure after a strong electron irradiation. The atom arrangement in the encircled area is close to that in η - Fe_2C . (b) Optically transformed pattern. Arrows indicate the spots appearing at the positions corresponding to the 210_η and 210_η spot positions.

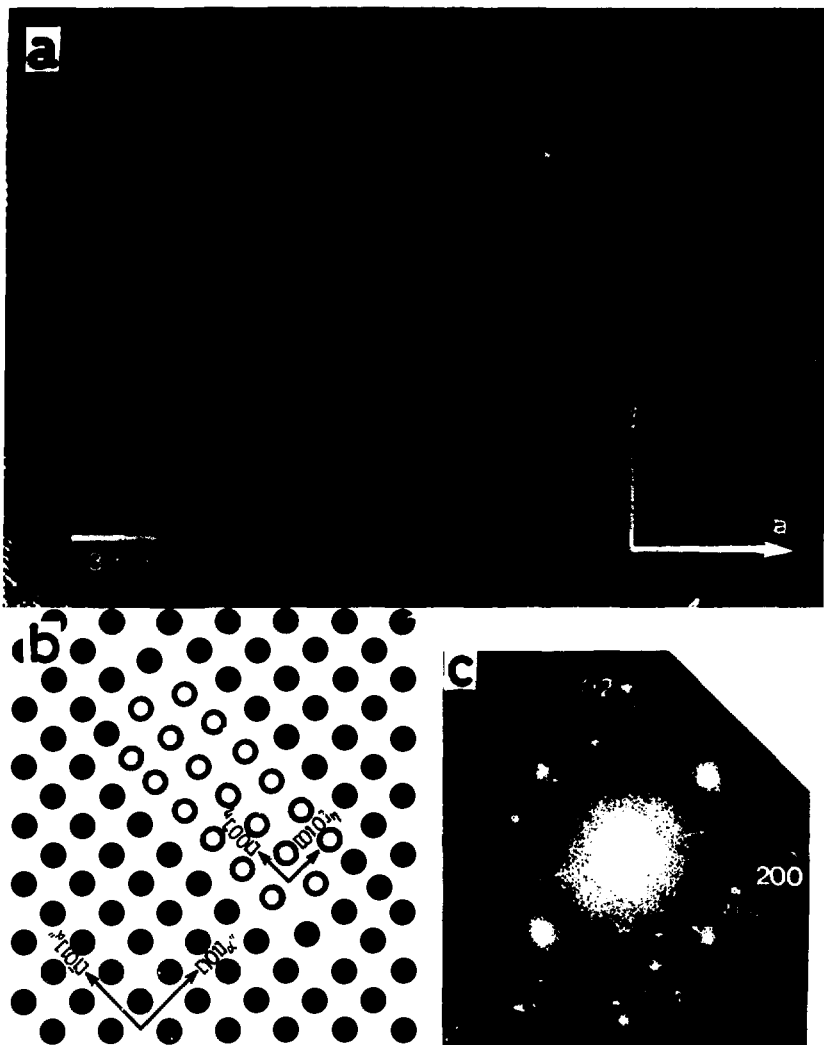


Fig. 5. (a) Structure image of martensite tempered at 420 K. The structure is made of η -Fe₂C and the low carbon martensite α'' . (b) Schematic illustration of the atom arrangements in η -Fe₂C (open circles) and in α'' (solid circles). (c) Optically transformed pattern of (a).

IN-SITU STUDY OF γ' PRECIPITATION IN Fe-N

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ABSTRACT

An in-situ study of γ' -Fe₄N precipitation in nitrogen-ferrite has been performed using a heating stage in a HVEM. The salient features of the reaction are those of bulk-aged material; however, it was found that the free surfaces influence the γ' variant that forms. The quality of the images recorded at temperature show the ability of the experimental technique to provide information regarding the nucleation, growth and dissolution processes during phase transformations.

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1. INTRODUCTION

HVEM has been shown to be a powerful tool for in-situ precipitation studies in many age-hardening alloys [1]. In one such system, nitrogen-ferrite, it has been suggested that the precipitation reaction in the thick regions ($> 0.3\mu\text{m}$) of thin foil specimens is typical of that found in bulk-aged material [2,3]. For this reason nitrogen-ferrite was used to assess the capability of the Berkeley 1.5MeV HVEM to follow dynamically entire precipitation reactions. The nucleation, growth and dissolution behaviour of individual γ' -Fe₄N precipitates was observed directly at the aging temperature and the results obtained are in good agreement with bulk-aging behaviour. Indeed the fine structural information recorded at temperature suggests that the potential exists to study in extreme detail the mechanism of γ' nucleation and the manner in which the system accommodates the large strains produced during the transformation.

2. EXPERIMENTAL

Supersaturated nitrogen-ferrite (0.08wt%N) was prepared by homogenizing zone-refined iron foils (0.1mm thick) in a 10.5NH₃:89.5H₂ gas mixture at 590°C followed by quenching into iced brine. Thin foil specimens were made using the window technique by electropolishing in a 68 vol% acetic acid: 16 vol% perchloric acid: 16 vol% butoxy-ethanol electrolyte at 0-5°C using 20 volts and a current density of 0.1 amp cm⁻². Aging of bulk material was performed in a vacuum furnace (< 1.0 cPa) whereas in-situ aging of thin foil specimens was achieved by using the double tilt heating stage (1°C sec⁻¹) of the Berkeley 1.5MeV Kratos HVEM operating at 500kV to avoid radiation effects [3].

3. RESULTS

3.1. General Features of γ' Precipitation

Generally morphological aspects of large semi-coherent precipitates ($> 1\mu\text{m}$) are studied using optical metallography or extraction replication techniques because of the extreme difficulty in retaining the particles in thin foil specimens. Metallographic observations on nitrogen-ferrite bulk-aged at $> 200^\circ\text{C}$ have shown that formation of the equilibrium precipitate $\gamma'\text{-Fe}_4\text{N}$ occurs both in the matrix and grain boundaries at the expense of the metastable $\alpha''\text{-Fe}_{16}\text{N}_2$ phase which dissolves until none of the latter remains [4,5]. By utilizing the HVEM in-situ heating capability, both of these precipitation events have been observed as shown in Figs. 1 and 2. Figure 1 shows extensive grain boundary γ' precipitation after in-situ aging Fe-0.08wt%N at 350°C ; however, some matrix precipitation has also occurred in agreement with bulk-aging behaviour. Another interesting feature of this micrograph is the way in which the grain boundary allotriomorphs spread into the matrix. An example is shown by the two arrowed precipitates in Fig. 1; their mutual orientation reflects the presence of the low angle boundary which separates the two (001) grains. This slight misorientation of the grain boundary is shown by the traces produced by oxidation of the dissolved oriented α'' precipitates. Figure 2 shows a typical micrograph of matrix γ' precipitation recorded at temperature (300°C) after in-situ aging. The characteristic 'V'-shaped platelet morphology associated with γ' and the detailed interfacial dislocation structure is clearly illustrated as are the dislocations generated in the matrix during the growth process. During cooling these latter dislocations are utilized for the



Fig. 1. Typical grain boundary γ' allotriomorphs observed at room temperature after aging 5 min. at 350°C .



Fig. 2. Matrix precipitation of γ' observed at temperature after aging 5 min. at 300°C .

heterogeneous precipitation of $\alpha''\text{-Fe}_{16}\text{N}_2$ as shown in Fig. 3. In between the $\gamma'\text{-Fe}_4\text{N}$ particles which have associated denuded zones due to the localized transfer of nitrogen from dissolving α'' particles, is a sigmoidal dispersion of α'' precipitates. The larger particles are produced by preferential heterogeneous nucleation and growth of α'' on matrix dislocations during the initial cooling, whereas the smaller particles are a result of homogeneous nucleation during further undercooling [3].

3.2. The $\alpha''\text{-}\gamma'$ transformation. The rate of $\alpha''\text{-Fe}_{16}\text{N}_2$ formation is dependent upon the initial nitrogen supersaturation and aging temperature [6] and its growth is controlled by the diffusion of nitrogen in ferrite [7,8] as is the coarsening of Fe_4N [9]. The intermediate precipitate b.c. tetragonal $\alpha''\text{-Fe}_{16}\text{N}_2$ forms on {001} matrix planes as discs thin in the c direction. The α'' structure consists of eight (2x2x2) body-centered-cubic ferrite unit cells distorted by ordered nitrogen atoms occupying two of the sixteen octahedral interstices whose tetrad axes are parallel with one of the cube directions, i.e. the c -edge. The equilibrium $\gamma'\text{-Fe}_4\text{N}$ precipitate has a f.c.c. arrangement of metal atoms with a single nitrogen atom occupying an ordered position in the central octahedral interstice. Fe_4N has the orientation relationship with the parent ferrite, $(112)_\gamma \parallel (210)_\alpha$; $[110]_\gamma \parallel [001]_\alpha$ [4], and the α'' structure can be considered as a distorted γ' lattice with alternate nitrogen atoms missing and which fits with the ferrite matrix in a Baker-Nutting orientation relationship, i.e. $(001)_\alpha \parallel (001)_{\text{Fe}_4\text{N}_{0.5}}$; $[110]_\alpha \parallel [100]_{\text{Fe}_4\text{N}_{0.5}}$, [0]. It seems likely, therefore, that $\gamma'\text{-Fe}_4\text{N}$ can be

nucleated from α'' by nitrogen enrichment and some evidence exists to suggest that this reaction indeed occurs [2]. In the present work this hypothesis was tested by



Fig. 3. Micrograph showing γ' particles formed by aging 3 min. at 300°C and fine scale α'' precipitation produced on cooling.

heating at 285°C an Fe-0.08 wt%N thin foil which initially contained oriented $\alpha''\text{-Fe}_{16}\text{N}_2$ precipitates. It is clearly seen in Fig. 4 that after 4 min. at temperature a 'V'-shaped γ' particle has nucleated at a shrinking α'' precipitate. The γ' particle once formed, readily grows with a complex double-'V' morphology as the surrounding α'' precipitates dissolve. The particle marked A is the broad face of a γ' platelet growing from an adjacent region. This observation of γ' nucleation at α'' particles was found in other similar in-situ experiments and supports the aforementioned mechanism by which Fe_{16}N_2 transforms to Fe_4N . However, it must be pointed out that nucleation of γ' precipitates in the matrix was initiated not only at dissolving α'' particles but also at other sites. At this aging temperature (285°C) the nitrogen solubility in solution due to the dissolving Fe_{16}N_2 is considerable and is of the order of $\sim 0.04\text{wt}\%$ [5] and therefore, it is not totally unexpected that Fe_4N

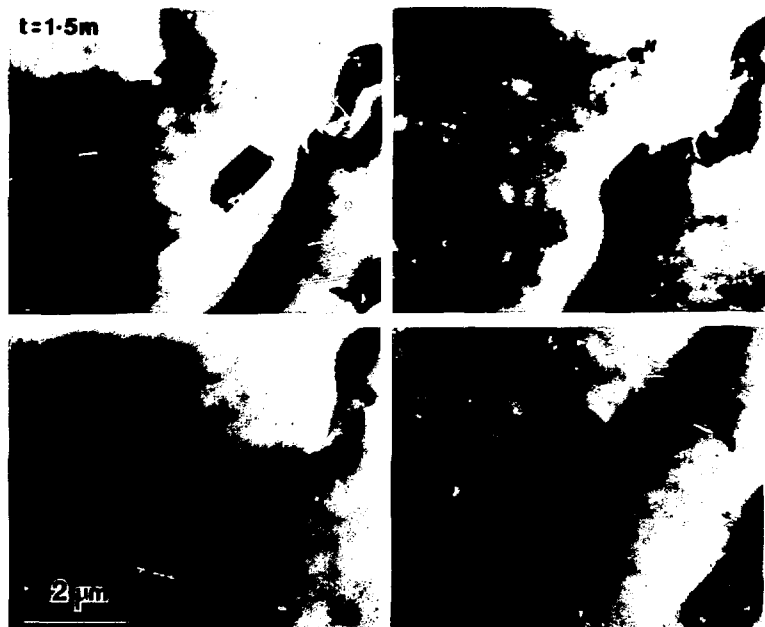


Fig. 4. Dynamic growth sequence at 285°C showing γ' nucleation at a dissolving α'' precipitate. Beam direction near to $[001]$.

nucleation would also occur on lattice defects. In the same way that γ' precipitation occurs at α'' , on cooling from the aging temperature the roles are reversed. An example of this is shown in the insert of Fig. 3 where an α'' precipitate has formed at the end of a γ' particle and grown into the matrix.

3.3. Strain Accommodation During γ' Precipitation. One of the aims of the present investigation was to address the problem of how the strain associated with the γ' transformation is accommodated. It has been postulated that a precipitate and matrix tend to be related by an invariant line strain [11] and this approach has been successful in interpreting the precipitation of semi-coherent platelets of Mo_2C in molybdenum [12]. A study on Fe_4N particles extracted from bulk-aged material has shown that the interface of individual single crystal platelets are characterized by a fine structure comprised of two sets of parallel straight lines [13]. Figure 5 shows that this fine structure is also a feature of γ' particles which form during in-situ aging. Similar fine structural lines observed on Mo_2C platelets in molybdenum [12] lie along the invariant line direction and are interfacial dislocations produced by shear between precipitate and matrix. A complete analysis of the crystallography of the present precipitation reaction requires the beam direction to be parallel to the invariant line direction which is predicted to be $\langle 112 \rangle_{\alpha'}$, [11], the same direction as that

experimentally observed for the fine structural lines on γ' platelets [13]. However, in the present study this analysis was hindered because it appeared that variants of γ' formed during in-situ aging were influenced by the free surface during nucleation, i.e. the preferred invariant line directions are ones making small angles to the foil surface. This is consistent with the hypothesis since it maximizes strain relief normal to the invariant line. Figure 3 shows formation of 'V'-shaped platelets mirrored about the $(\bar{1}10)_{\alpha}$ plane. These symmetrical 'V'-shaped groupings arise because the overall strain energy is reduced further by growing in pairs as shown in the γ' growth sequence of Fig. 4. In order to circumvent the difficulty of obtaining the invariant line direction parallel to the beam direction, work is in progress using initially bulk-aged material.

Figures 6a, b, and c emphasize the



Fig. 5. Fine interfacial line structure observed on γ' platelets after in-situ formation at 300°C.



Fig. 6. In-situ aging sequence showing γ' growth and dissolution: (a) immediately after reaching 290°C; (b) 5 min. at 290°C; (c) as (b) then heated to 350°C.

clarity of images recorded at temperature during an in-situ experiment. Both the strain-relieving dislocations formed in the interface and their counterparts in the matrix are clearly resolvable during γ' growth and dissolution. Figure 6a shows γ' platelets nucleating at the expense of shrinking α'' particles whereas Figs. 6b and c show γ' growth and dissolution stages respectively.

4. CONCLUSION

The present work has further demonstrated the potential for studying precipitation reactions in-situ in the HVEM. The high quality images recorded at temperature offer the exciting opportunity to follow nucleation and growth processes. All aspects of bulk aging behaviour are recognized during in-situ Fe_4N precipitation in nitrogen-ferrite and evidence has been obtained which has allowed the elucidation of the nucleation mechanism and the morphological character of γ' precipitates. However, in the thin-foil studies, a complete crystallographic analysis of the transformation using the invariant line strain concept has been hindered because the free surfaces dominate in determining the variants of γ' which form.

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A CRYSTALLINE-AMORPHOUS TRANSITION IN NiTi ALLOYS INDUCED BY HIGH-ENERGY ELECTRON IRRADIATION

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ABSTRACT

A crystalline-amorphous transition in NiTi alloys induced by electron irradiation has been studied by high voltage electron microscopy. The transition takes place in the following; A number of small amorphous regions are formed in the crystalline matrix at the beginning stages of irradiation, and then they grow in size until coalesce with each other into one body. The amorphous transition preferentially occurs along such defects as dislocations and grain boundaries in general. This is closely related to the high sink efficiency of these defects for interstitials induced by irradiation.

Crystalline-amorphous transition has also been investigated in various intermetallic compounds.

INTRODUCTION

Recently, it was found that a crystalline-amorphous (C-A) transformation could be induced by in-situ electron irradiation with HVEM in such intermetallic compounds as Fe₃B [1] and NiTi [2,3,4]. The finding is of interest not only from the view point that the electron irradiation provides a new technique of producing amorphous metals but also from the scientific standpoint to obtain a general view on the amorphization process in solids induced by particle irradiation. The present work is concerned with the detailed process of electron-irradiation induced amorphization in NiTi which shows an excellent shape memory and in various intermetallic compounds such as Zr₂Al, Fe₂Ti and others.

SPECIMENS AND EXPERIMENTAL PROCEDURES

Rods of nearly equiatomic NiTi alloys, kindly supplied by Furukawa Electric Co., Ltd., Tokyo, were hot- and cold-rolled to sheets of 0.3 mm thick. The sheets were annealed at 1173 K for 1200 s in a vacuum of 6×10^{-4} Pa and then water quenched. Foil specimens for HVEM were electrolytically prepared from these sheets using combination of jet and plate-cathode methods with a solution kept at 213 K. The electron irradiation was carried out with a Hitachi HU-3000 type 3 MV electron microscope operated at 2 MV. Irradiation temperature was varied from 150 to 230 K. A 125 kV electron microscope of Hitachi HU-12A type was also used in an attempt to avoid additional damages during the observation.

RESULTS

C-A Transition in NiTi

Figure 1 is an example showing the overall sequence of the electron irradiation induced transformations in a NiTi alloy. The arrow on each micrograph indicates a fixed position. In Fig.1, martensite structure, (a), changes to the parent phase of B2, (b), by the reverse transformation at the very beginning stage of irradiation. This can be explained in terms of the Ms temperature suppression induced by the introduction of a high density of point defects. The Ms temperature suppression is completely removed by the annealing of the specimens at 453 K for 900 s [5]. With continued irradiation, all the diffraction contrasts in the parent phase fade away and the corresponding S.A.E.D. pattern changes from a spot to a halo pattern, (c), showing that the parent phase undergoes a C-A transition by the electron irradiation.

Successive stages of this C-A transition are shown in Fig.2. Figure 2(a) shows an area of the parent phase just transformed from the martensite by pre-irradiation, in which a 002 bend contour is observed. The same areas after 10 s, 20 s, 110 s, 140 s and 180 s irradiation at a dose rate of 4×10^{23} e/m².s are shown in Figs.2(b) to (f), respectively, with corresponding S.A.E.D. patterns. With increasing total dose of electrons, the contrast of the bend contour becomes gradually vermiculated ((c) to (e)), and finally interrupted at the central part (†) of the irradiated area, (f). Figure 3, which is an enlargement of the framed part in Fig.2(f), clearly shows that the interruption is caused by the coalescence of small, isolated amorphous regions which appear gray in the micrograph. In the corresponding S.A.E.D. patterns, diffuse halo rings are formed around individual diffraction spots at the early stages of irradiation ((c'), (d')). With further irradiation, however, the halos successively disappear together with the corresponding diffraction spots in such a manner that the higher is the spot index, the faster is the rate of fading, as shown in Fig.2(e'). As a result of this, the halo rings appear only around the central spot in the final state (Fig.2(f')). These results indicate that the amorphization takes place in such a process that first a number of nuclei of amorphous phase are formed in the crystalline matrix at the initial stages of irradiation and then they grow in size until coalesce with each other into one body under irradiation.

The nucleation sites of the amorphous regions were examined by dark-field (DF) microscopy: DF images of the microstructures produced by irradiation were taken with a 125 kV EM by setting aperture on a part of a halo ring, and in a thin part of the specimen where the dislocation density is low enough to permit the image analysis. Figure 4 shows an example of the results, in which (a) and (b) are the bright-field (BF) and DF images of the same areas, respectively. It is evident from the micrographs that all the dislocations show extremely broad contrast, which appear dark and bright in BF and DF images respectively, indicating that the broad contrast is responsible for the halo ring. Namely, the contrast is related to the amorphous regions nucleated along dislocations. Stereomicroscopy has revealed that the amorphous regions take the shape of thin cylinders and are distributed in the crystalline matrix along the pre-existing dislocation lines[4]. This is the first time such a preferential C-A transition at dislocations has been observed in metal crystals.

Successive stages of the amorphous transition at dislocations are effectively studied in crystals with low dislocation densities, as shown in Fig.5. A Ni-49,5at%Ti alloy was chosen as the vehicle for the study because the alloy has a low Ms temperature so that it can be cooled down to the irradiation temperatures without introducing dislocations by martensitic transformation. Figure 5(a) shows a B2 area containing two dislocations with a[100] Burgers vector before irradiation. The same area was irradiated for 638 s, 1020 s and 1243 s, respectively, at 265 K with a dose rate of 7.6×10^{23} e/m².s, as shown

in Figs.5(b),(c) and (d). At the beginning stages of irradiation, the dislocations become slightly helical, as seen in Fig.5(b). With continued irradiation, cylinders of amorphous phase are formed along individual dislocations irrespective of the depth of the dislocations from the foil surface,(c), and then the cylinders make lateral growth as shown in (d). In this case, the diameter of the cylinders reaches about 40 nm.

It is ascertained that grain boundaries, which can be regarded as a slab of dislocation core, also act as a preferential site for the C-A transition, as shown in Fig.6. Figures 6(a) and (b) show an area containing a small-angle boundary and the same area after irradiation for 1310 s with a dose rate of $7.6 \times 10^{23} \text{ e/m}^2 \cdot \text{s}$ at 266 K, respectively, in the same specimen examined in Fig.5. In Fig.6, a Moiré pattern, associated with the sub-boundary, appears on a broad band. Comparison of Fig.6(a) with (b) reveals that the width of the band is decreased from 0.26 to 0.20 μm by the irradiation, and a pair of fringe-free zones, whose width is comparable with the diameter of the amorphous column along dislocations (white-arrowed), are formed at the same time along the surface trace of the sub-boundary, as indicated by black arrows in Fig.6(b). These facts show that a plate-shaped amorphous region, having a comparable thickness with the amorphous region along dislocations, has been formed along the sub-boundary, as schematically illustrated in Fig.6(c). This observation suggests that the preferred amorphous transition at these defects results from the high sink efficiency of dislocations and grain boundaries. This suggestion is substantiated by an experimental result that no C-A transition is observed at temperatures above 290 K, but screw dislocations become helical by absorbing interstitials and edge ones make a climb motion.

Based upon these results, the preferred C-A transition at dislocations is considered to occur as follows. A cylinder of a depleted zone, consisting of a region enriched in vacancies, is produced along the dislocation core due to the preferential annihilation of more mobile interstitials. The cylindrical region eventually transforms to an amorphous phase when the vacancy concentration exceeds a critical value. The interface between the crystalline matrix and the cylindrical amorphous phase can serve as a sink for interstitials, so that the amorphous regions can make a lateral growth by repetition of the same mechanism. Studies to evaluate the critical value of the vacancy concentration are in progress in this research center.

Thermal Stability of Amorphous NiTi Produced by Electron Irradiation

By step annealing experiments, it is revealed that the amorphous $\text{Ni}_{0.5}\text{Ti}_{0.5}$ produced by electron irradiation crystallizes at about 630 K. The crystallization temperature is fairly low compared with that of $\text{Ni}_{0.35}\text{Ti}_{0.65}$ amorphous alloy prepared by liquid-phase quenching, i.e., 760 K[6]. This is consistent with the reported inability to produce an amorphous $\text{Ni}_{0.5}\text{Ti}_{0.5}$ by conventional liquid-phase quenching.

C-A Transition in Other Intermetallic Compounds

The present study on NiTi, as well as the work on Fe_3B [1], raises a question whether a similar C-A transition can be produced in other intermetallic compounds or not. So, in this work, a series of intermetallic compounds with different physical properties, i.e., Fe_2Ti , FeTi , Zr_3Al , Zr_2Al , Ni_3Al , NiAl , CuZn and Nb_3Sn , were prepared and all irradiated with 2 MeV electrons at various temperatures, in an attempt to answer the question. The dose rate of electrons was fixed around $(6 \sim 9) \times 10^{23} \text{ e/m}^2 \cdot \text{s}$ throughout the experiment.

The results obtained are summarized in Table 1, where the symbol 0 denotes the occurrence of a C-A transition within 1 ks while the symbol X shows the absence of the transition. Here, a complete change in the S.A.E.D. pattern

Table 1 C-A Transition in Various Intermetallic Compounds

Materials	Irradiation Temperature (K)							
	0	100	100	200	200	300	300	300
NiTi		0	0	0	0	0	0	X
Fe ₂ Ti				0	0	0	0	X
Zr ₂ Al				0	0	X	X	X
FeTi				X	X			X
Zr ₃ Al				X	X			X
CuZn		X		X				X
Nb ₃ Sn				X				X
Ni ₃ Al				X	X			X
NiAl		X	X		X	X		X

(see text for notations)

from a spot to a halo pattern was used as a criterion for the C-A transition. It is found that of the 8 intermetallics investigated Fe₂Ti and Zr₂Al can undergo a similar C-A transition at low temperatures. It is interesting to note that the intermetallic compounds which undergo a C-A transition by electron irradiation (i.e., NiTi, Zr₂Al) are easily rendered amorphous by high-energy ion irradiation while those which remain crystalline by electron irradiation (i.e., Ni₃Al, NiAl) show a stout resistance to the amorphization by ion irradiation[7]. This suggests that the tendency toward amorphization by electron irradiation may also be predicted by a simple rule that the compounds with no or limited solubility in the phase diagram have a strong tendency of amorphous transition while those showing extensive solubility have a weak one, which well explain the C-A transition in intermetallic compounds induced by ion irradiation[7]. However, the present result shows that (1) Zr₂Al can be rendered fully amorphous while Zr₃Al remains crystalline although both are line compounds in the same alloy system, and that (2) Fe₂Ti becomes completely amorphous while FeTi remains crystalline although the former has a wider solubility range (i.e., ~7 wt%) than the latter (i.e., ~2 wt%)[8]. The presence of these exceptions to the rule indicates that understanding of such fundamental parameters as defect concentrations and formation energies of individual defects is required to predict the ease of amorphous formation in intermetallic compounds induced by electron irradiation.

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Fig.1 Overall sequence of the electron irradiation induced transformations in NiTi. $T=158\text{ K}$, $\phi=5 \times 10^{23}\text{ e/m}^2 \cdot \text{s}$. (a) before irradiation, (b) after 30 s irradiation, (c) 120 s.

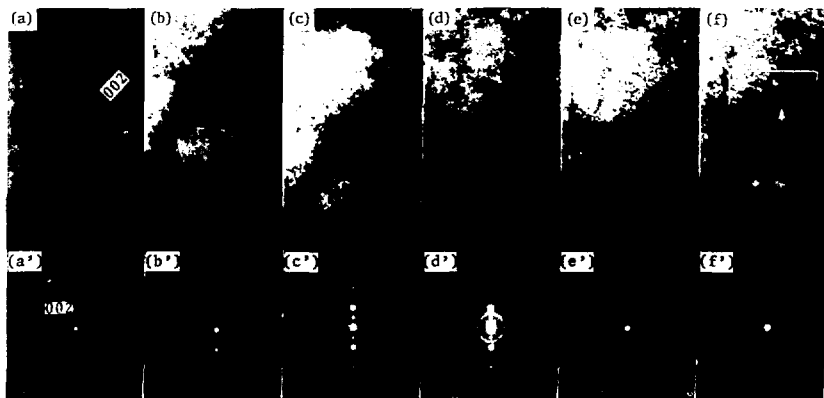


Fig.2 Successive stages of the amorphization of NiTi by electron irradiation. $T=230\text{ K}$, $\phi=4 \times 10^{23}\text{ e/m}^2 \cdot \text{s}$. (a) just transformed from monoclinic martensite to B2 parent phase by pre-irradiation for 10 s, (b) after additional 10 s irradiation, (c) 20 s, (d) 110 s, (e) 140 s, and (f) 180 s.



Fig.3 An enlargement of the framed part in Fig 2(f).

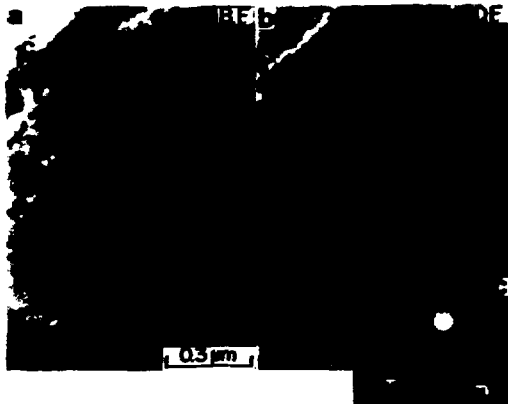


Fig.4 Preferential amorphization at dislocations in NiTi. (a) BF, and (b) DF images of the same area. Irradiation time was 3.0 ks. $T=190\text{ K}$, $\phi=4 \times 10^{23}\text{ e/m}^2\cdot\text{s}$. (c) shows the position of aperture.

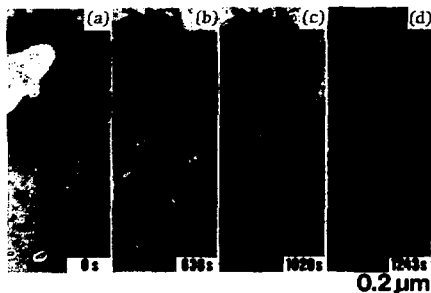


Fig.5 Successive stages of the C-A transition at dislocations in NiTi. $T=265\text{ K}$, $\phi=7.6 \times 10^{23}\text{ e/m}^2\cdot\text{s}$. (a) before irradiation, (b) 638 s, (c) 1020 s, (d) 1243 s

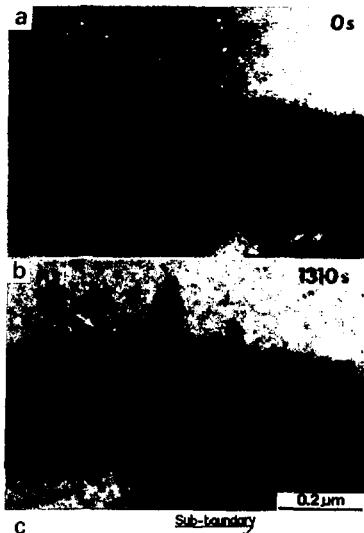
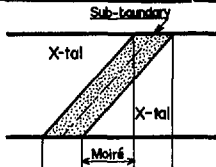


Fig.6 Preferred amorphous transition at a grain boundary. $T=266\text{ K}$, $\phi=7.6 \times 10^{23}\text{ e/m}^2\cdot\text{s}$. (a) before irradiation, (b) after irradiation for 1310 s, (c) schematic illustration of an amorphous region along the grain boundary.



COMPARISON OF THE EFFECT OF ELECTRON AND ION IRRADIATION ON CRYSTALLIZATION OF AMORPHOUS ALLOYS

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ABSTRACT

Electron irradiation during annealing in the HVEM, as well as heavy ion irradiation, lowered the crystallization temperature (T_c) of two amorphous alloys, but only heavy ion irradiation changed the mode of crystallization when compared to thermal annealing behavior. Heavy ion irradiation was more effective in lowering T_c than electron irradiation. The mode of crystallization during heavy ion irradiation was also different from either electron irradiation or thermal annealing in that ion irradiation produced an ultra fine grain, equilibrium phase directly from the amorphous matrix. The acceleration of crystallization was attributed to a radiation enhanced diffusion mechanism in the amorphous phase. The difference in crystallization mode was attributed to nucleation of the crystal phase in the displacement cascade region during heavy ion irradiation. During electron radiation, the absence of cascades precludes nucleation of the equilibrium phase.

INTRODUCTION

Concurrent irradiation during annealing can have a pronounced effect on the crystallization behavior of an amorphous alloy [1]. Previous studies of metal-metalloid amorphous alloys have shown that electron irradiation generally lowers T_c although there are some inconsistencies [2,3]. Electron irradiation can produce quite different effects than other types of irradiation because the atom displacement process is much more uniform and homogeneous than from heavy ions. The purpose of this research was to study the crystallization behavior of amorphous metal alloys during electron or ion irradiation to (a) confirm that irradiation does tend to accelerate the crystallization reaction and (b) determine how the mode of crystallization varies with the type of irradiation.

Specifically, amorphous iron based-tungsten and molybdenum-nickel alloys have been irradiated at elevated temperatures with 1.2-1.5 MeV electrons and the microstructures compared with those induced by irradiation with 5 MeV Ni^{++} ions. The results from both types of irradiation are compared with thermal annealing results.

EXPERIMENTAL PROCEDURE

Amorphous alloys of $Fe_{62}Cr_{16}Ni_8W_{14}$ and $Mo_{50}Ni_{50}$ were prepared by high rate sputter deposition. The former alloy was made from type 304 stainless steel with 14% tungsten added. Thinned foils of the alloys were electron irradiated with either 1.2 or 1.5 MeV electrons in the

HEM at Lawrence Berkeley Laboratory. Displacement cross sections varied between 28 and 35 barns for the NiMo alloy and 40-48 barns for the iron-tungsten alloy for this electron energy range. The current density was $\sim 1 \times 10^{20} \text{ e}^-/\text{cm}^2$ for the 1.2 MeV irradiation and $\sim 6 \times 10^{19} \text{ e}^-/\text{cm}^2$ for the 1.5 MeV irradiation. This produced displacement rates of $2.1 \times 10^{-3} \text{ dpa/sec}$ and $2.8 \times 10^{-3} \text{ dpa/sec}$ for the nickel-molybdenum and iron-tungsten alloys, respectively. The specimens were irradiated at elevated temperatures in a hot stage monitored with a thermocouple. Specimens were heated to a temperature considerably below T_c and irradiated for ~ 15 minutes. The temperature was then increased in 20-50 K intervals and held for 15-20 minutes at each temperature until significant crystallization occurred.

Similar amorphous alloys were bombarded with 5 MeV Ni^{++} ions at a displacement rate of $\sim 3 \times 10^{-3} \text{ dpa/sec}$ in the PNL tandem accelerator. The damage zone was analyzed in a Philips EM400 using standard techniques to extract a thin foil. Specimens were irradiated at several temperatures over a range of ion doses. Unirradiated thermal control material was annealed in a high vacuum furnace.

RESULTS

In both amorphous alloys, electron irradiation accelerated the thermal crystallization kinetics, but did not affect the mode of crystallization. Ion irradiation affected both kinetics and mode.

Amorphous $\text{Fe}_{16}\text{Cr}_{16}\text{Ni}_8\text{W}_{14}$

Crystallization began in the electron irradiated region of the amorphous alloy at dose levels greater than 3.6 dpa and a temperature of 480°C , fig. 1a. The dotted line outlines approximately the irradiated region. No evidence of crystallization was found outside the irradiated region at this irradiation temperature. Continued irradiation at 480°C produced more crystals but a saturation was reached after about 40 minutes (9 dpa). Increasing the temperature to 540°C produced crystals beyond the edge of the irradiated zone, fig. 1b. Further irradiation up to 20 minutes (5 dpa) at 540°C resulted in extensive crystallization throughout the foil. This compares with several hours at 550°C to reach similar stages of crystallization during thermal annealing in bulk material. Electron irradiation lowered T_c , but even in unirradiated regions of the thin foils, T_c was lower than that observed in bulk material. An example of the microstructure after annealing this alloy in bulk form is shown in fig. 2.

The crystals formed during irradiation were identified as the bcc, α -iron solid solution with a lattice parameter of 0.287nm. No other crystal phases were identified except an Fe_3O_4 phase in foils that had been irradiated to 600°C . The crystals found in the unirradiated region were the same and were also the same as that identified in material annealed in bulk form. A primary difference between the irradiation and thermal transformation was the formation of a χ phase in the remaining amorphous matrix during annealing of bulk material at temperatures

> 600°C. Oxidation at the higher temperature probably precluded the formation of this χ phase in the HVEM foils.

During heavy ion irradiation, an extremely fine grained χ phase crystallized directly from the amorphous matrix with no indication of a bcc phase, fig. 3 [1]. This was completely different from that found during electron irradiation as well as thermal annealing. In addition, T_c was even lower during ion irradiation than electron irradiation as shown by the appearance of the χ phase at temperatures as low as 400°C and doses less than 1 dpa. The smallest χ phase grains were at the resolution limit of the electron microscope but the size increased with dose up to a maximum size of 30-40 nm.

Amorphous Ni₅₀Mo₅₀

Crystallization of amorphous MoNi occurred at 650°C in the electron irradiated region after a dose of ~ 3 dpa, fig. 4a. Doses up to 10 dpa were required at 600°C before electron induced crystallization was observed. Unirradiated regions of the foil showed no crystallization at these times and temperatures. The crystals initially formed in the thinnest region of the irradiated foil. At 650°C, the crystallization eventually spread outside the irradiated region but only to the thinner areas fig. 4b. This is further evidence that surface nucleation of the crystals is also significant in the crystallization behavior of these amorphous thin foils. In bulk material, crystallization requires many hours at 700°C.[4]

Comparisons of the mode of crystallization were only partially successful due to apparent contamination from the HVEM environment. In a foil irradiated at 600°C, the crystals were a mixture of α -Ni (nickel-molybdenum solid solution) and a phase tentatively identified as Mo₂C. In another foil, irradiated up to 650°C, a phase tentatively identified as Ni₃Mo₃ (C,0) was also observed. This phase has the crystal structure of the eta phase. This phase was only observed in the thicker regions of the foil as shown by the large grains in fig. 4b. The smaller grains were composed of the mixture of α -Ni and Mo₂C.

The crystallization during thermal annealing of the bulk material was complex. At 700°C, a mixture of pure Mo and MoNi₃ formed whereas at 800°C, there was a mixture of Mo and α -Ni crystals.[4] An example of these mixed phases is shown in fig. 5. After long times or high temperatures, these duplex structures transformed to the equilibrium δ phase. The electron irradiated microstructure was similar to the bulk material annealed at 800°C except that there was Mo₂C in the thin foils rather than pure molybdenum as in the bulk material. Temperatures near 800°C were not used in the HVEM to determine if δ phase eventually formed because of contamination problems.

Ion irradiation caused an even lower T_c and a completely different mode of crystallization compared to electron irradiation. Crystallization began at temperatures as low as 550°C and at doses less than 1 dpa during ion irradiation. An extremely fine grained δ phase formed directly from the amorphous phase, fig. 6. No intermediate phases formed. The mode of crystallization during ion irradiation was, therefore, similar for the two amorphous alloys.

Discussion

Accelerated crystallization caused by electron irradiation or heavyion irradiation can be attributed to radiation enhanced diffusion. Diffusion controlled crystallization kinetics are enhanced by the creation and migration of point defects. Defects analogous to vacancies and interstitials in crystals can be created in the amorphous phase. Annealing stages have been observed in low temperature irradiated amorphous alloys which implies migration and annihilation of point defects [5]. As electrons have only sufficient energy to displace one or two atoms from their sites, a uniform distribution of vacancies - described as excess free volume - is created.

In contrast to the uniform distribution of the defects produced by electron irradiation, heavy ions produce displacement cascades which promote nucleation of the crystal phase. The high defect density and hence atomic mobility within the cascade region allow the complex, equilibrium phases such as δ and χ to form directly from the amorphous structure. Metastable phases form because it is energetically easier to pass through a series of intermediate phases than to nucleate the final equilibrium phases directly from the amorphous matrix. However, the high concentration of displaced atoms or excess free volume can provide sufficient activation to nucleate the equilibrium phases directly. The minimum crystal size of 2-3 nm is comparable to reported displacement cascade dimensions.[6]

Electron irradiation, in which no cascades are formed, does not affect the nature or type of crystallization process. The maximum energy transfer for 1.5 MeV electrons is about 200 ev. This energy would produce only about 4 displacements. The defect distribution is therefore characterized by a uniform distribution of isolated defects. The presence of these isolated defects increases the overall long range atomic mobility but there is not the highly localized defect concentration found in cascades which affects short range mobility and crystal nucleation.

ACKNOWLEDGEMENT

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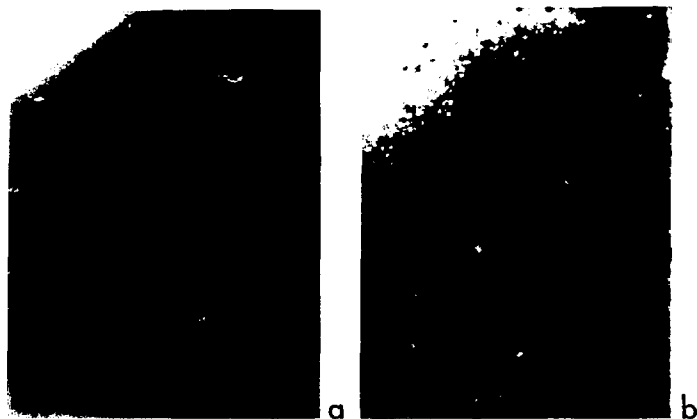


Fig. 1 Amorphous Fe-Cr-Ni-W, irradiated with 1.2 MeV electrons
(a) 480°C to 4 dpa b) 480°C to 9dpa + 540°C to 3 dpa.

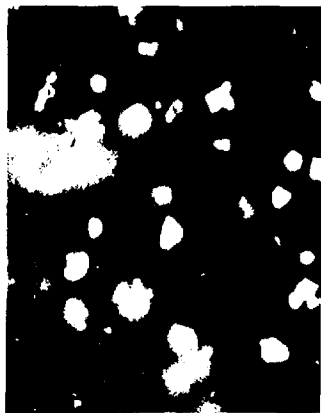
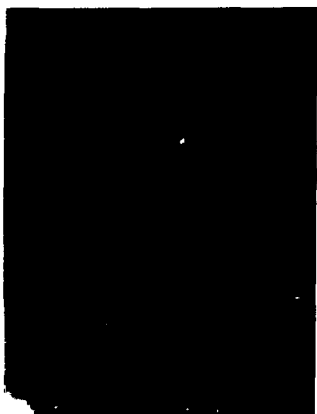


Fig. 2 Amorphous Fe-Cr-Ni-W, annealed 550°C for 24 hours.



Fig. 3 Amorphous Fe-Cr-Ni-W, ion irradiated 400°C to 2 dpa.



a



b

Fig. 4 Amorphous MoNi, irradiated with 1.5 MeV electrons
(a) 650°C to 3 dpa (b) 650°C to 10 dpa



Fig. 5 Amorphous MoNi annealed
700°C for 48 hours

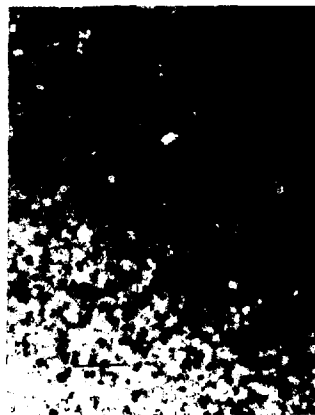


Fig. 6 Amorphous MoNi, ion
irradiated at 600°C to 3 dpa

EFFECTS OF HVEM IRRADIATION ON ORDERED PHASES IN Ni-Ti

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ABSTRACT

Various ordered phases in the Ni-Ti system were subjected to electron irradiation in the Berkeley HVEM. Austenitic NiTi (B2 structure) disorders and turns amorphous with room-temperature irradiations at accelerating potentials between 1 and 1.5 MeV. Total doses for the onset of amorphiticity range between 0.7×10^{22} and 3×10^{22} e.cm⁻² (0.4 to 1.0 dpa). At 90K the dose requirement decreases to 4×10^{20} e.cm⁻² ($\sim 10^{-2}$ dpa). Martensitic NiTi (distorted monoclinic structure) readily detwins and transforms to austenite when irradiated for short times (~ 10 seconds). Vapor-deposited amorphous films were crystallized to produce NiTi, Phase X (ordered nickel-rich phase with unknown structure) and Ni₃Ti (DO₂₄ structure). Upon electron irradiation, NiTi and Phase X disorder and become amorphous, while Ni₃Ti disorders but does not turn amorphous with doses up to 4×10^{22} e.cm⁻² at 90K. These results are discussed in terms of the requirement of a critical concentration of defects and their relative mobilities. Brimhall's solubility criteria for amorphization of ordered alloys by ion bombardment is apparently applicable to electron-induced crystalline to amorphous transitions in this alloy.

The author acknowledges stimulating conversations with Drs. G. Thomas, K. H. Westmacott and R. Sinclair. Raychem Corporation provided some of the alloys. This work was supported by the NSF-MRL Program through the Center for Materials Research at Stanford University.

INTRODUCTION

Electron irradiation in a high voltage electron microscope (HVEM) produces a variety of effects on the structures of materials as discussed in several review papers (e.g. [1]). Recently, there has been increased interest in the influence of electron irradiation on ordered phases. Carpenter and Schulson [2] studied the disordering of Zr₃Al by 1 MeV electrons and observed that the phase became partially amorphous after a dose of a few displacements per atom (dpa). They additionally observed that the dose requirement for the onset of amorphization decreased with decreasing irradiation temperatures. Similar results were obtained by Mogro-Campero, et al. [3] who investigated the crystalline to amorphous (C/A) transformation in Fe₃B by 1 MeV HVEM irradiation. They found that the intermetallic phase became amorphous at 130K with damage levels less than 1 dpa, whereas at room temperature the reaction did

not occur after several dpa. More recently, C/A transitions in NiTi have been studied by Thomas, et al. [4] and by Mori, et al. [5,6], who observed that the transition occurs between 1-2 MeV. Similar to Zr₃Al and Fe₃B, the critical dose for amorphization in NiTi has a steep temperature dependence above ~200K and obtains nearly constant doses below ~100K [6]. The purpose of the present paper is to report on the effects of electron irradiation on the structures of various phases in the Ni-Ti system using the 1.5 MeV HVEM at the National Center for Electron Microscopy in Berkeley.

EXPERIMENTAL

The materials used in this investigation were prepared by two methods. NiTi_{48.5} and NiTi_{49.5} samples were obtained as rolled sheets from Raychem Corporation in Menlo Park, California. These samples were then annealed in vacuum at 900°C and water quenched. After this treatment, the microstructure consisted of 100% austenite (ordered B2 structure) for NiTi_{48.5} (Ms ~100°C) and a mixture of austenite and martensite (distorted monoclinic structure [7]) for NiTi_{49.5} (Ms 30°C). Electron transparent foils were obtained by jet-electropolishing 3mm discs in either a perchloric-acetic solution at room temperature or in a nitric-methanol solution at -55°C. An addition sample was obtained from J. Brimhall in the as-polished condition. Although the precise composition of this sample is unknown, it is estimated to be NiTi₄₇.

Other compositions of Ni-Ti were vapor-deposited as amorphous films and subsequently crystallized to obtain various metastable and equilibrium phases [8]. The results reported here concern NiTi₄₄ which was crystallized at 500°C. TEM samples from NiTi₄₄ were prepared by ion milling at low ion currents to prevent the formation of surface artifact phases.

Specimens were irradiated at several combinations of accelerating potentials (0.6 to 1.5 MeV), beam currents (0.5 to 20 A cm⁻²), temperatures (90 - 300K) and specimen orientations. Typical condensed beam sizes ranged from 1.6 to 4 μm. Images and diffraction patterns were recorded on photographic film or videotape. Damage rates were calculated using damage cross sections (σ_d) from weighted mean values based on effective displacement threshold energy values of 40 eV for nickel and 30 eV for titanium [9]. At 1.5 MeV, σ_d is approximately 27 barns for NiTi; with a typical electron density of 3X10¹⁹ e.cm⁻² sec⁻¹, the damage rate is 2.0dpa .sec⁻¹.

RESULTS

Results from the HVEM irradiations of the various phases in Ni-Ti will be presented in this section. For clarification, irradiation of the austenitic and martensitic phases from the conventionally-prepared material will be initially discussed and followed by the results from the crystallized, vapor-deposited films.

Austenite

The B2 austenite phase from the NiTi₄₇, NiTi_{48.5} and NiTi_{49.5} samples become amorphous when irradiated between 1.0 and 1.5 MeV at room temperature. An example of an irradiation sequence at 1.5 MeV of a NiTi_{49.5} sample is shown in Fig. 1 (courtesy of R. Sinclair and K. H. Westmacott). The extinction contour pattern is from a [351]A zone axis as determined from the selected area diffraction pattern (SADP) in Fig. 1a. Elapsed times (in minutes) are shown in the upper right-hand corner of each micrograph. The onset of amorphiticity, as evidenced by the breakup of the extinction contours, begins after approximately 3.5 minutes, Fig. 1b. This corresponds to an electron dose of $\sim 7 \times 10^{21}$ e.cm⁻² or a damage level of ~ 0.4 dpa. Longer irradiation times produce larger amorphous areas as seen in Fig. 1c. After 16 minutes (~ 2 dpa) the amorphous region is approximately 1 μ m in diameter. The amorphous halo in Fig. 1c. has a d-spacing corresponding to 0.21 ± 0.01 nm.

Several different zone axes from the three compositions of NiTi were irradiated at 1.5 MeV. Presently, however, there is insufficient data to infer any systematic changes in electron dose requirements as a function of composition. The critical dose level for the onset of the C/A transition in these samples ranges from 0.7×10^{22} to 2×10^{22} e.cm⁻² (0.4 to 1.0 dpa). The effects of accelerating potential on the critical dose requirement were additionally investigated. Austenitic grains from the three compositions became amorphous down to 1.0 MeV at levels of approximately 3×10^{22} e.cm⁻² (~ 1.0 dpa). The NiTi phase did not turn amorphous at 0.6 MeV with doses up to 2×10^{23} e.cm⁻².

Martensite

Only the NiTi_{49.5} sample contained martensite at room temperature. Electron irradiation of this structure caused an almost immediate transformation to austenite. Figure 2 shows a transition from (100)_M (Fig. 2a.) to (001)_A (Fig. 2b.) which occurred in less than 10 seconds; this entire sequence, and others, were recorded on videotape. The as-transformed austenite becomes amorphous upon further irradiation as described above.

Vapor-Deposited Films

The vapor-deposited and crystallized NiTi₄₄ films consisted of NiTi matrix grains with Ni₃Ti (ordered hexagonal - DO₂₄ structure) precipitates and a nickel-rich ordered phase of undetermined crystal structure referred to as Phase X [8,10]. Electron-induced order-disorder reactions in Phase X and Ni₃Ti were initially studied. Figure 3a. shows a [111]_A SADP with 1/7 [321] superlattice reflections from Phase X. (The habit plane of Phase X is (111)_A.) After room-temperature irradiations at 1.2 MeV for a total dose of 6×10^{22} e.cm⁻² (1.3 dpa) the superlattice reflections have completely disappeared (Fig. 3b.). Ni₃Ti disorders under similar irradiation conditions.

None of the phases in this material became amorphous with room temperature irradiations. At 90K, however, Phase X and austenite undergo C/A transitions. For example, Fig. 4 shows a region in which Phase X disorders and starts to turn amorphous after ~ 10 seconds ($\sim 4 \times 10^{20} \text{ e.cm}^{-2}$), Fig. 4b. A $\sim 2 \mu\text{m}$ diameter area becomes fully amorphous after 90 seconds, $\sim 4 \times 10^{21} \text{ e.cm}^{-2}$ as seen in Fig. 4c. Ni_3Ti precipitates (arrowed) did not become amorphous under these conditions with doses as high as $4 \times 10^{22} \text{ e.cm}^{-2}$ (0.8dpa). Low temperature irradiations of [001]A austenite grains were recorded on videotape which documented that $\langle 100 \rangle$ A superlattice reflections gradually disappear as the amorphous halos appear around the fundamental reflections.

DISCUSSION

HVEM irradiations cause disordering reactions in all of the NiTi phases considered in this paper. Of these phases, austenite and Phase X subsequently become amorphous, whereas martensite initially transforms to austenite and Ni_3Ti does not turn amorphous with electron doses up to $4 \times 10^{22} \text{ e.cm}^{-2}$. C/A transitions in NiTi also occur by ion-bombardment at dose levels equivalent to $\sim 1.0 \text{ dpa}$ [11-14]. Although the displacement mechanisms for ion and electron irradiation differ (e.g., there are no thermal spikes with electrons) it is likely that these methods produce identical amorphous states based on the atomic spacing measurements. These spacings are similarly obtained from vapor-deposited NiTi amorphous films by X-ray and electron diffraction [15]. Brimhall, et al. [13,14] proposed that irradiation-induced amorphization of intermetallic alloys may be explained in terms of the degree of solubility in the crystalline phase; generally those alloys which become amorphous have low solubilities. These authors further illustrated that their model is consistent with the concept of the requirement of a critical concentration of defects for amorphization. Phases with narrow solubility limits which are strongly ordered, such as the B2 structure of NiTi, can not be disordered by severe quenching from high temperatures. Disordering of these structures by particle bombardment produces a condition in which the free energy of the defected crystalline state exceeds that of the amorphous state [16]. According to the limited-solubility model, the amorphous state consists of randomly misoriented regions possessing short-range order. Long range reordering is prohibited below some temperature due to the low mobilities of the defects.

The results from the present and previous [4-6] irradiation-induced amorphization studies of NiTi are consistent with the model outlined above. The markedly reduced electron dose requirement at low irradiation temperatures suggest that the defects become relatively immobile below $\sim 100\text{K}$, thus allowing accumulation of a critical defect concentration. The C/A transition in NiTi is also consistent with the temperature criteria model proposed by Naquib and Kelly [17]. This model, although originally derived for ion-implanted, non-metallic alloys, states that amorphization occurs if the crystallization temperature (T_c) of the amorphous material is > 0.3 of the melting temperature (T_m). In NiTi, $T_c \sim 750\text{K}$ as determined by DSC [15] and by *in situ* heating [11]; thus, $T_c/T_m \sim 0.48$. The above arguments may also be applicable to Phase X due to the experimental ease of disordering and amorphization under electron irradiation. That Ni_3Ti does not become amorphous is consistent with the relatively high solubility of titanium in nickel ($\sim 10\%$). Thus, upon disordering, the phase is able to accommodate a large critical concentration of defects which was not exceeded by electron or ion [14] irradiations.

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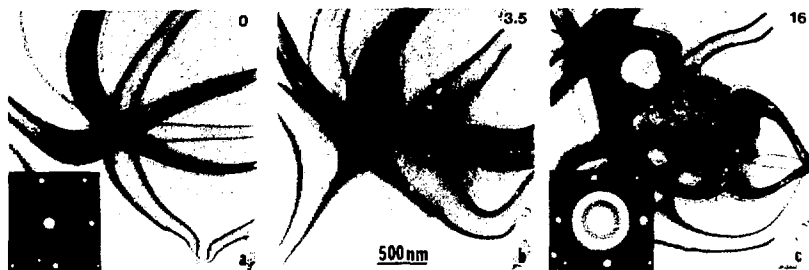


Figure 1: Room temperature amorphization sequence of NiTi_{49.5} at 1.5 MeV with (a) 0dpa, (b) 0.4dpa and (c) 2dpa.



Figure 2: Irradiation-induced transformation from (a) (100) martensite to (b) (001) austenite.

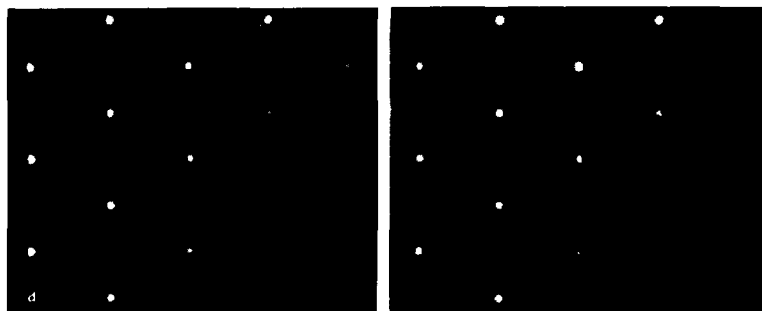


Figure 3: $[111]_A$ SADP's with superlattice reflections from Phase X at 1.2 MeV after (a) 0 dpa, (b) 1.3 dpa.

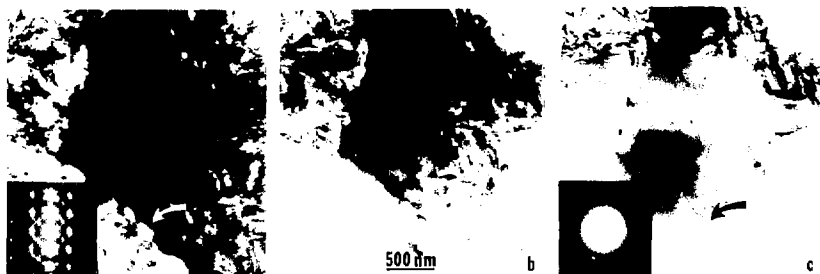


Figure 4: Disordering and amorphization reactions at 1.2 MeV and 90K after (a) 0 dpa, (b) 10^{-2} dpa and (c) 10^{-1} dpa.

ORDER-DISORDER TRANSITION IN Ni_4Mo
INDUCED BY ELECTRON IRRADIATION IN A HIGH-VOLTAGE MICROSCOPE

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ABSTRACT

A brief report is given on a study on the order-disorder reaction in Ni_4Mo induced by electron irradiation at low temperatures. Analysis of the steady states occurring as a result of the competition of radiation disordering and radiation-enhanced reordering yielded information on the basic transformation behaviour of the alloy. The results corroborate the spinodal ordering model. A kinetic treatment of the order-disorder reaction under irradiation is outlined. It permits to calculate the steady-state degree of long-range order in fair agreement with experimental data.

1. INTRODUCTION

High-energy electron irradiation of ordering alloys may induce disordering by displacement and replacement of crystal atoms as well as ordering by radiation-enhanced diffusion. Under irradiation, the ordering transition can be studied at temperatures where purely thermal treatments cannot induce the transition at a detectable rate. Therefore, information obtained on the radiation-induced ordering transition is not only of interest from the point of view of radiation damage production but it can contribute to a better understanding of the basic transformation behaviour. High-voltage electron microscopy is particularly useful for such studies since it provides high radiation dose rates and allows to record, in situ, the specimen structure by micrographs and electron diffraction patterns.

We have applied this technique to the order-disorder transition in Ni_4Mo . In this brief report we present some results of this study concerning the basic transformation behaviour. In addition we give results of a kinetic treatment of the radiation-induced order-disorder transition. A detailed account of this work will be published elsewhere /1,2/.

2. THE ORDER-DISORDER TRANSITION IN Ni_4Mo

Ni_4Mo has a critical ordering temperature, T_c , of 1140 K. When quenched from the disordered state it exhibits a short-range order (SRO) structure characterized by pronounced maxima at $\{1 \ 1/2 \ 0\}$ positions in the diffraction pattern. These maxima are not coincidental with the $1/5 \ \{4 \ 2 \ 0\}$ superlattice reflections of the long-range order structure (LRO) /3/. The formation of SRO and its nature have been the subject of a large number of partly controversial papers. The discussion yielded as a result two models, the structural microdomain model /4/ and the thermodynamic spinodal ordering model /5/.

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The microdomain model starts from the assumption that at $T > T_c$ the material contains small partially ordered domains. The SRO structure observed after quenching is that of these microdomains which are frozen-in by the fast cooling. In particular, it is assumed that the characteristic SRO reflections originate from Ni_4Mo domains containing a sinusoidal composition fluctuation and non-conservative anti-phase boundaries $/4/$.

In the spinodal ordering model the SRO structure is formed at $T < T_c$ out of the disordered material. At temperatures just below T_c Ni_4Mo develops LRO by a nucleation and growth mechanism. However, if the material is rapidly quenched through this temperature range it can, below a characteristic temperature, develop a spinodal-type instability. This means, it can transform continuously from the disordered to the ordered state. Free-energy considerations indicate that in Ni_4Mo two ordered structures can occur $/5/$. The first, the SRO structure, is energetically favourable for small deviations from the disordered state. For higher degrees of order, however, the energy is lower for the second structure, the LRO structure. It is important that the theory yields for the spinodal temperature of the SRO structure a higher value than for that of the LRO structure. Thus, if the transition to LRO by nucleation and growth (close to T_c) is impeded by quenching, the alloy adopts the SRO structure as soon as its spinodal temperature is reached. During further cooling, LRO can in principle develop after the spinodal temperature of this structure is reached. However, the SRO structure remains frozen-in if at that temperature the atom transport required for the transition has become too slow.

3. EXPERIMENTAL METHODS AND RESULTS

We have irradiated Ni-20at% Mo alloy with 1 MeV electrons at $50K < T < 1050K$ in an AEI electron microscope. The transformation behaviour was studied in situ by means of micrographs and electron diffraction. The starting material was available in as-quenched condition exhibiting SRO and in order-annealed form exhibiting LRO with a domain size of about 2 μm . From the experimental results we are selecting here three items corroborating the spinodal ordering model.

At $200K < T < 450K$ we observed the formation of SRO in initially long-range ordered material (Figure 1). It is important to note, that SRO did only form after LRO was destroyed completely. At this relatively low temperature the re-ordering rate is, due to the low atomic mobility, so small that under irradiation only a very low level of order can be maintained. In agreement with the results of the spinodal ordering model, the alloy then adopts the SRO structure since so close to the disordered state it is the energetically most favourable one. Further support for the spinodal ordering model is that SRO forms at $T < T_c$ and under conditions where LRO is completely unstable. This is difficult to explain in the framework of the structural model which explains SRO by a structure forming at $T > T_c$ and which is derived from the LRO structure by introduction of non-conservative anti-phase boundaries.

At $450K < T < 550K$ we found that long-range ordered as well as short-range ordered material remains virtually unaltered during irradiation (Figure 2). Due to the relatively high temperature, there is now a strong reordering tendency which counteracts irradiation disordering. The driving force for ordering is especially large for that structure which, under the given conditions, is the energetically most favourable one. Thus, in short-range ordered material, i.e. at small deviations from the disordered state, the SRO structure is continuously regenerated. In the long-range ordered material the LRO structure has the

lower energy and is therefore maintained.

At $T > 550$ K long-range order develops from short-range order (Figure 3). Diffraction and micrographs indicate that, at $T < 800$ K, this transition occurs continuously without nucleation. Above this temperature, nuclei form rapidly after starting the irradiation. This allows to fix the spinodal temperature of the LRO structure at about 800 K. In agreement with the expectations of the spinodal ordering model this temperature lies in a range where purely thermal atom transport is negligible.

4. THE KINETICS OF THE RADIATION-INDUCED ORDER-DISORDER REACTION

In /2/ a model is presented which describes the order-disorder reaction under irradiation. It is assumed that radiation-induced disordering is opposed by radiation-enhanced reordering. The ordering process is modeled by a chemical reaction /6/ whose elementary step occurs via vacancy jumps. The vacancy jump rate depends on the degree of long-range order, S , and is given by

$$v_{\pm} = v_0 \exp\{-(E_m \pm 3VS)/kT\} \quad (1)$$

(k -Boltzmann's constant, T -abs. temperature, v_0 -attempt frequency). The lower activation energy holds for a jump in which an atom changes from the wrong to the right sublattice, i.e. for an ordering jump (v_+), while the higher value refers to a disordering jump (v_-). E_m is the migration activation energy in disordered material. The pair energy parameter, V , is derived from T_c by adjusting it in such a way that the ordering rate outside irradiation becomes zero at the critical temperature. The ordering rate is given by

$$dS/dt = -\epsilon PS + k_+ 4(1-S)^2/25 - k_- \{S + 4(1-S)^2/25\} \quad (2)$$

$$k_{\pm} = v_{\pm} 12 C_V^{\alpha} C_V^{\beta} / (C_V^{\alpha} + 4C_V^{\beta}). \quad (3)$$

The number of disordering events per atom displacement, ϵ , depends on the disordering mechanism and is for electron irradiation and not too high vacancy concentrations close to one. P is the defect production rate. In /2/ a set of rate equations is derived which permit to calculate C_V^{α} and C_V^{β} , the vacancy concentrations on the Mo (α) and the Ni (β) sublattice. In general, these concentrations are different and depend on the degree of order.

Numerical results for the steady-state degree of order are given in Figure 4 together with experimental data. Considering the difficulty and appropriate inaccuracy of a determination of S by means of electron diffraction the agreement is good.

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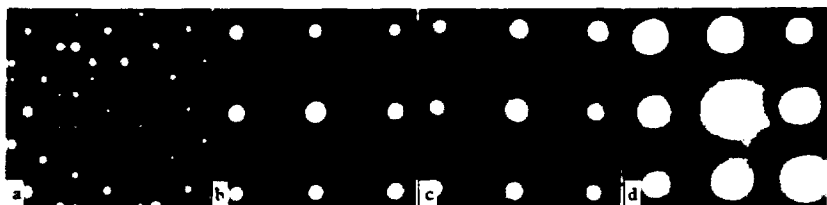


Figure 1: Short-range order develops in initially long-range ordered material during irradiation at 300 K. After: (a) 0 s, (b) 60 s, (c) 120 s, (d) 240 s. $P = 5 \times 10^{-3} \text{ dpa/s}$; zone axis: $[001]$.

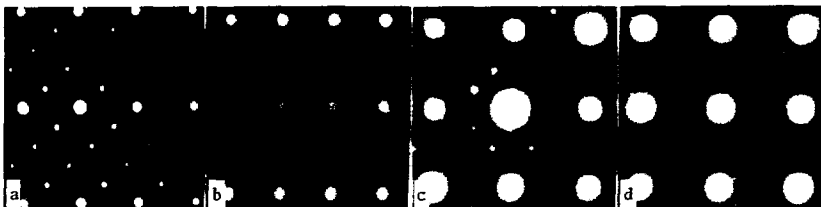


Figure 2: Persistence of LRO (a,b) and of SRO (c,d) during irradiation at 470 K. After: (a) 0 s, (b) 240 s, (c) 0 s, (d) 600 s. $P = 5 \times 10^{-3} \text{ dpa/s}$; zone axis: $[121]$ in (a,b) and $[001]$ in (c,d).

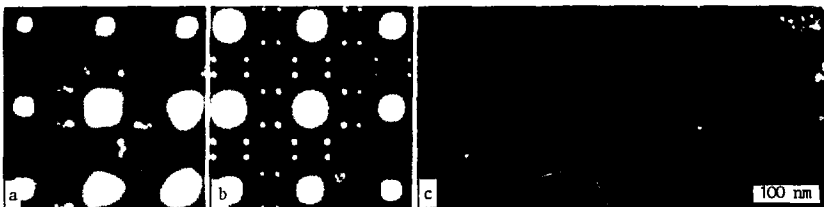


Figure 3: Transition to LRO in initially short-range ordered material. (a) Continuous transition at 750 K; SRO and LRO reflections connected by diffuse intensity after 15 s. (b) Domain nucleation at 820 K indicated by sharp LRO reflections after 5 s, and (c) dark-field picture of LRO domains after 10 s.

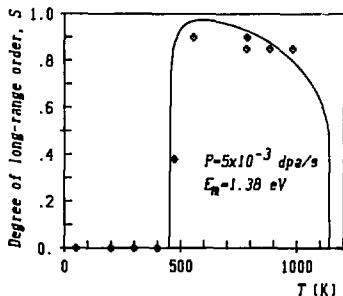


Figure 4: Calculated steady-state degree of long-range order and experimental data (open squares). For E_m the value for pure nickel was used.

IN SITU ION IMPLANTATION OF N^+ IN ALUMINUM

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ABSTRACT

High purity (99.999%) aluminum foils were implanted with N^+ ions at various temperatures in the Argonne National Labs HVEM-TANDEM facility. The evolution of the ion damage was observed as the implantation occurred up to doses of 2×10^{16} ions cm^{-2} (~ 0.1 dpa). Subsequent annealing of implanted specimens in the HVEM at $.89 T_m$ caused the clustering of implanted nitrogen to form nitrogen gas bubbles.

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1. INTRODUCTION

Ion implantation is one method by which the near surface properties of various materials can be improved [1,2,3,4]. This includes increases in hardness, and also increased resistance to wear, corrosion, and fatigue. TEM investigations of various materials after implantation sometimes show the presence of newly created second phases [5,6]. In many of these experiments the average range of the implanted ions can be large compared to the thickness of the TEM foil. In the present investigation, the ANL HVEM facility which incorporates an ion beam interface [7] has been utilized to study microstructural changes during nitrogen ion implantation in relatively thick specimens of Al over a wide range of temperatures.

2. EXPERIMENTAL PROCEDURE

Electrolytically polished, recrystallized aluminum foils (99.999% purity) were implanted at room temperature in the HVEM ($.32 T_m$) with N^+ ions. Beam energies of 40 and 100 keV were employed with fluxes typically $1 \cdot 10^{12}$ ions $cm^{-2}sec^{-1}$. For these energies the average depth of the implanted ions was calculated to be 130 and 230 nm respectively utilizing the distribution predictions of the Lindhard-Scharff-Schiøtt (LSS) theory. The effect of specimen temperature during implantation was also investigated by performing similar implantation experiments at elevated temperatures (100, 300 and 560°C),

and at low temperature (-120°C). Post in situ high resolution observations were performed in a Siemens 102.

3. RESULTS

A) Implantation at Room Temperatures and Subsequent Annealing

At low doses of approximately 2×10^{14} ions cm^{-2} individual dislocation loops were observed in specimens implanted at both 40 and 100 keV (Fig. 1). Contrast and tilting experiments performed on a foil for which the implantation was terminated at this dose showed that most of these loops were faulted $1/3 \langle 111 \rangle$ Frank loops lying on $\{111\}$ planes (Fig. 2). The fault contrast is clearly discernible for $g=200$ (Fig. 2a). The lack of clear fault contrast in the micrograph for $g=220$ (Fig. 2b) is presumably due to the larger extinction distance of 220 and the fact that $g \cdot b = 0$ for half the loops. It is also observed that irregularly shaped and larger loops (A & B in the figure) appear unfaulted for all g vectors. It is deduced that these loops have unfaulted and transformed into perfect $1/2 \langle 110 \rangle$ loops.

Further irradiations ($\sim 8 \cdot 10^{14}$ ions cm^{-2}) under these conditions produced a high density of damage. This heavily damaged microstructure persisted as the implantations were continued up to doses of 2×10^{16} ions cm^{-2} (Fig. 3). Weak-beam dark field images taken during implantation showed the presence of small dislocation loops and a fine dislocation network (Fig. 4). No extra reflections indicating the presence of a second phase (e.g., aluminum nitride) were observed in the diffraction patterns.

After the implantations with 40 and 100 keV N^+ ions were terminated, the specimen was annealed in the HVEM. Coarsening of the fine dislocation network was observed to begin near 250°C . At this point individual dislocations could again be resolved under bright-field conditions (Fig. 5). Continued annealing of specimens at 560°C (.89 Tm) for one hour failed to reduce the dislocation density further. Subsequent weak-beam microscopy performed after this annealing showed that these dislocations had become pinned on very small (~ 2.0 nm) strain centers (Fig. 6). Lines of no contrast for these strain centers are observed perpendicular to g in the weak-beam images which rotate as g is varied. No extra reflections are observed in the diffraction patterns. The most likely interpretation is that these strain centers are very small nitrogen bubbles formed during annealing. The high density and small size of these strain centers is presumably due to nitrogen having a very low diffusivity even at these relatively high temperatures.

B) Implantation at Elevated Temperatures

Specimens were also implanted at 100, 330, and 560°C . The general changes in the microstructure that occur as the specimen temperature is increased is that the density of dislocation loops produced during implantation decreases and that their growth rate increases. It is not clear whether the loops unfault at a very early stage or whether the loops are initially unfaulted. In addition, a high density of background damage is observed which is presumably due to nitrogen bubbles or some earlier stage of nitrogen atom clustering. For the specimen implanted at 560°C , the dislocation loops produced by the implantation process grew so rapidly that they climbed out of the foil soon after they were formed.

C) Implantation at Low Temperatures

Individual dislocation loops and other strain centers were too small to be resolved in the specimen implanted at -120°C , presumably due to the low mobility of defects. The microstructure contained a very high density of black spot damage which increased with increasing dose until a steady state was achieved (Fig. 7). Re-examination of this specimen in another microscope after removal from the HVEM showed that some kind of defect coalescence had occurred upon allowing the specimen to warm up to room temperature (Fig. 8). The nature of these defects is not presently understood, and a further investigation of them is currently in progress.

4. CONCLUSIONS

- 1) Faulted $1/3 \langle 111 \rangle$ Frank loops are initially formed in pure Al during nitrogen implantation at ambient temperatures. Further irradiation causes these loops to grow and eventually unfault to give perfect $1/2 \langle 110 \rangle$ loops.
- 2) The clustering of implanted nitrogen to form nitrogen bubbles only occurs at relatively high temperatures ($\sim 500^{\circ}\text{C}$) presumably due to the low mobility of nitrogen in Al.
- 3) No evidence of nitride formation is observed in the diffraction patterns, and only nitrogen bubble formation is deduced to occur.
- 4) Implantation at low temperatures (-120°C) produces a high density of black spot damage. Clustering of these defects occurs upon warming the specimen to room temperature.

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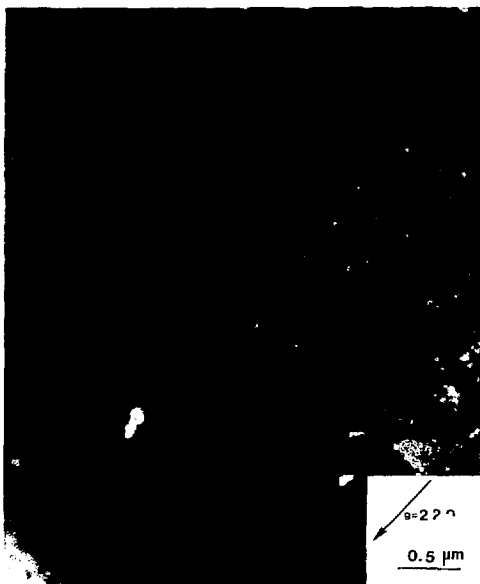


Fig. 1. Dislocation loops formed by implantation of 100 keV N^+ ions (dose $\sim 2 \times 10^{14}$ ions cm^{-2} ; 0.001 dpa) in Al at room temperature.

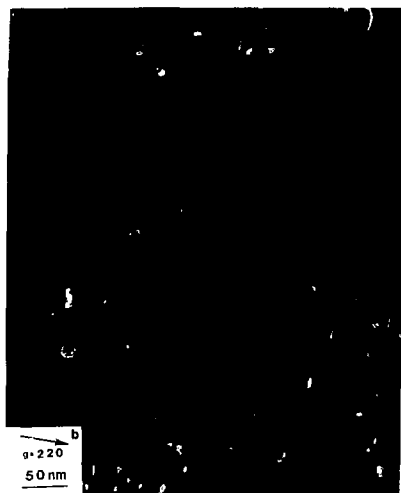
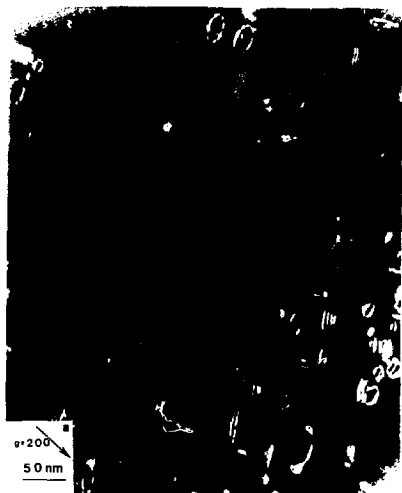


Fig. 2. Weak-beam dark field micrographs of loops formed under similar conditions to those in Fig. 1. a) shows fault contrast for $g=200$; b) shows lack of clear fault contrast for $g=220$.



Fig. 3. Bright-field micrograph showing high density of damage formed by 100 keV N^+ ions (dose $\sim 2 \times 10^{16}$ ions cm^{-2} ; 0.1 dpa) at room temperature.



Fig. 4. Weak-beam dark field micrograph of damage shown in Fig. 3.

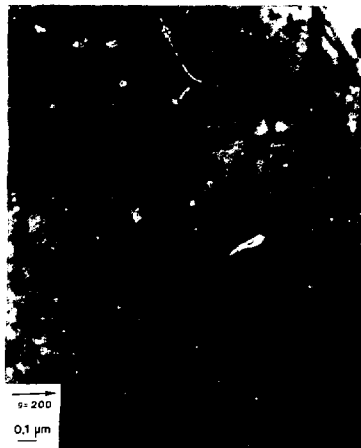


Fig. 5. Bright-field micrograph showing dislocation network formed by annealing the damage in the HVEM shown in Figs. 3 and 4 for one hour at 560°C.

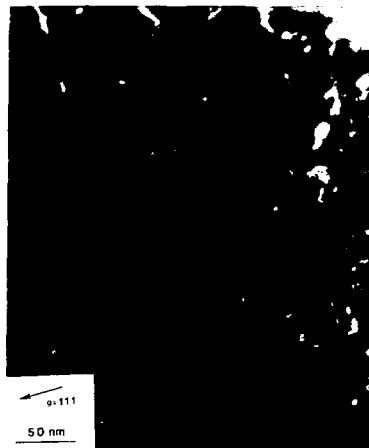


Fig. 6. Weak-beam micrograph of strain centers responsible for pinning the dislocations shown in Fig. 5. Note the lines of no contrast for these strain centers are approximately perpendicular to g .

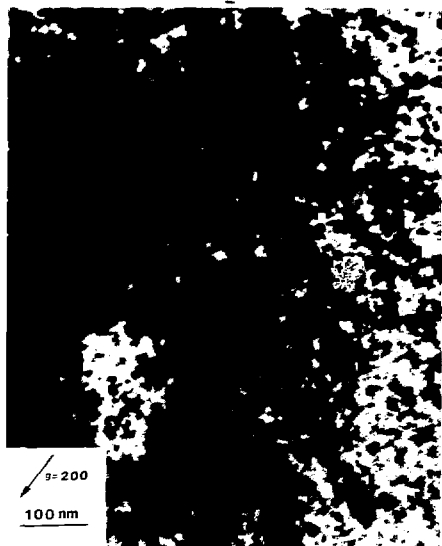


Fig. 7. Heavy density of damage formed during implantation of 100 keV N^+ ions (dose $\sim 2 \times 10^{15}$ ions cm^{-2} ; 0.01 dpa) at $-120^\circ C$.

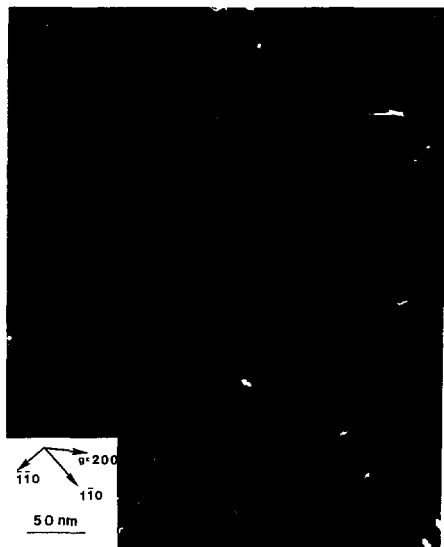


Fig. 8. Weak-beam dark field micrograph of specimen shown in Fig. 7 after being warmed up to room temperature.

TEM STUDIES OF OXIDATION AND PASSIVATION OF IRON

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ABSTRACT

The growth of oxide nuclei on iron at 600 to 700°C has been investigated both in-situ and ex-situ by electron microscopy. At high P_{O_2} (20 torr) randomly oriented magnetite is the first oxide phase to nucleate, while at low P_{O_2} (10^{-5} torr) wustite nucleates first and shows a strong orientation relationship with the iron substrate. The passive film formed electrochemically on iron has been studied using conventional TEM and also an environmental cell containing moist N_2 gas. The passive films formed in neutral buffer solution (pH = 8.4) are found to be crystalline spinel oxides, $Fe_3O_4/\gamma-Fe_2O_3$, with strong orientation relationships to the iron substrate. This work was supported by NSF Materials Research Laboratory Grant No. DMR 78-24150. One of the authors (K.K.) acknowledges the financial support from Kazato Foundation.

INTRODUCTION

The formation of a passive film during oxidation of iron in both aqueous and gaseous environments is a subject of considerable practical importance since effective corrosion resistance in service requires such passive protection. However, the fundamental mechanism by which passivity is imparted, i.e., the composition and structure of the passive film, is not well understood. For example, even though the composition of thermal scales on iron is well defined, very little is known of the microstructural factors which control oxidation kinetics and adherence of the scales. Regarding the structure and composition of anodically-formed passive films of iron, a multi-layer model similar to that which occurs in air-formed oxide films has been proposed. While others believe that hydrogen and hydroxide ions inherently present in an electrochemical cell must play a major role in the formation of the passive film.

OXIDATION OF IRON

The materials and experimental techniques have been described previously [1,2,3]. Thin foil specimens of 99.998% pure iron were oxidized and observed in-situ at temperatures in the range of 600^o to 700^oC in 3 kPa dry O₂ (20 torr) and 1 mPa (10⁻⁵ torr) air using gas environments in an environmental cell [4] and the microscope column of a Hitachi HU-650B high voltage electron microscope, respectively.

The oxidation of iron at 700^oC in 3 kPa dry O₂ for 30 s indicates that the first oxide phase to form consists of highly-strained and randomly-oriented fine grains, as shown in Figure 1. Analysis of the selected area diffraction pattern (SADP) in Figure 1(c) suggests that the first oxide phase is magnetite and the hematite (α -Fe₂O₃) forms on further oxidation. In the early stages of high temperature oxidation, magnetite generally nucleates first and grows until the partial pressure of oxygen at the metal/oxide interface is low enough for wustite (Fe_{1-x}O) to form. On the outer surface the magnetite oxidizes to hematite and so a three layer scale develops. However, further oxidation of the specimen in 3 kPa dry O₂ gives only hematite formation. Wustite never forms because the foil is too thin.

Wustite nucleation and growth can be studied in-situ by oxidation at O₂ pressures of 1 mPa, as shown in Figure 2. The dark field (DF) micrograph of Figure 2(b) imaged with a Fe_{1-x}O reflection indicates that oxide nuclei exhibit a strong orientation relationship to the iron substrate. Black/white strain contrast observed across an island in the bright field (BF) image of Figure 2(a) suggests that formation of oxide nuclei is similar to the surface nucleation of coherent precipitates. Fe_{1-x}O nuclei were observed after an incubation period, typically 10 to 20 minutes. On pure iron it was always observed that Fe_{1-x}O nucleated at temperatures higher than 600^oC and at oxygen pressures of ≈ 1 mPa. The presence of a pre-existing oxide film on the surface may be responsible for the reduction of the partial pressures of oxygen at the metal/oxide interface compared to that in the gaseous environment and thus for the nucleation of Fe_{1-x}O rather than Fe₃O₄ or Fe₂O₃ [5]. In-situ experiments provide useful information about nucleation and growth processes in real time (Figure 3). Once oxide nuclei are formed, very few additional nuclei occur. Individual oxide nuclei grow more rapidly in lateral directions than in normal directions to the surface. During this stage, oxygen must diffuse through the pre-existing oxide film and react in a way that favors the growth of the original nuclei rather than to form new nuclei.

Oxidation induced stress effects in growing oxides have been considered by a number of investigators. For example, epitaxially induced stresses which originate at the phase interface led to the development of the growth stress theory by Pilling and Bedworth [6] based on atomic volume differences between the two structures. Figure 4 illustrates micro-bend contours present in Fe_{1-x}O nuclei resulting from such elastic strains. Stresses generated at the Fe/Fe_{1-x}O interface should be short range since the Fe can deform plastically and the Fe_{1-x}O is known to creep extensively during high temperature oxidation [7].

The SADP in Figure 5(a) was taken during in-situ oxidation of iron at 650^oC for 26 minutes. The oxide formed is wustite. However, the SADP in Figure 5(b) taken from the same area after in-situ oxidation at room tempera-

ture clearly shows magnetite reflections. Wustite has transformed to magnetite near the wustite/gas interface during specimen cooling to room temperature. Below the 570°C eutectoid temperature, aging treatments in air have been found to produce a multi-stage decomposition of the wustite [8]. Magnetite is one of the decomposition products. In Figure 6, an example of a microdiffraction pattern taken from an oxide island at the very edge of the specimen after in-situ oxidation, the orientation relationship appears to be: $[100] \text{Fe}_3\text{O}_4 // [100] \text{Fe}_x\text{O}$ // $(010) \text{Fe}_3\text{O}_4$, suggesting a topotactic relation between wustite and magnetite. The diffuse intensity maxima around wustite reflections indicate vacancy ordering in wustite.

PASSIVATION OF IRON

Thin foils of iron specimens for passivation studies were prepared so as to be free of primary oxides and overlayer oxides or oxyhydroxides. The materials and experimental techniques have been described previously [9]. The Swann environmental cell [4] in an AEI EM7 electron microscope was used with moist He gas at 100 torr. Figure 7 shows SADP's from the iron passivated electrochemically in borate buffer solution, pH 8.4. Figure 7(a), taken in moist He gas, exhibits weak $\{113\}$ oxide reflections (arrowed). About 7 minutes after stopping the supply of moist gas, as shown in Figure 7(b), the $\{113\}$ reflections are clearly observed. The intensities of the oxide reflections have increased relative to the iron reflections. This observation suggests that the crystallinity of the passive film may change after exposure to vacuum in the environmental cell. Even so, the passive film of iron, in either hydrated or subsequently dehydrated environments, is thought to be crystalline spinel-type iron oxide. However, it is possible that structural changes accompany the transfer of the passivated specimens into the environmental cell, because even in the environmental cell there is no electric potential and a very small amount of water compared to the electrolyte.

The orientation relationships between the oxide and iron substrate were determined from SADP's using a Siemens Elmiskop 102. Figure 8 shows the SADP's from the passivated iron. The oxide in Figure 8(a) has the orientation relationship: $[111] \text{oxide} // [\bar{1}10] \text{iron}$; $(101) \text{oxide} // (111) \text{iron}$ and $(0\bar{1}1) \text{oxide} // (001) \text{iron}$. In Figure 8(b), $[\bar{1}10] \text{oxide} // [2\bar{1}1] \text{iron}$; $(001) \text{oxide} // (011) \text{iron}$ and $(\bar{1}10) \text{oxide} // (\bar{1}11) \text{iron}$. The orientation relationship of the passive film to the iron has been discussed in terms of atomistic matching at the interface [9]. A definitive distinction between Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ could not be made from the diffraction patterns. Recently obtained a-c impedance data and ellipsometry data [10,11] have been explained in terms of the exponential variation of the Fe^{2+} concentration with distance in the film with an upper limit of 10% in the local concentration. The electrochemical analysis is incompatible with the presence of Fe_3O_4 and suggests that $\gamma\text{-Fe}_2\text{O}_3$ may be the dominant oxide. The suggested structure of the passive film is a crystalline iron spinel oxide consisting of a varying iron concentration from the metal/oxide interface to the oxide/solution interface.

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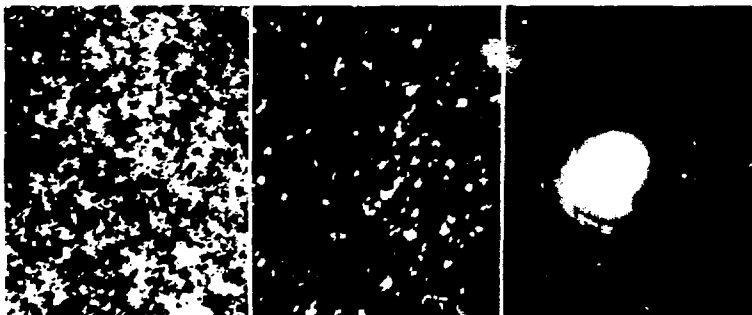


FIGURE 1: Pure Fe foil oxidized in 3 kPa dry O_2 at $700^\circ C$ for 305: (a) B F, (b) D F and (c) SADP.

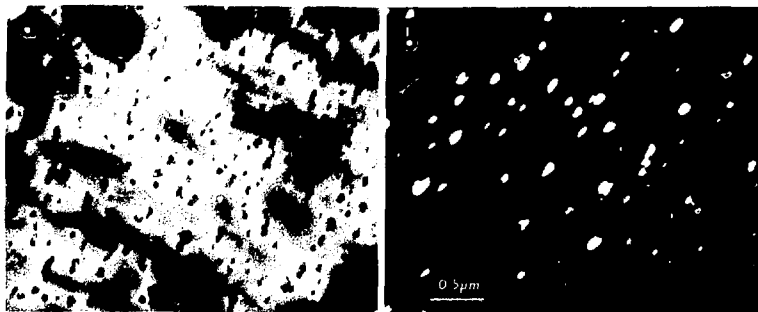


FIGURE 2: Pure Fe foil oxidized in-situ in 1 mPa air at $650^\circ C$ for 30 minutes; (a) B F and (b) D F.



FIGURE 3: B F micrographs showing growth sequence of Fe_{1-x}O in 1 mPa air at 650°C : (a) 18 (b) 47 and (c) 96 minutes.



FIGURE 4: B F micrograph showing micro-bend contour in Fe_{1-x}O nuclei formed in 1 mPa air at 650°C for 17 minutes.

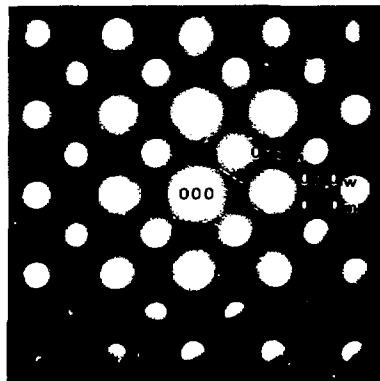


FIGURE 6: Microdiffraction pattern from an oxide island formed in 1 mPa air at 650°C for 15 minutes.

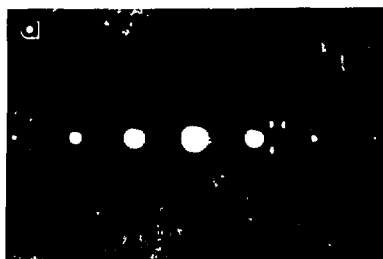


FIGURE 5: SADP's from Fe oxidized in 1 mPa air: (a) in-situ at 650°C for 30 minutes and (b) after in-situ at room temperature.



FIGURE 7: SADP's from passivated Fe using environmental cell: (a) in moist He gas and (b) about 7 minutes after stopping gas supply.

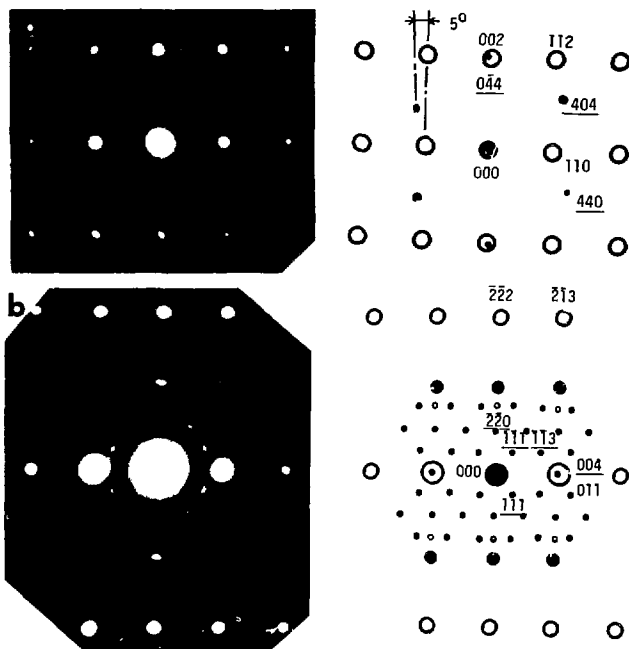


FIGURE 8: SADP's from passivated Fe: (a) $(\bar{1}10)$ Fe and (b) $(2\bar{1}1)$ Fe substrate.

AN IN SITU STUDY OF THE OXIDATION OF MAGNOX A180 BY HIGH-VOLTAGE ELECTRON MICROSCOPY

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ABSTRACT

In situ oxidation in a gas reaction cell in a 1 MeV microscope has been used to study the oxidation of Magnox A180 in moist carbon dioxide. At low temperatures ($<200^{\circ}\text{C}$) epitaxial growth of MgO occurs whereas at higher temperatures a compact polycrystalline MgO film is formed. In thin foils preferential growth of polycrystalline oxide from the foil edge along the $\langle 10\bar{1}0 \rangle$ directions leads to breakdown of protective behaviour and growth of a flocculent form of MgO via vapour transport. This process parallels breakdown which occurs on bulk samples and which is strongly inhibited by the presence of beryllium in the dilute magnesium-aluminium alloy.

INTRODUCTION

The low absorption cross section of magnesium to thermal neutrons, compatibility with uranium metal, good thermal conductivity and relative low cost constitute the principal factors that have contributed to the choice of this metal, suitable alloyed, for cladding the uranium fuel in carbon dioxide cooled, graphite moderated nuclear reactors in the U.K. For this application an alloy containing 0.8% aluminium and $\sim 0.01\%$ beryllium (Magnox A180) was developed for the United Kingdom Atomic Energy Authority (U.K.A.E.A.) which showed considerably improved resistance to oxidation, in the reactor environment, over that of the pure metal. This has been successfully employed in power producing reactors for many years.

Higher operating temperatures could lead to beneficial increases in efficiency. However, oxidation of the Magnox cladding within the reactor can lead to significant losses in heat transfer due to the build up of reaction products and therefore reduced generating efficiency. In extreme cases penetration of the cladding might occur. It is necessary therefore, to study the interaction of carbon dioxide of controlled purity with Magnox at elevated temperatures. Direct observation of the reaction between a metal and a gas at high temperature can be carried out at a resolution of $\sim 40\text{\AA}$ using the environmental cell, developed by Swann [1] at Imperial College, for use in an AEI EM7 million volt microscope. Such a study coupled with results from bulk oxidation studies should lead to an understanding of the oxidation mechanisms involved, especially the role of aluminium and beryllium and thus to practical methods of further inhibition of the corrosion.

EXPERIMENTAL TECHNIQUES

Samples of partially extruded Magnox A180 alloy fuel cans having typical analyses, Mg, 0.87% Al, 50 ppm. Zn, 60 ppm. Si, < 100 ppm. Zr, + O, 20, 78 and 160 ppm. Be were supplied by the Materials Development

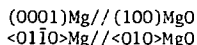
Division of the U.K.A.E.A. Harwell, U.K. Thin slices (~1 mm thick) were spark machined from these samples parallel to the extrusion direction. The average grain size was 150 nm and the texture was typical of a hot extruded c.p.h. metal with {0001} planes aligned with the extrusion axis.

Slices for bulk oxidation studies were polished mechanically to 1 μ m diamond and chemically polished in 30% nitric acid in methanol. Thin foils were prepared as 3 mm discs and electropolished in the same solution.

In situ oxidation was carried out using a GATAN, single-tilt hot stage and environmental cell in the HVEM, the accelerating voltage used was 500 kV in order to minimise radiation displacement damage in the foils. The environment chosen was ~60 torr CO₂ saturated with water at room temperature at temperatures up to 550°C.

RESULTS

On heating the samples from room temperature in the oxidising environment oxidation was first detectable at ~100°C with the nucleation of an epitaxial surface film of fine MgO crystals (Figure 1a). The orientation relationship between the metal and oxide was observed to be:



The interface plane was principally (2 $\bar{1}\bar{1}$ 0)Mg which dominated the sections of highly textured metal employed in this study. With increasing time and temperature this film was seen to thicken and at ~150°C polycrystalline MgO blades, producing ring diffraction patterns, were seen to form at the thinnest areas of the foil. These blades proceeded to grow preferentially in directions orthogonal to [0001] giving rise to a pronounced crystallographic morphology (Figure 1a, b and c), being elongated in [01 $\bar{1}$ 0] on the predominant (11 $\bar{2}$ 0) surface. Above ~230°C, epitaxy was lost and the entire metal surface became covered with a fine grained polycrystalline MgO film. This initially thickened as the oxide blades continued to grow into the metal under the surface oxide film. In the zero and 20 ppm. beryllium alloys formation of the spinel MgAl₂O₄ was detected by electron diffraction but MgO remained the principal product of the oxidation. Eventually cracks develop in the polycrystalline oxide present in the blades, often at the metal/oxide interface. When this occurs a rapid flocculent oxide growth takes place at the oxide/gas interface (Figure 2). As can be seen from Figure 2 the flocculent growth continues even when the metal/oxide interface (arrowed) has retreated and is no longer in direct contact with the site of the flocculent growth. When the metal has been completely consumed the positions of the flocculent outgrowths act as markers for the local positions of the metal/blade oxide interfaces when this growth began (Figure 3).

Results identical in form to those seen in the in situ experiments are obtained on bulk samples, for example Figure 4, which shows the flocculent outgrowth from a crack in the surface oxide film. Detached samples of such flocculent films have been examined and are seen to consist of crumpled sheets of material identified by electron diffraction to be crystalline

MgO (Figure 5). The in situ experiments show essentially identical behaviour for all beryllium levels. However, bulk studies clearly show that the development of the flocculent outgrowths is strongly inhibited with increasing beryllium content.

DISCUSSION

The in situ results show that the predominant product of oxidation is MgO. The morphology and microstructure of this oxide varies with oxidation temperature. The observation of epitaxy at low growth temperatures and breakdown of epitaxy above a critical temperature ($\sim 230^{\circ}\text{C}$) is qualitatively similar to many observations made of epitaxial growth of films and is not therefore unexpected. It does not appear to be critical with regard to oxidation resistance since the compact polycrystalline oxide formed above 230°C is initially protective. Oxide blade growth is probably a thin-foil artifact. The anisotropy of the growth rate within the blade regions may simply be related to the ease of removal of magnesium atoms from non-close packed planes relative to the close packed (0001) plane. The faster growth of the polycrystalline blades relative to the thickening rate of the compact surface film may also be explained in terms of the much larger density of short circuit diffusion paths present in the polycrystalline blades. It is likely that some vapour transport is also involved since the blades continue to grow faster than the compact surface film even under conditions when the latter is also polycrystalline. Since the specific volume of magnesium oxide is less than that of magnesium (Pilling and Bedworth ratio 0.81) and the oxide blade extends through the foil thickness the oxide in this region must be relatively porous. This porosity will allow fast gas transport to the advancing reaction interface enabling continued growth under the otherwise protective compact surface film as shown by the in situ sequence, Figure 1.

Stresses developed within the blades due to their lower specific volume can also lead to cracking of the compact oxide especially at the blade/metal interface. The vapour pressure of magnesium is relatively high (~ 0.3 mm Hg) at 550°C [2], and therefore vapour transport of the metal to the oxide/gas interface can take place down the cracks leading to the development of the crystalline flocculent outgrowths. This behaviour is clearly seen in Figure 2 where the sites of metal consumption and flocculent oxide formation are physically separate and are connected only by a crack in the oxide within a blade. This behaviour dominates in thin foils which do not therefore distinguish between materials with different beryllium levels. In bulk samples beryllium appears to increase the resistance of the compact oxide to cracking in the absence of blade growth. The tendency toward flocculent oxide formation is therefore reduced. The cause of the increased resistance to cracking has not yet been ascertained. It is not believed that the observed formation of small amounts of the spinel MgAl_2O_4 in the zero and low beryllium content materials is directly related to cracking although one effect of beryllium may be to limit the transport of aluminium to the oxide phase.

CONCLUSIONS

In situ experiments can mirror the initial stages of the bulk oxidation of Magnox A180 and demonstrate the processes of breakdown of the otherwise protective compact oxide film. However, oxide blade growth, which is a thin

foil effect masks the beneficial effect of beryllium additions.

ACKNOWLEDGEMENTS

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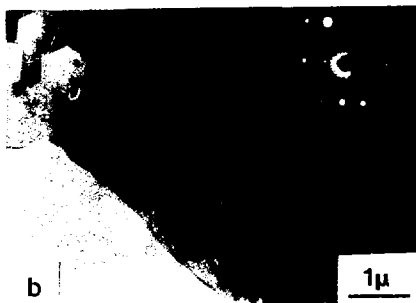


1a

164°C.



2a

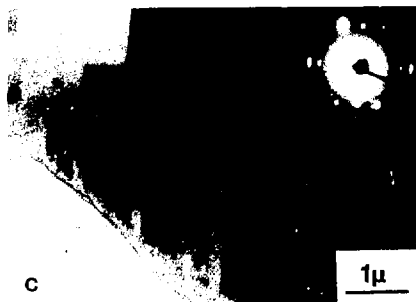


b

323°C.

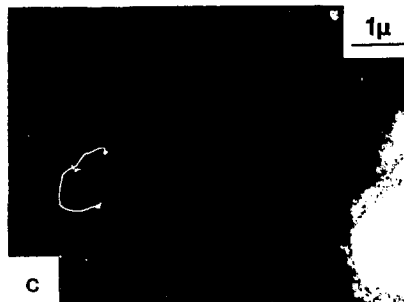


b



c

423°C.



c

Fig 1a,b&c. Development and breakdown of epitaxial oxide film on Magnox AL80 and the concurrent growth of polycrystalline oxide blades in an $[01\bar{1}0]$ direction.

Fig 2a,b&c. Rapid deposition of flocculent MgO from the vapour phase at 525°C in 60 Torr 'wet' CO_2 .



Fig 3.T.E.M. of flocculent MgO growing from boundaries between polycrystalline oxide blades.

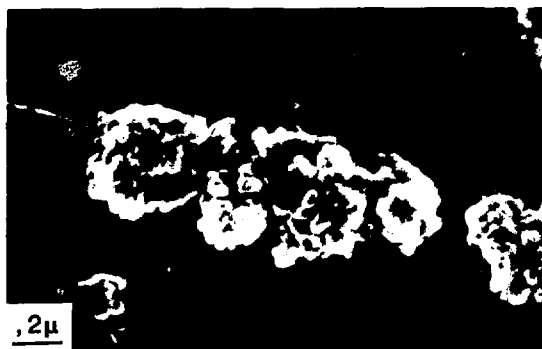


Fig 4.S.E.M. of flocculent MgO growing from cracks in 'primary' oxide film formed on bulk samples oxidized for 24 hrs in 760 Torr 'wet' CO_2 .



Fig 5.T.E.M. of strip-ped flocculent oxide showing 'crumpled film' type morphology.

IN-SITU OXIDATION STUDIES OF VANADIUM-20% TITANIUM ALLOY

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ABSTRACT

V-20Ti alloys have been oxidized in-situ in the ORNL HVEM at temperatures from 300-600°C, and at an oxygen pressure of 3×10^{-5} torr. Results show the initial formation of a fine tweed structure with the associated diffraction pattern characterized by short, well defined streaks through the matrix reflections due to $\langle 110 \rangle$ rel rods. At 400-600°C, this tweed structure is followed by a transformation to a bct structure with a c/a ratio of ~ 1.2 . Surface oxide was formed in the 400-600°C range and was identified as $V_2O_3(R\bar{3}c)$, but containing some titanium. No evidence for long period superlattices such as occur in the oxidation of vanadium was found. This research was partially supported through the SHaRE program with Oak Ridge Associated Universities.

INTRODUCTION

Many refractory metals and alloys dissolve considerable amounts of oxygen interstitially, even at moderate temperatures. The formation of oxide will depend on the oxygen pressure and the temperature, and a competition will normally exist between internal and external oxidation. At very low pressures and moderate to high temperatures, oxygen solution predominates, and oxidation may proceed without the formation of appreciable amounts of surface oxide. In this study, the pressure was maintained at a reasonably low value, so that (using in-situ high voltage electron microscopy) the interstitial-induced phase transformations occurring in a V-20Ti alloy could be studied with a minimum amount of complication from surface oxide formation.

Only one previous study of the formation of internal oxide in a V-Ti alloy has been reported [1], and this study involved high temperature (1100°C), atmospheric oxygen pressure, followed by prolonged aging at 700°C. The only oxide phase reported in this TEM study was TiO (Fm3m), which was formed internally.

This in-situ study of the V-20Ti alloy follows previous studies of the oxidation of vanadium [2,3], and was designed to determine the effect of the alloying element Ti on the oxidation, and in particular to attempt to follow initial changes in structure and morphology.

EXPERIMENTAL

The V-20Ti alloy used in this study was furnished by the Oak Ridge National Laboratory (ORNL) and was vacuum heat treated for 1-2 hours at 1000-1200°C. Three millimeter discs were punched from the material and electron transparent areas were obtained by electropolishing with an electrolyte consisting of 80% CH_3OH and 20% H_2SO_4 . The best polish occurred when the electrolyte was kept between 0°C and -30°C, and the closed circuit potential was 25 volts. The in-

situ oxidation was carried out in the GRNL Hitachi HU-1000 high voltage electron microscope (HVEM). Good access to the pole piece gap allowed pressure measurement (ion gauge) and residual gas analysis (mass spectrometer) of the specimen environment. A baseline pressure of 7×10^{-7} torr could be obtained with the KGA showing approximately equal amounts of H_2O , CO, and N_2 . Oxidation experiments were carried out by leaking controlled amounts of oxygen directly into the specimen area with pressures up to 10^{-4} torr showing no significant effects on the operation of the microscope. All of the experiments reported here were carried out with an oxygen pressure of 3×10^{-5} torr. The specimen temperature could be varied up to 800°C using a Gatan double tilt heating stage.

RESULTS AND DISCUSSION

300°C . At this temperature, the first observable change in the microstructure occurs after 8 minutes in oxygen. The Bragg contours in the image take on a mottled appearance, and at the same time diffuse scattering is observed around the matrix reflections in the diffraction pattern. This is followed by the gradual formation of a fine $\langle 110 \rangle$ tweed structure and the development of well defined, short $\langle 110 \rangle$ rel rods at the matrix reflections (Fig. 1). This type of modulated structure has been observed in a number of alloy systems [4,6]. It has also been observed in alloys with fcc or bcc crystal structures; in substitutional and interstitial alloys; and preceding order-disorder transformations and general precipitation processes.

It has been suggested by Takezawa and Sato [5] that the tweed microstructure is due to the presence of small particles with a 2H (orthorhombic) structure. Although there are other analyses [6,7] which conflict with this conclusion, a model has been developed [8] using the assumption of a high density of body centered orthorhombic strain centers with unrotated $\{110\}$ type habit planes, which appears to explain all observed $\langle 110 \rangle$ streaking in the diffraction patterns and the modulated structure in the bright and dark field micrographs of internally oxidized V-20Ti alloys.

After two hours at 300°C , no change could be observed in the tweed morphology or the diffraction patterns. The transformation sequence in vanadium specimens oxidized in-situ under similar conditions was observed to be: bcc solid solution (α) $\rightarrow$ tweed structure $\rightarrow$ long range ordered bct (α') (Fig. 2). This occurred rapidly in vanadium, whereas no evidence for the formation of similar long period superlattices was observed in the oxidized V-20Ti alloy, even for much longer oxidation times. Clearly the presence of Ti in the alloy has prevented the formation of long period superlattice structures, and has slowed the rate of formation of discrete oxide phases.

400°C . The initial stages of the oxidation process at 400°C are characterized by the presence of the tweed structure as in the 300°C oxidation. However, after 68 minutes' oxide ion, although there was little change in the image other than a coarsening of the tweed structure, it was apparent that structural changes were taking place, since the $[010]$ diffraction pattern showed marked tetragonal distortion (Fig. 3a).

After two hours at temperature, the $[010]$ diffraction pattern corresponded to a bct structure having a c/a ratio of 1.19, with a lattice constant of 3.52 Å in the $[001]$ direction and a 2.96 Å in the $[100]$ direction. The bright field micrograph shows a relatively coarse tweed with the variants parallel to the

traces of the bct (101) and (10 $\bar{1}$) which have an angle of $\sim 80^\circ$ (Fig. 3b). At this stage a few isolated surface oxide nuclei are also observed.

This type of bcc $\rightarrow$ bct transformation appears to be similar to the α (bcc) $\rightarrow$ β (bct) transformation occurring in the V-O system above 500°C , where the β phase is reported to have a maximum c/a ratio of 1.19 [9]. It has been observed by Lawless, Kenik and Bentley [3] that when in-situ oxidized thin foils of vanadium containing the β phase are cooled from the reaction temperature the order-disorder, $\beta \rightarrow \beta'$, transformation will occur. However, there is no evidence that long period superlattices are formed in internally oxidized V-20Ti alloy either at the 400°C reaction temperature or upon cooling.

500°C and 600°C . The transformation sequence at these temperatures, although differing substantially in rate, are essentially equivalent and may be easily followed using electron diffraction (Fig. 4a-c). The first observable change in the [010] diffraction pattern is diffuse $\langle 100 \rangle$ streaking which could be interpreted as being due to the presence of two-dimensional, coherent platelets on {100}. This type of precipitation has been observed in other refractory alloys containing interstitials, but attempts to image the platelets in the internally oxidized V-20Ti thin films were unsuccessful. However, in a parallel study in which V-20Ti bulk specimens oxidized at 750°C and 4×10^{-5} torr O_2 coherent platelets $\sim 300 \text{ \AA}$ in diameter were found to exist on {100} planes (Fig. 5).

After oxidation for 21 minutes at 500°C , the [010] diffraction pattern shows tetragonal distortion (Fig. 4b), which increases with time, and after 46 minutes, the diffraction pattern shows strong bct characteristics (Fig. 4c). The spacing for (001) is calculated to be 3.66 $\text{\AA}$ and 2.94 $\text{\AA}$ for (100) giving a bct structure with c/a ~ 1.24 .

Surface oxide, identified as $\text{V}_2\text{O}_3(\text{R}\bar{3}\text{c})$ from the diffraction data, appears at about 20 minutes oxidation time, and increases markedly with increasing time, the diffraction patterns showing well-defined rings from small crystallites. Auger analysis of the surface oxide indicated the presence of titanium in the oxide and it is likely that the oxide is in fact a mixed (V-Ti) $_2\text{O}_3$ oxide.

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Figure 1. $\langle 110 \rangle$ tweed in V-20Ti alloy oxidized for 2 hours at 300°C and associated $[001]$ diffraction showing $\langle 110 \rangle$ streaks at the matrix reflections.



Figure 2. a) Order-disorder transformation sequence in V foil oxidized in-situ for 15 minutes at 350°C and 1×10^{-5} torr O_2 . b) [011] diffraction pattern from tweed showing the inclined $\langle 110 \rangle$ rel rods as described in [6]. c) [011] diffraction pattern from α' .



Figure 3. a) [010] diffraction pattern after 68 minutes at 400°C. b) Coarse tweed in V-20Ti alloy after 2 hours with the [010] diffraction pattern showing strong bct characteristics.

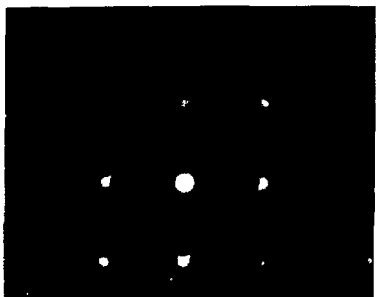
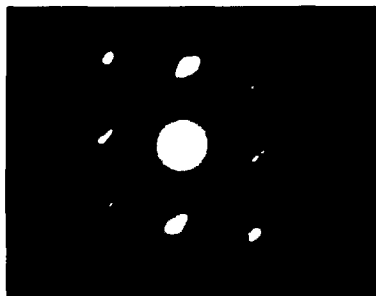
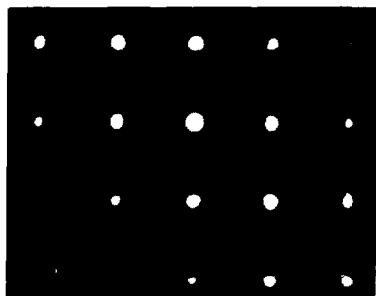


Figure 4. [010] diffraction pattern of specimen oxidized in-situ at 500°C a) 6 minutes, b) 21 minutes, c) 46 minutes.



Figure 5. Bright field image of coherent platelets in bulk oxidation specimen.

IN-SITU STUDIES OF HETEROGENEOUS CATALYSTS UNDER CONTROLLED ATMOSPHERIC CONDITIONS

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ABSTRACT

Dynamic Microstructural changes which occur in commercially important bismuth molybdate and iron molybdate catalysts and $\text{Cu}/\text{Al}_2\text{O}_3$ supported metal particle catalysts in hydrocarbon oxidation and methanol reactions have been studied under operating conditions using a gas reaction cell fitted to a high voltage electron microscope. Reactions with propylene on α -bismuth molybdate ($\text{Bi}_2\text{Mo}_3\text{O}_{12}$) have shown formation of an ordered intermediate phase close to $\text{Bi}_2\text{Mo}_2\text{O}_9$ and in methanol oxidation, the ferric molybdate is reduced to lower oxides and Fe metal. Sintering of copper particles is observed in CO/H_2 reactions using $\text{Cu}/\text{Al}_2\text{O}_3$.

INTRODUCTION

Heterogeneous Catalysis has played a major role in the development of the petrochemical industry. Metal oxides and supported metal particle catalysts are used e.g., for the selective oxidation of hydrocarbons to produce key industrial chemicals. The activity and selectivity of the catalysts, however, are critically dependent upon the microstructural changes under operating conditions and despite extensive solid state structural work such changes in these complex systems are not well understood. It is likely that the conventional X-ray or neutron diffraction methods are not well suited for the microstructural elucidation of these often multiphasic and microcrystalline powdered systems and post-reaction examination of the static catalyst is not always representative of the dynamic system (under reacting conditions). In-situ electron microscopy (EM), on the other hand, is a useful technique to examine catalysts directly under operating conditions, to obtain an insight into reaction mechanisms as a function of temperature, gaseous environments; nucleation of defects, metastable phases, catalyst degradation and reoxidation. Such studies are necessary to determine correlation between microstructure and reactivity as well as to optimise catalyst performance. In the present paper, in-situ observations of commercially important metal oxide catalysts such as bismuth molybdates, iron molybdates and copper catalysts supported on alumina are described. Bismuth molybdate based systems are used e.g., for the selective (amm)oxidation of propylene (C_3H_6) to acrylonitrile/acrolein (feedstocks for polymers) and iron molybdates are used for the oxidation of methanol (CH_3OH) to formaldehyde (HCHO). $\text{Cu}/\text{Al}_2\text{O}_3$ based systems are used in CO/H_2 reactions to produce methanol.

EXPERIMENTAL

The three major phases in the catalytically active region of the phase

diagram of bismuth molybdates, i.e. $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ (α -phase), $\text{Bi}_2\text{Mo}_2\text{O}_9$ (β) and Bi_2MoO_6 (γ) were prepared [1] by coprecipitating aqueous bismuth nitrate and ammonium paramolybdate in appropriate proportions. Samples were also prepared by solid state fusion of Bi_2O_3 and MoO_3 . Iron molybdates were prepared using iron oxide and molybdenum trioxide in FeCl_3 solution.

Model $\text{Cu}/\text{Al}_2\text{O}_3$ catalysts were prepared (by I.C.I.) by evaporating 30 Å Cu on amorphous alumina. In-situ reduction and reoxidation experiments were carried out using a gas reaction cell capable of operating with realistic gas pressures up to 1 atm. and temp. upto $\sim 1000^\circ\text{C}$, fitted to an AEI-EM7 high voltage EM (HVEM) at 1 MeV. The dynamic events were recorded using low beam currents on a video system coupled to a low light level TV camera and also on films. Blank experiments (without the beam) were also carried out to confirm the direct observations. Microstructural characterisation from such studies was complemented where necessary by high resolution EM (HREM) using a JEM 200CX EM at 200 keV (with a point resolution of $\sim 1.7\text{\AA}$) coupled to an on-line image analysis (Intellect) system [2] and the local chemical composition was analysed by using the Oxford field emission gun STEM and by using an automated Cameca microprobe. Parallel experiments (under conditions identical to those in the HVEM) were conducted on bulk catalysts using a gas chromatograph and mass spectrometer (GC-MS) system.

RESULTS

1. Bismuth molybdates:- $\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$: The (010) samples were reduced in the HVEM from room temp. (R.T.) to $\sim 550^\circ\text{C}$ in a continuous flow of C_3H_8 at 100 torr. (α is monoclinic, $a = 7.68\text{\AA}$; $b = 11.491\text{\AA}$, $c = 11.92\text{\AA}$, $\beta = 115.4^\circ$, space group $\text{P}2_1/\text{C}$). At operating temperature of $\sim 440^\circ\text{C}$ an ordered superlattice was observed in the diffraction pattern with spacings of $\sim 8.4\text{\AA} \times 10.8\text{\AA}$. Figs.1(a) to (d) illustrate the sequence of reduction observed frequently, with (a) the fresh sample at R.T. (b) its diffraction pattern (c) the sample at $\sim 440^\circ\text{C}$ showing crystallites and (d) the corresponding diffraction pattern with the superlattice. The superstructure was somewhat unstable outside the reducing conditions but could be stabilised for short periods by annealing. Microanalysis of the reduced crystallites indicated Bi:Mo ratio of $\sim 1:1$ suggesting the presence of a phase similar to $\text{Bi}_2\text{Mo}_2\text{O}_9$ and indicating reduction of the α -phase (and abstraction of lattice oxygen). Some MoO_3 crystallites were also present. At $\sim 500^\circ\text{C}$, metallic bismuth and MoO_2 were observed. HREM and electron diffraction analysis of pure β samples showed that the superstructure is close to (101) β as shown in Fig. 2(a) and (b). In $\text{C}_3\text{H}_8\text{-O}_2$ mixtures, a similar superstructure was observed (at operating temp. $\sim 400\text{--}440^\circ\text{C}$) but reduction to bismuth metal was slowed in the presence of gas O_2 as was the carbon deposition (coking). Parallel GC-MS experiments revealed enhanced selectivity in the presence of the superstructure (β). Similar observations were recorded in the reduction of $\gamma\text{-Bi}_2\text{MoO}_6$.

2. Iron molybdates: Dynamic microstructural changes which occur in ferric molybdate catalysts ($\text{Fe}_2\text{Mo}_3\text{O}_{12}$, $a = 15.70\text{\AA}$, $b = 9.23\text{\AA}$, $c = 18.20\text{\AA}$, $\beta = 125.1^\circ$) in reducing environments of 10% H_2 in He, CH_3OH balanced by He as well as in $\text{CH}_3\text{OH}/\text{O}_2$ mixtures (at 100 torr) have been studied up to $\sim 400^\circ\text{C}$ to obtain an insight into CH_3OH oxidation. It is generally believed that the mechanism of methanol oxidation on ferric molybdates proceeds involving the release of lattice oxygen (resulting in a partially reduced surface) which is replenished by gaseous oxygen, but different opinions exist regarding the rate determining step, i.e. whether it is the reoxidation of the surface or desorption of

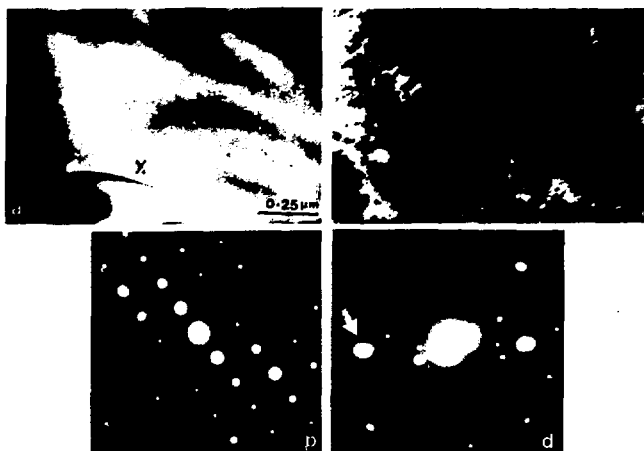


Fig. 1. In-situ sequence of reduction of $\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$ in C_2H_6 . (a) sample at R.T. (b) its diffraction pattern (c) the sample at $\sim 440^\circ\text{C}$ showing crystallites (d) diffraction pattern with a superlattice.

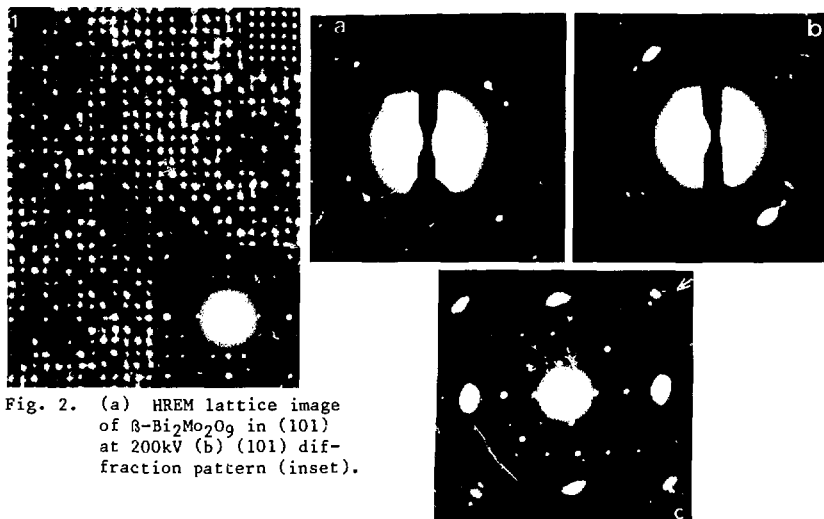


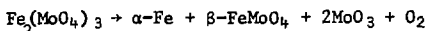
Fig. 2. (a) HREM lattice image of $\beta\text{-Bi}_2\text{Mo}_2\text{O}_9$ in (101) at 200kV (b) (101) diffraction pattern (inset).

Fig. 3. Pure ferric molybdate diffraction pattern near to (010) projection shown in (a) is replaced by a ring pattern (b) during in-situ reduction in $\text{H}_2\text{-He}$ (c) $\beta\text{-FeMoO}_4$ reduced product showing an orientation relationship $[110]_\beta // [001]_{\alpha\text{-Fe}}$.

HCHO [3].

(a) Reduction with 10% H₂-He and with CH₃OH/He: Reduction of the molybdate in H₂/He resulted in the formation of a variety of lower oxides with α -Fe₂O₃ as the dominant phase present. In addition, Fe₂MoO₄ (spinel), β -FeMoO₄, Fe₃O₄, γ -Fe and α -Fe were also observed. The reduction reaction appears to proceed via several simultaneous routes. One which is frequently observed is the decomposition of the ferric molybdate into fine-grained polycrystalline aggregates either as a single phase or as a mixture of various reduced species. The HREM lattice imaging showed these crystallites to be free of defects.

During the course of the reduction, the single crystal ferric molybdate diffraction pattern close to (010) (Fig. 3(a)) disappeared being replaced by a ring pattern (Fig. 3(b)) and the fresh sample decomposed into polycrystalline aggregates. Another mechanism which was also observed in reduction experiments revealed transformation of Fe₂Mo₃O₁₂ to relatively larger single crystallites of α -Fe₂O₃, β -FeMoO₄, etc. Frequently, these crystallites were found to be defect-free, but in some cases, twins, dislocations and 'porosity' type defects were observed. In addition, subsequent selected area diffraction patterns of the specimens revealed the presence of both α -Fe (suggesting segregation of iron) and β -FeMoO₄ with an orientation relationship $[110]_{\alpha\text{-Fe}} // [001]_{\beta\text{-FeMoO}_4}$ as shown in Fig. 3(c). This suggests a possible mechanism for the reduction of the type



The β -FeMoO₄ may be further reduced to α -Fe₂O₃ or Fe₃O₄ before finally reducing to Fe metal. Other possible reaction mechanisms are under consideration. The results in CH₃OH/He were somewhat similar to those in H₂/He with α -Fe₂O₃ as the main reduced species. The lower oxides existed as single crystallites or as fine polycrystalline aggregates.

(b) In CH₃OH-O₂ environments preliminary results have indicated that reduction of ferric molybdate occurs in the presence of gaseous oxygen (suggesting abstraction of lattice oxygen) and that the predominant reduced species are Fe-Mo oxides (e.g. β -FeMoO₄, occurring as large, defect-free single crystallites or as aggregates), iron oxides and γ -Fe. HREM images were consistent with the in-situ observations. Parallel GC-MS experiments confirmed the direct observations with no significant coking in the presence of gaseous oxygen. The in-situ methanol studies have revealed that Fe₂Mo₃O₁₂ is reduced to lower oxides and Fe metal under operating conditions. Further work is in progress to elucidate the exact reduction mechanism and to correlate the microstructure with the catalytic activity and selectivity.

3. Cu/Al₂O₃ catalysts: In-situ HVEM is well suited to examine sintering mechanisms of small metal particles on ceramic substrates, under a variety of gaseous conditions, providing reliable data on reaction kinetics since some systems are oxidised when exposed to air. Preliminary experiments have been conducted on Cu/Al₂O₃ using H₂ and CO gases independently and together, to examine their effect. Samples heated in H₂ for an hour at ~200°C followed by further heating up to 240°-300°C for 1 hour, showed coarsening of the metal particles. The in-situ observations suggested that coarsening occurred predominantly by migration of atomic/molecular species (from smaller to larger particles) [4] rather than by particle migration/agglomeration. Predominantly

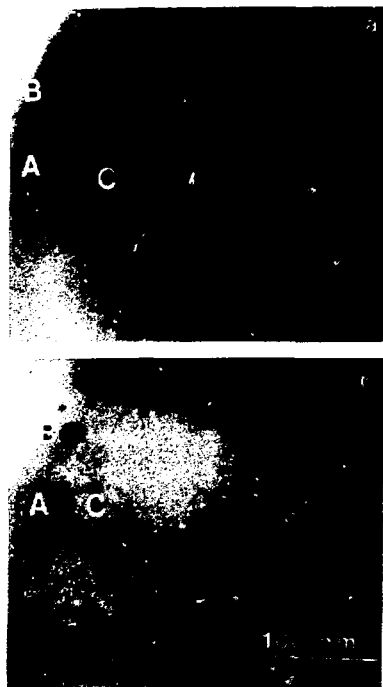


Fig. 4. Sequence showing particle migration (e.g. A, B, C, D) in Cu/Al₂O₃ catalyst in H₂ at ~350°C. (a) after 1.5 hours and (b) 1.75 hours.

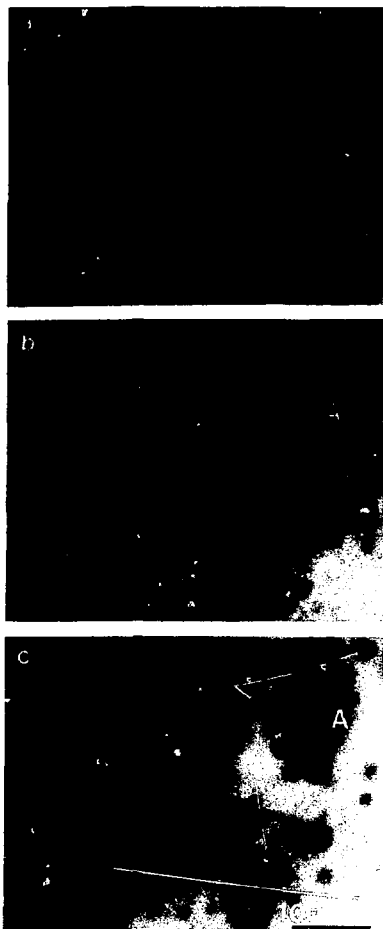


Fig. 5. Particle motion (e.g. at A) in CO/H₂ (a) after 1 hour (b) 1.5 hours (c) 2 hours.

two types of particle sizes were observed with sizes around 10nm-35nm. At a higher temperature of $\sim 350^\circ\text{C}$, direct observations revealed particle migration as shown in Fig. 4. Particle migration and coalescence were also observed in a CO/H_2 mixture at $\sim 350^\circ\text{C}$ as shown in Fig. 5. Some larger particles were observed to move at a rate of $\sim 200\text{nm/hr}$. In CO , the diffraction patterns exhibited additional rings. The alumina substrate showed a 'mottled' contrast and particles with different sizes - 35nm and $\sim 10\text{nm}$ were observed. The dynamic studies have thus provided useful information about the metal particle sintering mechanisms (which play a key role in the deactivation of the catalyst) under a variety of gaseous conditions. The samples taken out of the HVEM showed oxidation to Cu_2O confirmed by selected area and micro diffraction. Investigation of these samples in the 200CX EM also showed that particle sizes were larger than in the in-situ controlled (H_2 , CO) conditions suggesting that sintering in air had occurred. Many particles were faulted and twinned. Attempts are being made to calculate contrast from metal particles using multislice methods on the Intellect system [5]. Fig. 6(a) shows a 30Å silver particle on a 30Å amorphous alumina support and (b) a simulated image of the amorphous film.

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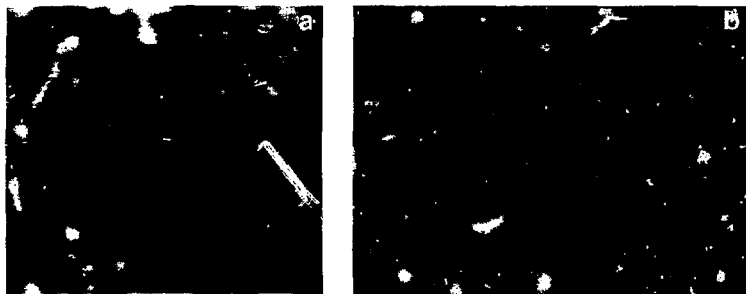


Fig. 6. Calculated images of (a) $\sim 30\text{Å}$ silver particle $[100]$ zone on a 30Å amorphous alumina support (b) the amorphous film. Silver atom positions are superimposed in (a).

IN SITU OBSERVATION OF NUCLEATION AND COLLAPSE OF BUBBLE DOMAINS
IN COBALT BY HIGH VOLTAGE LORENTZ ELECTRON MICROSCOPY

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ABSTRACT

The cylindrical bubble domains were nucleated in the h.c.p. cobalt of (0001) orientation within the electron microscope, using strong objective lens field along the optical axis as a bias field, and the nucleation process was observed. Bubble structures in the remanent state and the process of collapse of bubbles with temperature increase were also studied.

INTRODUCTION

Thin crystals of h.c.p. cobalt in a basal, (0001) orientation, which generally have the plate magnetic domain structure, exhibit the cylindrical "bubble" domains when a large magnetic bias field is applied in the c-axis normal to the foil. The bubbles in cobalt were observed first by Grundy et al. [1,2,3,4] directly in the electron microscope. They observed the domain structures in various conditions of bias field and specimen temperature by Lorentz electron microscopy, to investigate the nucleation and stability of bubble domains, and discussed the results in relation to theories of bubble formation.

Among several techniques of observing magnetic domains, electron microscopy is the only method to observe the domains in a submicron scale and the magnetization distribution in the domain wall. Although cobalt is not a suitable material for application to memory and logic devices in computer system, it is the most suitable material to study the fine details of bubble domains by electron microscopy, and the results will be useful for understanding the physics of bubble domains. Recently, we have extended the study of magnetic domains in single crystal cobalt by the use of 1000 kV electron microscope equipped with a new device for in situ observation of domain wall motion [5]. The results on bubble domains are described in the present paper.

EXPERIMENTAL

Plates of 1.5 mm thick with (0001) orientation were cut out of the single crystal ingot grown in an alumina crucible by the Bridgman method in a vacuum. Then disks of 3 mm diameter were cut out of the plates by the spark-cutter, thinned to 0.5 mm thick by mechanical polishing, and thin sections for electron microscopy were prepared by electropolishing and ion-thinning techniques. These were examined by the defocused mode of Lorentz electron microscopy, using 1 MV (JEM-1000) and 200 kV (JEM-200B) electron microscopes.

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Two kinds of objective pole-piece were used for JEM-1000, i.e. the ordinary pole-piece for top-entry (or side-entry) goniometer and the one designed for magnetic domain observation. In the ordinary pole-piece, strong objective lens field along the optical axis is available as a bias field along the c-axis of the specimen, and the strength at the specimen position can be calibrated by measuring the lens current at different accelerating voltages and different values of defocus, Δf . When the other type of pole-piece is used, magnetic field due to the lens along the optical axis is less than 3 Oe at the specimen position [5], and it is possible to observe the domain structure at remanence. The similar type of field-free pole-piece was used also in the JEM-200B.

RESULTS

Formation of bubble domains

Figs. 1 and 2 show typical examples of the Lorentz image of bubble domains observed at 1000 kV under the bias field of 9.2 kOe. Two types of bubble are present, in agreement with the observation by Grundy et al. [1]. In the type 1, the domain wall is continuously magnetized either clockwise or anticlockwise (Fig. 3(a), (b)), and the contrast in the center of the bubble is either bright or dark in the Lorentz image (Fig. 3(a'), (b')), depending on the sense of rotation of magnetization in the wall as well as on the defocus condition, overfocus or underfocus. In the type 2, the magnetization is opposed in the two halves of the wall forming a pair of Bloch lines (Fig. 3(c)), and the contrast as shown in Fig. 3(c') is produced.

These two types of bubble form a large hexagonal network with the spacing of 0.3-0.5 μm ; as the crystal becomes thicker the bubble diameter and the spacing become larger, in accordance with theoretical prediction [1]. Compared with Fig. 2, all the bubbles seen in Fig. 1 are of type 2. This is attributed to the presence of a component of magnetic field in the foil plane, denoted by $H_{\parallel}$ in Fig. 1. In fact, it was confirmed that the bubble state converts from type 1 to 2 and vice versa and the line joining Bloch lines changes, when a double-tilt goniometer is operated.

In order to observe the process of nucleation of bubbles, the bias field (lens field) was changed by changing the degree of defocus (Δf) and/or the accelerating voltage. The bubbles begin to appear from the plate domains when the field is increased to about 6 kOe and disappear in the field larger than 16-18 kOe, achieving the saturation magnetization. Fig. 4 shows the Lorentz images taken successively from the same area by changing Δf from +0.6 mm to +1.2 mm, i.e., by increasing the bias field from 9.7 kOe to 9.8 kOe. It is clearly seen that plate domains change into rows of bubbles and the subtle rearrangement of domain configuration occurs as the field is increased by 0.1 kOe. These observations support the pinching mechanism of bubble formation proposed by Grundy et al. [4].

Domain structures at remanence

After a hexagonal array of bubble domains such as shown in Figs. 1 and 2 was produced in the strong field of objective lens, the specimen was re-examined with the field-free pole-piece and the domain structures at remanence were observed. Although the plate domains and dumbbell-shaped domains appear



Fig. 1. Lorentz image of bubble domains under the bias field of 9.2 kOe. 1000 kV, $\Delta f = -1.2$ mm. H indicates in-place component of magnetic field.

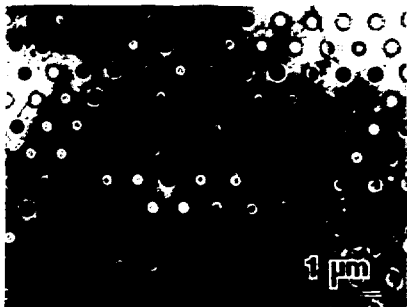


Fig. 2. Lorentz image of bubble domains under the bias field of 9.2 kOe. 1000 kV, $\Delta f = -1.2$ mm.

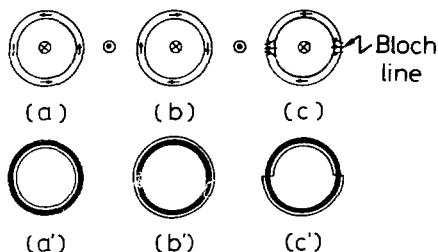


Fig. 3. Wall structure of bubble. (a) and (b) are the type 1, and (c) the type 2. (a'), (b') and (c') are the corresponding contrast in the overfocused image.

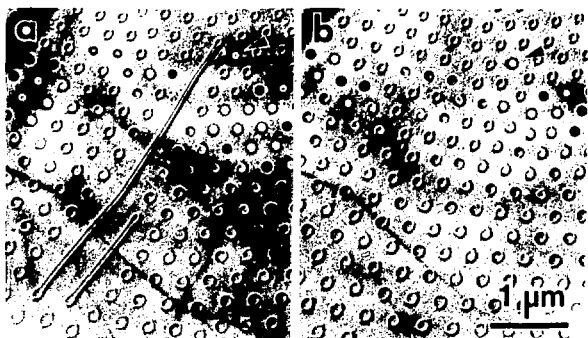


Fig. 4. Lorentz images showing the change in bubble array with bias field, (a) 9.7 kOe, (b) 9.8 kOe. Arrows indicate the same bubble. 1000 kV.

throughout the specimen, a large number of bubbles remain, as shown in Fig. 5. While the spacing of bubble array does not change very much, the bubble diameter in the remanent state is larger than that in a magnetic field, and the total volume occupied by bubbles is almost equal to that outside bubbles, so that overall magnetization becomes zero.

Collapse of bubble domains with temperature increase

The magnetic anisotropy perpendicular to the foil (parallel to the c -axis), which is responsible for the formation of bubbles, decreases with temperature increase in the h.c.p. cobalt: the first magnetocrystalline anisotropy constant, K_{u1} , decreases from large positive value with temperature increase and becomes negative at temperatures above 240°C, while the second anisotropy constant, K_{u2} , remains positive. As a result, the easy direction of magnetization begins to deviate from the c -axis towards the c -plane at about 240°C and becomes parallel to the c -plane at 330°C. The rotation of easy direction was confirmed experimentally by observing the changes of domain structures with temperature in the crystals of (1120) and (1010) orientations, by Lorentz electron microscopy [6].

In the crystals of (0001) orientation, the stability of bubble domains will be lowered as the temperature becomes higher, because of the decrease of K_{u1} , and they can not exist at temperatures above 240°C. It is of interest, therefore, to observe the process of collapse of bubbles with temperature increase. For this purpose, the field-free pole-piece and side-entry specimen heating holder were used in the present study.

Fig. 6 shows a sequence of the Lorentz images of domain structure at remanence taken from the same area in the (0001) cobalt of 0.25 μm thick at 20, 170 and 234°C. Upon heating, a noticeable change in bubble contrast occurs. At about 100°C, the spot appears at the center of bubbles, either white or black, as well as in the plate domains and outside the bubbles. As the temperature becomes higher the contrast of the spot becomes stronger, and the subtle rearrangement of bubble array occurs. At about 200°C, individual bubbles begin to collapse or coalesce to form dumbbell domains. If the specimen is cooled down to room temperature before bubbles collapse, however, the bubble array without center spot is recovered. Upon re-heating, and spot appears again at about 100°C. The Lorentz images shown in Fig. 6 were taken after one cycle of heating and cooling. At about 230°C, a large number of bubbles collapse simultaneously, but some bubbles remain and align linearly, exhibiting the contrast very similar to that of the cross-tie wall, as shown in Fig. 6(c). At temperatures above 240°C, the bubbles disappear completely, and the "cross-tie" walls change gradually to the normal 180° walls as the temperature increases. Once the bubbles disappear, they never recover in zero field even if the specimen is cooled down to room temperature.

In the remanent state, magnetic energy of the type 2 bubble is larger than that of the type 1 bubble, because of the existence of the Bloch lines. In fact, the number of the type 2 bubbles is very small compared with the case in the bias field (compare Fig. 5 with Figs. 1 and 2), and almost all the type 2 bubbles have converted into the type 1 after one cycle of heating and cooling, as seen in Fig. 6(a).

The contrast of the spot appearing in the bubble center is generally the

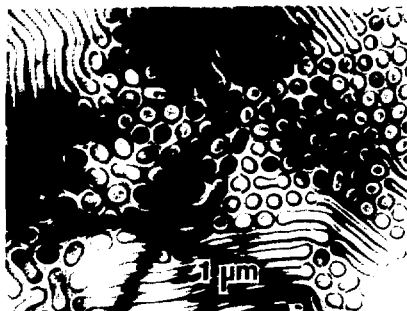


Fig. 5. Lorentz image at remanence.
1000 kV, $\Delta f = +76 \mu\text{m}$.

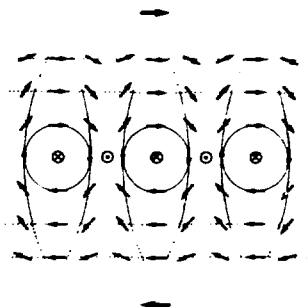


Fig. 7. A model for magnetization distribution in the "cross-tie" wall observed in Fig. 6(c).

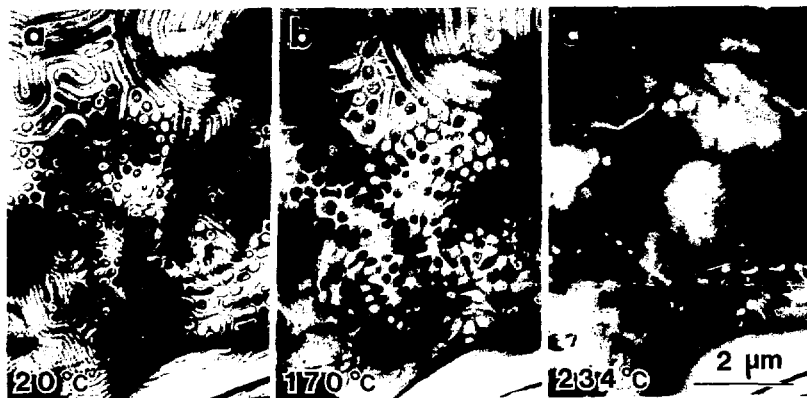


Fig. 6. A sequence of the images of domain structure at various temperatures. 200 kV, $\Delta f = -170 \mu\text{m}$. Arrows in the right-hand side show the same place, and those in the upper side of (b) point out the spots outside bubbles.

same as the inside contrast of bubble wall: the spot is white when the inside of wall contrast is white and vice versa. This contrast can be explained by the tilting of magnetization inside bubble, as postulated by Grundy et al. [2]: around a central region called a "core", where the magnetization is normal to the foil (parallel to the c-axis), the magnetization tilts away from the normal towards the foil plane by a small angle and the in-plane component rotates in a similar manner to the magnetization in the wall. Using the expression for the total magnetic energy of the hexagonal array of type 1 bubbles, given by Grundy et al. [2], the critical temperature T_0 at which the magnetization begins to tilt away from the c-axis, and the core radius r_0 were estimated from the present experimental condition. The results were $T_0 \approx 150^\circ\text{C}$ and $r_0 \approx 40 \text{ \AA}$, in qualitative agreement with the present observation.

There are exceptions to the contrast of the center spot, however. Sometimes, the reverse contrast appears, compared with the inside contrast of the wall in the type 1 bubble, meaning that the sense of rotation of in-plane component is different from that of the bubble wall. In the type 2 bubble, the spot having black and white contrast appears. These exceptional contrast has also been observed in the sputtered Ho-Co films [7]. Models for the magnetization distribution for these cases will be reported elsewhere.

It is noteworthy that the "cross-tie" wall appears in the process of collapse of bubbles. The bubbles having the same sense of rotation of magnetization in the wall align linearly, while other bubbles nearby are collapsing. From the contrast of the wall (Fig. 6(c)), a model for the magnetization distribution can be derived, as shown in Fig. 7, which bears a striking resemblance to that of the cross-tie wall observed in the ferromagnetic thin films [8]. It must be mentioned, however, that there is a big difference in size between two cases: the period of Bloch lines or cross-walls is $0.3\text{--}0.5 \text{ }\mu\text{m}$, corresponding to the spacing of bubble array, in the present case, while it is longer than a few microns in the evaporated films.

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MICROSTRUCTURE IN INTERMETALLIC COMPOUND PHASE OF Pd₅Ce

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ABSTRACT

The crystal structure of Pd₅Ce was analyzed by means of electron diffraction and high resolution microscopy. It was found that Pd₅Ce has two poly-types of stacking structure, or (I)- and (II)-types, which consist of a definite number of "blocks". The block is composed of two kagome-network-layers of Pd atoms, a close-packed layer of Pd and a nearly close-packed layer of two Ce and one Pd atoms. The stacking structures in Pd₅Ce(I) and (II) can be described as 2H and 3R with respect to the sequence of the blocks, respectively. The actual structure of Pd₅Ce is found to contain various kinds of stacking faults and long range modulation, the latter giving rise to the satellite-spots flanking major reflections in the diffraction pattern.

INTRODUCTION

Since Pd-Ce is one of the alloy systems of rare earth and VIII elements, their magnetic properties are of great interest. From a practical viewpoint, in the meanwhile, some research workers[1] were interested in Pd alloys as hydrogen storage materials and studied the diffusion kinetics of hydrogen in the alloys. As such physical properties depend strongly upon the microstructure in the alloy, it is important to clarify the phase-relation in the alloy-system. It is known that the solubility limit of aPd-Ce is about 13 at% Ce and there is an equilibrium phase of Pd₃Ce which has an ordered structure of Ll₂. Rossi et al.[2] suggested that there is an intermetallic compound phase around 17 at%Ce, but no comprehensive work on the phase diagram or the crystal structure has been carried out. Recently, the present authors confirmed the existence of Pd₇Ce and Pd₅Ce phases by means of electron diffraction and high resolution microscopy. It was already reported [3,4] that Pd₇Ce has an ordered structure which is isomorphous with Pt₇Cu. In this paper, we will report the results for the crystal structure of Pd₅Ce.

EXPERIMENTAL

An alloy ingot with 20 at% Ce was prepared from pure metals of palladium and cerium in an electron beam furnace. The ingot was remelted several times to promote homogenization. Discs 3 mm in diameter were cut out from the ingot by spark machining. The discs were sealed in an evacuated quartz capsule, annealed at about 1173 K and then quenched into iced brine. It was observed with an optical microscope that the alloy was composed of two phases. An EPMA examination indicated that one of the phases was of 25 at% Ce and the other 17 at% Ce. The former phase was confirmed by electron diffraction to have an Ll₂ structure. The foil specimens for electron microscopy were made from the discs by a conventional jet method in an electrolyte of a mixture of LiCl, Mg(ClO₄)₂ and CH₃OH. Electron diffraction patterns and high resolution images were observed for Pd₅Ce using JEM-200B and JEM-1000 with a side entry goniometer, at HVEM LAB, Kyushu University. The microscope JEM-1000 has been improved for high resolution observation[5].

RESULTS

(1) Electron Diffraction

It was found that there are two modifications of crystal structures in the phase of Pd_5Ce . The electron diffraction patterns for the both structures are shown in Figs. 1 and 2. We designate them (I)- and (II)- types, or $\text{Pd}_5\text{Ce(I)}$ and $\text{Pd}_5\text{Ce(II)}$, respectively. The diffraction patterns are quite similar to each other. In particular, the patterns with an incident beam parallel to $[\bar{1}20]$, or $[\bar{1}20]$ patterns, are the same. There is a difference between the two types in the way of splitting of the diffraction spots along $[001]$ in the $[0\bar{1}0]$ pattern, revealing that $\text{Pd}_5\text{Ce(I)}$ and (II) are "poly-types".

We will consider first (I)-type to analyze the crystal structure of Pd_5Ce . One can see six-fold satellite spots flanking major reflections, but they are ignored for simplicity. It is easily seen that the diffraction spots in Fig. 1 can be classified into two groups; the spots with the indices of $h + k = 3m$ and the others with $h + k = 3m+1$. The former spots appear at every reciprocal lattice point of $l=n/4$, and the latter at $l=n/8$. Here, m and n are arbitrary integers, and the spacing between the nearest atomic layers⁶, or c_0 , is taken as a unit length along $[001]$. The patterns indicate that the unit cell of $\text{Pd}_5\text{Ce(I)}$ is made of two "blocks" which are composed of four atomic layers, and one block is stacked on the other with a displacement of $\pm[1/3, 1/3, 0]$. As the displacement vector in a structure which is purely made of close-packed layers is $\pm[1/3, 0, 0]$, it is not the case for the present. If the block contains kagome network layers, the displacement vector can be $\pm[1/3, 1/3, 0]$. And, it is known that in alloy-systems of rare earth and VIII elements there are many phases which have a structure related with a Laves phase. Thus, it is considered reasonable to assume that Pd_5Ce has also a stacking structure containing kagome layers. We propose here a new model for the crystal structure of the block which contains ten Pd and two Ce atoms, as shown in Fig. 3. The block is composed of two parts, X and A, both of which are made of a kagome layer and a close-packed one. The layers in part X are made of Pd atoms. In part A, however the kagome layer consists of three Pd atoms but the close-packed layer is of two Ce and one Pd atoms. As Ce atoms are significantly large in diameter compared with Pd, one of the two Ce atoms, or Ce(1), should be stacked on a hexagonal hole of the kagome layer, being shifted downwards by a small amount s . Then, the other Ce atom, Ce(2), can occupy either of the rest two atomic sites, being shifted upwards. Consequently, one can see that there are two variants of part A which can be distinguished by which site Ce(2) occupies. Hereafter, we designate A^+ when Ce(2) occupies the site of $(x,y)=(1/3,1/3)$, and A^- if $-(1/3, 1/3)$. Thus, the kagome layer has to be shifted by $\pm[1/3, 1/3, 0]$ when it is stacked on $A^\pm$. When the parts derived from X and $A^\pm$ by a shift of $\pm[1/3, 1/3, 0]$ are designated as Y and $B^\pm$, or Z and $C^\pm$, respectively, the sequences of the parts XA^+ , A^+Y , A^+Z and their cyclic ones are allowed. Consequently, the two-block structure of $\text{Pd}_5\text{Ce(I)}$ can be determined uniquely to be XA^+YB^- . These ways of description of the layers and the possible manners of stacking were reviewed in detail by Komura and his co-workers [6,7].

From the diffraction patterns shown in Fig. 2, it is found that $\text{Pd}_5\text{Ce(II)}$ has the same blocks as $\text{Pd}_5\text{Ce(I)}$ but a different way of stacking of the blocks. In $[0\bar{1}0]$ pattern shown in Fig. 2(c) there are reflections at the rel-points of $h+k=3m+1$ and $l=3n+1$. But when a small aperture for selecting area was used, a half of the reflections disappeared as shown in Fig. 4. This indicates that the pattern in Fig. 2(c) is the one for the twinned crystal, and that the unit cell of the untwinned crystal consists of three blocks, the sequence of which is $XA^+YB^+ZC^+$ or $XA^+ZC^+YB^+$. The sequences are the identical to each other but in the relation of twinning with respect to the basal plane.

The calculated structure factors for $\text{Pd}_5\text{Ce(I)}$ and (II) are tabulated in

⁶The layer corresponds to (111) plane in an fcc lattice.

Table 1, where the atomic scattering factors of Pd and Ce are put to be 48 and 58, for simplicity. One can see a good agreement between the observed diffraction patterns and the calculated ones. However, it is found that there is a quantitative difference in intensity. This seems to be due to a dynamical effect in electron diffraction as mentioned by other investigators[8].

(2) High Resolution Images

In order to verify the crystal structure proposed for Pd_5Ce , high resolution images were observed. Some of the results for $\text{Pd}_5\text{Ce(I)}$ are shown in Figs. 5 to 7, where the projected crystal structures are attached. Figure 5 shows the image taken with an incident beam parallel to $[120]$, or the image corresponding to the structure projected onto (010) plane. We call it (010) image. One can see in the image that white dots are configured in the shape of rectangles of about $0.25 \text{ nm} \times 0.45 \text{ nm}$ and the bright dots and dimmed ones are arranged alternately along $[001]$. If the brightness of the image-contrast is assumed to be proportional to the projected potential of the crystal, the bright dots are considered to correspond to the groups of two Ce and one Pd atoms, and the dimmed ones to those of three Pd atoms. Alternatively, if the brightness is reversely proportional, the bright dots correspond to the holes between the groups of three Pd atoms, or H_1 , and the dimmed ones to H_2 . Which explanation is adequate for the present case cannot be known before examining by the image simulation. But, it is clear that the periodicities in the observed image contrasts agree well to those in the projected potential of the proposed structure.

Figure 6 shows the image taken with an incident beam parallel to $[0\bar{1}0]$, or (120) image, and the corresponding projected structure. The observed image is characterized by rectangularly arranged white dots and dark lines which are perpendicular to $[001]$. If the assumption is accepted that the dark lines correspond to the atomic layers containing Ce atoms which have a high potential and the white dot to a pair of holes marked with H in the projected structure, the present model is found to be coincident with the image.

Figure 7 shows the image taken with a $[001]$ incident beam, or (001) image. On the projected structure shown together in Fig. 7, the atomic columns of two Ce and two Pd are arranged hexagonally, and the columns of three Pd exist at the centers of the hexagons. One can see in the observed image that bright dots and the dimmed ones are arranged in the manner expected from the present model. Judging from the agreements between the observed images and the projected structure, it is concluded that the present model is acceptable for Pd_5Ce .

(3) Faults and Modulation

It was found that in the actual structure of Pd_5Ce there are various kinds of "faults". In the ideal structure the atomic layers containing Ce atoms exist regularly at an interval of about 0.9 nm . But one can find that the regularity is disturbed in some places in the observed image shown in Fig. 5. It is thought that this is due to faults with a displacement of $[002]$. In Fig. 7, on the other hand, some white dots which should have been dimmed are bright comparably to those which correspond to the atomic columns containing Ce atoms. This is probably due to the existence of stacking faults of the blocks.

In the diffraction patterns there are distinct satellite spots which were ignored in the present analysis of the structure. They surely indicate that there is some kind of modulation in the structure. It is believed that the modulation is attributable to a periodic arrangement of "faults" including the ones mentioned above.

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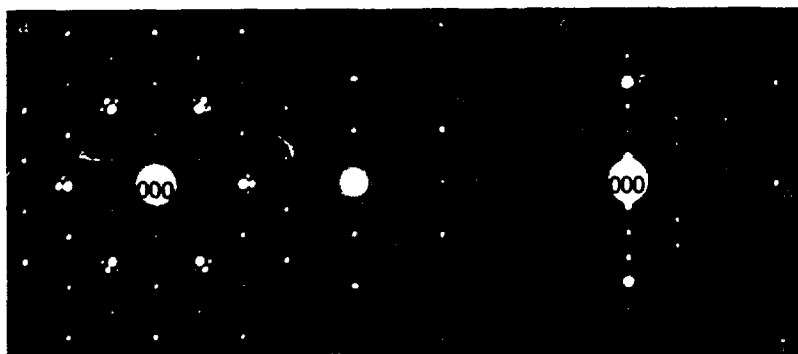


Fig. 1 Electron diffraction patterns for Pd₅Ce(I) Incident beams are (a) [001] (b) [1-20] and (c) [010]



Fig. 2 Electron diffraction patterns for Pd₅Ce(II) (a) [001] (b) [1-20] (c) [001]



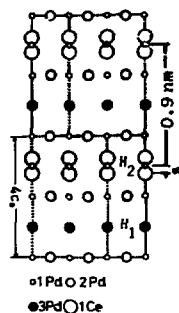
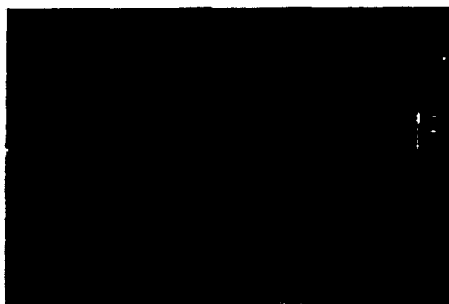


Fig. 5 (010) image and projected crystal structure of Pd₅Ce(I)

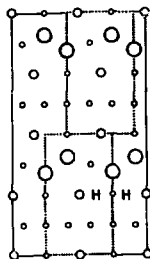
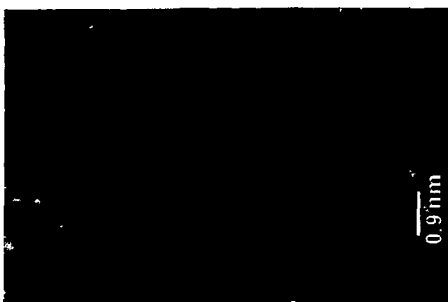


Fig. 6 (120) image and projected crystal structure of Pd₅Ce(I)

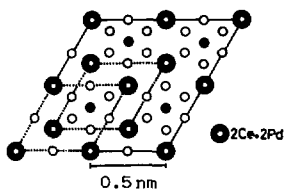
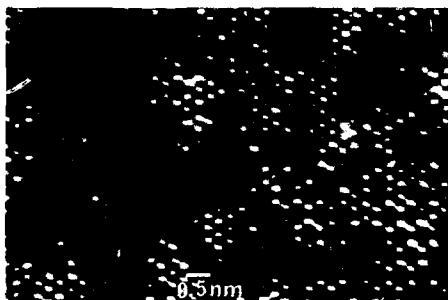


Fig. 7 (001) image and projected crystal structure of Pd₅Ce(I)

SERIAL SECTION RECONSTRUCTIONS OF MOUSE TASTE BUDS
USING HIGH VOLTAGE ELECTRON MICROSCOPY

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ABSTRACT

Using HVEM of serial sections and computer generated three-dimensional reconstructions, we are analyzing intercellular relationships, cellular morphology and patterns of synaptic connectivity in the vertebrate taste bud (TB). HVEM is especially suited for this; it is much easier to cut serial thick sections (0.5-1.0 μm) than thin ($<0.1 \mu\text{m}$) sections.

With the combination of HVEM and the computer we are able to generate models of taste buds and taste cells in the mouse more rapidly and efficiently than with serial reconstructions using conventional transmission electron microscopy (CTEM).

We thank G. Wray for assistance with the HVEM, and Ms. T. Sherman for excellent technical assistance. The Univ. of CO HVEM facility is funded by NIH Biotechnology Resources grant RR-00592 to K.R. Porter and M. Fotino. This study was supported by grants from Procter & Gamble to S. Roper and the MacArthur Foundation to P. M. Groves.

INTRODUCTION

Interpretation of three-dimensional (3-D) structures from electron micrographs is often a difficult task. One approach is to serial section the tissue, take micrographs of every section, and then produce a visual aid or reconstruction embodying the desired information from all of the sections. A reconstruction can be as simple as a series of tracings onto a piece of acetate [1], or it may be complex, such as models made from modelling clay [2], paraffin wax [3], styrofoam [4], or plexiglas sheets [2].

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Certain factors may limit the usefulness of a 3-D reconstruction. Modelling clay, due to its opacity, is inappropriate for the demonstration of internal structures. Plexiglas sheets allow one to look "inside" a structure, but plexiglas is expensive and bulky. Further, it is difficult to view plexiglas reconstructions from the sides due to refractive distortions. In general it is often difficult to utilize a 3-D model effectively because of weight, size or general unwieldiness, hence making it difficult to use solid reconstructions for presentations.

A variety of approaches for computer generated reconstructions are now available [5, 6, 7, 8]. The general features are as follows: (1) Data are entered into the computer by tracing contours onto a digitizing tablet or by using a video system in which a camera views a negative or print and the information enters into the computer memory as a series of densities. Data can then be conveniently stored on disks or magnetic tape. (2) Depending upon the sophistication of the software, features may be available such as: hidden line processing, shading and surface reconstructions, color, real-time rotation of x, y, and z axes, quantification of morphological features such as surfaces, volumes, densities, etc. (3) Hard copies can readily be produced with a graphics plotter or with photography directly from the computer terminal. (4) Stereopairs of reconstructions are easily produced and can conveniently be made into slides or prints for presentation or publications.

We have found the combination of HVEM of serial thick sections (0.5-1.0 μm) and computer-assisted 3-D reconstructions to be a powerful approach for our ultrastructural studies of taste buds in the vallate papillae of the mouse. Although it is possible to create computer 3-D reconstructions from thin sections, that process is tedious and time-consuming. It generally takes from 5 to 10 thin sections to equal the thickness of one HVEM section (0.5-1.0 μm); hence it follows that a reconstruction from serial thin sections would require not only taking 5 to 10 times as many micrographs, but also digitizing that many more contours into the computer.

In the present study we have used the techniques of HVEM of serial thick sections and computer generated 3-D reconstructions to elucidate features of TBs such as: (a) sizes and shapes of TBs, (b) numbers, types and shapes of cells found in TBs, and (c) the numbers and types of synaptic foci.

MATERIALS AND METHODS

Electron Microscopy

Mice were anesthetized with sodium pentobarbital and then fixed by perfusion with heparinized 2.5% glutaraldehyde + 1% paraformaldehyde in 0.05 M sodium cacodylate buffer (pH 7.3). Small samples of lingual epithelium were dissected and postfixed in buffered 2% osmium tetroxide followed by ethanolic dehydration, acetone rinsing and infiltration in 1:1 acetone-Epon/Araldite before curing in fresh resin. Serial thick sections (0.5-1.0 μm) were cut with a diamond knife, mounted onto formvar coated slot grids, stained in ethanolic uranyl acetate followed by triple lead stain [9], then carbon coated and examined in a JEOL JEM-1000 at 1 MeV.

Computer Reconstructions

Information from serial electron micrographs was traced onto a Summagraphics Bit Pad One and entered into our laboratory computer (PDP 11/2, Terak Corp.) using a FORTRAN program "3DDATA". Contours from each section were stored sequentially in data files on floppy diskettes.

Reconstructions were obtained using a FORTRAN program "HDLIN3". In the program the average x, y and z coordinates for an entire structure are determined in order to locate the centroid of the reconstruction in the center of the viewing screen. A hidden line algorithm is used so that higher contours cover overlapping regions of lower contours, giving the reconstruction the appearance of a solid. Each structure within a contour (eg. nucleus, plasma membrane, synapse) can be displayed in a different color. One may view the reconstruction at different perspectives by rotating the reconstruction in three axes and/or manipulating the size and viewing distance of the reconstruction. Once an appropriate view is achieved, a color drawing onto paper or mylar is made using a Houston Instruments DMP-4 color plotter.

RESULTS

The vertebrate taste bud is a barrel-shaped cluster containing from 30 to 150 cells which extend from the basal lamina of the epithelial layer to the surface of the tongue. A typical TB from the vallate papilla of a mouse is shown in Figure 1. In this 1 micrometer section it is possible to recognize the two major types of cells found in TBs: Dark cells (Type I) and Light cells (Type II). Because of the section thickness, it is possible to observe the full length of the apical process as it extends to the taste pore. A computer reconstruction of another longitudinally sectioned TB reveals that the taste pore is not necessarily located in the center of the apical region (Figure 2). In that case the taste pore is located to one side of the TB.

A 0.5 μ m cross section through a TB demonstrates our method for recording data from serial sections (Figure 3). Each TB cell is traced through the serial sections, classified according to type, and then given an identification number. Sensory neuronal processes and taste cell-neuronal synapses are also identified. Data from three TBs are shown below:

TABLE 1

Cell Types and Synapses in Mouse Vallate Taste Buds

TASTE BUD #	1	2	3*	TOTALS
CELL NUMBERS(# of Synapses)				
Dark	48(13)	72(16)	75	195(29)
Light	27 (4)	26 (8)	38	91(12)
Intermediate	6	2	14	22
Mitotic	0	0	6	6
Total/TB	81(17)	100(24)	133	314(41)

*synapses not counted for TB #3

Using the serial micrographs of the two TBs summarized in Table 1, we generated computer reconstructions of individual taste cells (e.g. Figure 4) as well as taste cells within the outlines of the TB (e.g. Figure 5). Note that the cell in Fig. 4 has a synapse near its nuclear region. This juxtaposition of synapses with the nuclear region of the taste cell was found to be a consistent feature. After reconstructions of 12 taste cells together with the outlines of the TB as in Figure 5, we found that most (approx. 80%) taste cells do not extend all the way from the base to the apical taste pore of the TB.

DISCUSSION

We have found computer reconstructions from HVEM serial thick sections well-suited to study the ultrastructure of taste buds. TBs are small enough (approx 100 μm long and 60 μm in diameter) so that relatively few serial sections are needed to include an entire TB. Using serial thin sections for CTEM would have required much more time, effort and expense. However, use of the HVEM does not mean a trade-off in resolution. At a section thickness of 1 μm the resolution of the HVEM is similar to that of CTEMs. The limiting factor in the choice of section thickness for our taste bud studies is not resolution, but the difficulty in interpretation of structures stacked on top of each other as section thickness is increased.

Computer reconstructions of entire TBs have revealed that the location of the taste pore is variable. More importantly, we have learned from computer reconstructions that taste cell synapses are found on both Light and Dark cells and are associated with the nuclear region of the taste cell. The significance of this is unknown at present. We believe the application of computer generated 3-D reconstructions from HVEM micrographs of serial thick sections to be a valuable experimental approach which may be applied at the organellar, cellular and multicellular levels of organization.

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Fig. 1. High voltage electron micrograph of 1 μ m longitudinal section of TB. Light cell (L), Dark cell (D), taste pore (tp), crypt (cr). X 3,300.

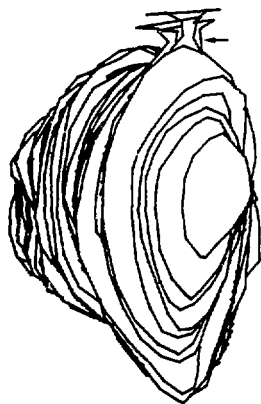


Fig. 2. Computer reconstruction of TB from 1 μ m serial sections. Note that taste pore (arrow) is to one side of the TB.



Fig. 3. High voltage electron micrograph of 0.5 μ m cross section through TB; Identification numbers have been given to each cell. Sensory neuronal processes are outlined in black and synaptic foci are indicated by arrows. X 3,000.

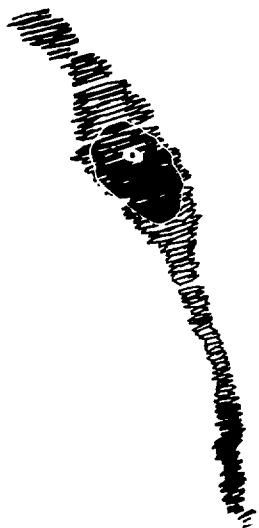


Fig. 4. Computer reconstruction of a Light cell from 0.5 μ m serial HVEM section. Synapse (s) is located near nucleus.

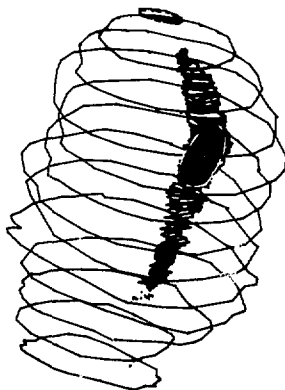


Fig. 5. Computer reconstruction of Light cell with outline of the entire TB to demonstrate the location of the cell within the TB, nucleus (n).

HIGH-VOLTAGE ELECTRON MICROSCOPY OF PERIPHERAL LINKS IN AXONEMES

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ABSTRACT

In this paper the axoneme of sea urchin spermatozoon is examined under H.V. electron microscope. In preparations "in toto" the nexin links system appears to be arranged in trasverse fibers 6-8 nm thick, connecting the A-tubule of a doublet with the B-tubule of the adjacent doublet. The links are spaced at ~ 80 nm distance along each doublet, inclined at an angle of $\sim 30^\circ$ to the axis of the doublet, so that the whole system forms a spiral with a pitch of ~ 80 nm. Nexin seems not to belong to the intermediate filaments class.

INTRODUCTION

Adjacent doublet microtubules in axonemes are bound to each other by transverse links discovered by Gibbons [1], isolated, and named "nexin" by Stephens [2], and described as attached at ~ 86 nm intervals along the doublets by Linck [3,4], Dallai et al. [5], Warner [6] and Witman et al. [7].

It is unclear whether the nexin links interconnect the A tubules of adjacent doublets [1,2,3] or connect the A tubule of one doublet to the B tubule of the adjacent doublet [6,7]. The longitudinal views of the nexin links complex are possible only after negative staining of dissociated flagella, where the general arrangement of the axoneme has been lost. To avoid this disruption we have examined whole sea urchin sperm axonemes by H.V. electron microscopy.

MATERIALS AND METHODS

Sea urchin (*Paracentrotus lividus*) alive spermatozoa were fixed 1 h in 2.5% glutaraldehyde in artificial sea water, post-fixed 1 h in 1% osmium tetraxide in cacodylate, washed in the same buffer, dehydrated through ethanols, attached on grids by polylysine, critical point dried, carbon coated. Other specimens

were briefly extracted by 1% Triton in cacodylate, fixed, and treated as previously reported. Part of the material was embedded in Epon-Araldite and cut in ultrathin sections. All the specimens were observed under the SEM 1,000 microscope in the Department of Molecular, Cellular and Developmental Biology of the University of Colorado, Boulder, Colorado.

OBSERVATIONS

Whole sea urchin sperm tails appear under the H.V. electron microscope as a bundle of longitudinal fibers, clearly visible through the plasma membrane, interconnected by a complicated system of transverse links. The three dimensional organization of this complex clearly demonstrates that the longitudinal fibers are doublet tubules and that they are bound to each other by superficial fibers forming a system of transverse links. It is apparent that this arrangement is the nexin filament system. The thickness of these links is about 6-8 nm. They appear bound to the doublets by dense knobs at 80 nm longitudinal intervals. Two knobs occur at the same level in each doublet one on the tubule A, one on the tubule B. It implies that each A-tubule is bound to the B-tubule of the adjacent doublet. Examination of stereo micrographs suggests moreover that the nexin links are not perpendicular to the doublet, but inclined on angle at about 30°, so that the nexin system forms a kind of continuous linkage arranged spirally with pitch of 80 nm around the inside of the cylinder of 9 doublets. Near the tip of the axoneme, where the number of doublets is decreasing, the two opposite nexin links starting from each doublet are no longer in register but the general spiral arrangement of the system appears still conserved with the same pitch.

Ultrathin longitudinal sections of Epon-embedded axonemes did not give any further information on the nexin arrangement; due to the reduced thickness of the area visible, where arms, radial links and projections are constantly present. Triton extracted axonemes appear to loose the nexin links along with membranes, and only the doublets and arms can be seen in the extracted axonemes.

DISCUSSION

The H.V. electron microscope examination of sea urchin sperm axoneme has given evidence that the nexin system binding doublets each to the other is made up of 6-8 nm thick filaments binding the A-tubule of a doublet to the B of the adjacent doublet, and

that the links are inclined at an angle of about 30° to the axis of the doublets. The general arrangement of the nexin system suggests the presence of a spiral fiber with a pitch of ~80 nm connecting the nine doublets. A 30° helix with a similar period (88 nm) has been suggested by Warner and Satir [8] for the arrangement of each triplet of radial spokes on the 9 walls of the 9 doublet tubules. Also Warner [6] observed in sections that nexin links are not perpendicular to the doublet's axis, but form angles of about 45°. The value of this angle may well vary according to the elasticity of the system and the displacement of the doublets.

Linck [4] summarizes the function of nexin system as playing a structural role during the "resting" state of the axoneme, and an active role as elastic elements to regulate the displacement during movement. Our observations, mainly on the tip region of the axoneme, support both of these hypotheses, and allow us to evaluate the variability of the filament thickness depending on its degree of stretching.

Although it is difficult to specify the class of proteins to which the nexin links belong, they are only about 8 nm thick and have a closer structural resemblance to the microtrabeculae than to intermediate filaments.

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NOTES

DISORDERING UNDER HVEM IRRADIATION

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ABSTRACT

An investigation has been made of the effects of high energy electron irradiation on the degree of long-range order S in fully ordered Ni₃Al, Ni₃Fe, NiAl and FeAl. The irradiations were carried out at temperatures between 15K and 305K and accelerating voltages of 600 kV and 1 MV. At low temperatures, below which vacancies can be considered immobile, all the alloys, except NiAl, became fully disordered when irradiated above the threshold displacement energy and the disordering rate increased with decreasing temperature and increasing accelerating voltage. The results are consistent with disordering by the propagation of replacement collision sequences down mixed-atom rows, with the energy of the primary knock-on defining the length of the sequence and the temperature dependence arising from an attenuation of sequence length due to lattice vibrations. Non-stoichiometric Al-rich NiAl is resistant to disordering having a high ordering energy and concentration of nickel vacancies which favour correlated athermal recombination events.

INTRODUCTION

It has been well established experimentally that irradiation of an ordered alloy above its threshold displacement energy can lead to changes in S (For a recent review see [1]). In a fully ordered alloy, each atom displaced produces a decrease in the state of order in the crystal which can only be restored if mutual recombination of an interstitial and a vacancy of the 'right' type occurs. In simple theories of disordering [2-4], where reordering is neglected, it is assumed that

$$S = S_0 \exp(-\epsilon \sigma_d \phi t) \quad (1)$$

where S_0 is the initial degree of long-range order, ϵ is a multiplication factor which depends on the assumptions of the particular model, σ_d is the displacement cross-section, ϕ is the irradiation flux and t is the irradiation time. At temperatures where the irradiation-produced and/or thermal defects are mobile enough to restore order to the lattice disordering is resisted. Theories which assume a balance between disordering and ordering under irradiation with change in temperature have been developed [5,6] and are supported by experimental evidence [7-9]. The exponential dependence of S on dose has also been experimentally verified [2, 10-14]. Some of these more recent investigations have indicated that disordering by mechanisms based on both uncorrelated recombination and replacement collision sequences can occur under electron irradiation but the mechanisms have not been studied systematically, and there are many details which require clarification. Notable in this respect are the effects of temperature and accelerating voltage.

MATERIALS AND METHODS

The ordered alloys investigated were Ni₃Al and Ni₃Fe having an L1₂ superlattice based on the fcc structure and NiAl and FeAl having a B2 superlattice based on the bcc structure. The alloys were heat treated to develop a fully ordered structure.

Electron diffraction was used to monitor changes in the degree of long-range order during electron irradiation by recording diffraction patterns sequentially from the irradiated volume and then measuring the intensities of the superlattice and fundamental reflections, as has been previously described [8,15]. Although this technique is experimentally straightforward and allows convenient variation of experimental conditions, it is necessary to be aware of its limitations and factors which can affect the determination of an accurate value of S . In practice, reproducible measurements of the disordering response can be achieved, even at low temperatures, if certain conditions are imposed. These are:

- (i) the specimen should be orientated with a systematic row diffracting and only the lowest $\pm g$ superlattice/fundamental ratios should be used,
- (ii) the irradiations should be carried out in thin foils ($<1000 \text{ \AA}$) so that rescattering is minimised. The fundamental reference intensities should not change by more than $\pm 10\%$.

All the irradiations were carried out in the AE1 EM7 equipped with double-tilt cooling (liquid N₂ and He) stages.

RESULTS

Ni₃Al and Ni₃Fe

A range of electron energies from 350 keV to 1000 keV at temperatures down to 15K was employed with all the irradiations carried out with the specimens close to the $\langle 110 \rangle$ orientation along a $\langle 001 \rangle$ systematic row of the diffraction pattern. For temperatures around 300K the incident flux was 1.5×10^{19} electrons/cm².sec; below this the flux used was 5×10^{18} electrons/cm².sec.

For Ni₃Al, 1000 kV electron irradiation resulted in an increased disordering response as the temperature was reduced. At 305K the alloy would not disorder completely and a steady-state value of S was attained; below 305K the alloy became fully disordered and the initial disordering rate continued to increase as the temperature was decreased. Ni₃Fe behaved similarly but was much easier to disorder completely at low temperatures. The results were initially plotted as $\ln S$ versus dose and it was found that the linearity implied by equation (1) was obeyed below $\sim 305\text{K}$ for both alloys. An effective disordering cross-section, σ_d , was determined from these plots at each temperature and for the two accelerating voltages. The results appear in Figure 1. It can be seen that there is a temperature dependence to the disordering rate and at any particular temperature the disordering rate is greater the higher the electron energy.

NiAl and FeAl

The response of fully ordered NiAl and FeAl to 1000 kV electron irradiation was investigated at temperatures between 305 K and 15 K with the samples close to the $\langle 100 \rangle$ orientation. The results, plotted as $\ln S$ versus dose, are shown in Figure 2. It can be seen that NiAl does not disorder completely even after extended irradiation at 15K, whereas FeAl readily disorders at a rate which increases with decreasing temperature.

DISCUSSION

The temperature dependence of the disordering cross-section cannot be explained by a temperature dependence of the threshold displacement energy; recent investigations into the temperature dependence of the $\langle 110 \rangle$ displacement energy in Cu have shown, for example, an increase in E_d with decreasing temperature [16]. Similarly the dependence cannot be due to an increase in the extent of uncorrelated recombination with decreasing temperature since literature evidence again points to an opposing variation [17]. The results are consistent with disordering by the propagation of replacement collision sequences down mixed-atom rows, as we have previously concluded for Mg_3Cd , Ni_3Al , Ni_3Si and Ni_3Fe [15]. With increasing temperature the lattice vibrations cause the atoms to be displaced away from the collision axis leading to a decrease in the efficiency of energy transfer and also to an increase in the amount of energy absorbed by the atoms surrounding the collision axis. To analyse the temperature dependence via the parameter ϵ (the number of replacements/displacements) it is necessary to use calculated theoretical displacement cross-sections.

Cross-sections (in barns) were taken as 55 and 28 for Ni_3Al and 45 and 32 for Ni_3Fe at 1000 kV and 600 kV respectively, and 57 for NiAl and FeAl at 1000 kV. For the $L1_2$ alloys, ϵ increases by a factor of 2 between 305 and ~ 105 K. For Ni_3Al at 15K ϵ is ~ 10 , for Ni_3Fe at 154 K ϵ is ~ 14 for 1000 kV electron irradiation. The magnitude of ϵ is greater for the higher energy electrons, when it is not limited by lattice vibrations, because the energy of the p.k.o. directly determines the length of the collision sequence. The creation of a replacement collision sequence is a low energy phenomenon and it is generally accepted that the critical focusing energy is less than ~ 100 eV. The maximum energies transferred in a primary electron-atom collision to Ni, Al and Fe atoms, for the range of electron energies used in the present work are below this (apart from primary displaced Al at the higher electron energies), so collision sequences can be created.

NiAl is more resistant to disordering than the other alloys investigated. With a damage rate of 10^{-3} d.p.a./sec, the alloy remains fully ordered at temperatures above 300K and even after extended irradiation at 15K the alloy is only partially disordered (see Figure 2). ϵ is ~ 2 at 158K and ~ 6 at 15K; however these values are subject to error due to the reordering component. The large constitutional vacancy concentration of Al-rich NiAl ensures that there is always likely to be a high degree of spontaneous recombination. The high ordering energy of NiAl further favours correlated recombination [13], which would account for the resistance of the alloy to disordering at temperatures approaching absolute zero. Unlike NiAl, FeAl disorders readily at temperatures below 300K. For both alloys however increases in the

disordering rate with decreasing temperature are again consistent with disordering by a replacement collision sequence mechanism.

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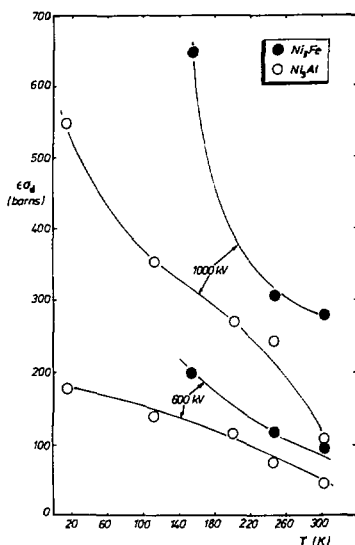


Figure 1: The experimentally determined disordering cross-section of $\langle 110 \rangle$ Ni_3Al and Ni_3Fe as a function of temperature and accelerating voltage.

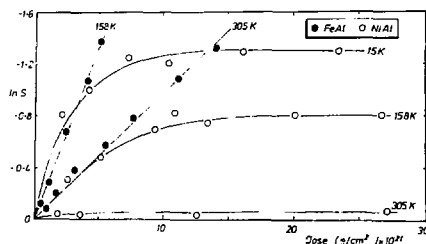


Figure 2: The disordering response of $\langle 100 \rangle$ NiAl and FeAl under 1000 kV electron irradiation as a function of temperature, plotted as $\ln S$ versus dose.

INTERVARIANT INTERFACES IN TWINNED MARTENSITES

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ABSTRACT

Conventional diffraction contrast and high resolution TEM at 200kV and 500kV have been used to examine the martensite intervariant interfaces in an equiatomic nickel-titanium alloy. Our results show that on an atomic level the intervariant interfaces are extremely irregular. The variants appear to be all approximately twin related to one another. The migration of the intervariant interfaces is briefly discussed.

INTRODUCTION

In a recent study of an internally twinned Ag-Cd martensite, Saburi and Wayman [1] found that the martensite formed in self-accommodating groups of four variants, each variant being composed of twin related lamellae of two orientations. Deformation of the martensite, which forms the basis of the shape memory effect, proceeded by a combination of detwinning within each variant, variant-variant coalescence and group-group coalescence. An essential requirement for such processes is that the intervariant interfaces are glissile [2]. Whilst detwinning can be accomplished by the passage of twinning dislocations through successive twin planes, the details of the migration of the variant-variant interfaces are less well understood. For this reason, it is pertinent to look at the variant morphology in other thermoelastic martensitic systems in which the martensite is internally twinned. In this paper, we report TEM observations of intervariant interfaces in an equiatomic nickel-titanium alloy and discuss current understanding of the migration of such interfaces. These were accomplished by examining thin foils of an alloy investigated previously [3-4] at 200kV in a side entry JEM 200CX electron microscope and at 500kV in the Cambridge H.R.E.M. which now has an instrumental resolution of about 1.8Å [5].

RESULTS AND DISCUSSION

The microstructure of this alloy is complicated by the occurrence of two twinning modes, the predominant one a Type II transformation twinning mode and the other a Type I deformation twinning mode [4]. Close inspection of the microstructure failed to find any regions in which four transformation twinning variants were grouped together, as in the case of Ag-Cd martensite. Instead, areas were frequently found in which two such variants had a common macroscopic interface derived from a $\{110\}_{P_2}$ plane of the parent cubic phase. Figure 1 is a bright field electron micrograph of such an area and Figures 2(a) and 2(b) the diffraction patterns corresponding to the three regions defined in Figure 1. Both Figure 2(a) and Figure 2(b) are derived from $\langle 111 \rangle_{P_2}$ zones and are themselves twinned diffraction patterns [4]. Analysis suggests that there are

approximate twinning relationships between the various lamellae. For example, the $\{110\}$ zone diffraction pattern in Figure 2(a) is approximately related to the one in Figure 2(b) by a rotation of Π about the $\langle 111 \rangle$ plane normal. The plane is derived from a $\{110\}_{B_2}$ plane and is the approximate intervariant interface plane.

At higher magnification, the intervariant interface in Figure 1 is extremely irregular and contains highly faulted regions, as can be seen in Figure 3. Further examples of intervariant interfaces are shown in Figures 4 and 5, the former between a Type I and a Type II internally twinned region and the latter between two Type I internally twinned regions. In both cases the foil is oriented with zones derived from $\langle 111 \rangle_{B_2}$ and, as in Figure 1, approximate twinning relationships between the variants can be derived.

Lattice imaging enables one to characterise further the intervariant interfaces and examples have already been given in a previous paper [4]. One aspect for which this technique is particularly suited is the determination of the orientation of small pockets of martensite at the intervariant interfaces. Thus by choosing an objective aperture which only includes the 001 and 010 beams of the monoclinic martensite, one can readily confirm the pockets of martensite in Figure 4 are faulted on 001 planes and that they are approximately twin related to the Type I and Type II internally twinned variants, as Figure 6 demonstrates. Another example is shown in Figure 7, an enlarged photograph of the intervariant interface in Figure 5, showing that the interface irregularity extends down to the atomic level.

Our experimental observations therefore present a picture of microtwinning in nickel-titanium martensite on a large scale, although it should be emphasised that the twinning relationships between different internally twinned variants are at best approximate because of the nature of the martensitic transformation. This strongly suggests that the migration of the intervariant interface involves mechanisms similar to detwinning and will probably depend on the ability of any mechanism to accommodate small angular deviations from ideal twin orientations. One particular mechanism has been proposed by Christian [2] in which the intervariant interfaces are assumed to be rotated away from an invariant plane condition by the formation of steps in the interface. Glide of these steps causes one variant to grow at the expense of the other. However this mechanism is only valid for relatively small angular deviations away from the invariant plane. The high irregularity of the intervariant boundaries in nickel-titanium may preclude such a mechanism.

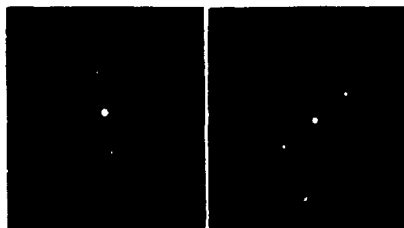
We would like to thank the Science and Engineering Research Council for financial support for this work.

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Fig.1. Bright field electron micrographs of three Type II internally twinned variants 1,2 and 3 in nickel-titanium martensite.



(a)

(b)

Fig.2(a) Diffraction pattern from regions 1 and 3 of Fig.1.
(b) Diffraction pattern from region 2 of Fig.1.

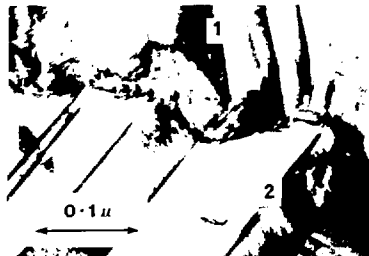


Fig.3. 1-2 intervariant interface at higher magnification.



Fig.4. Intervariant interface between a Type I and a Type II internally twinned variant.

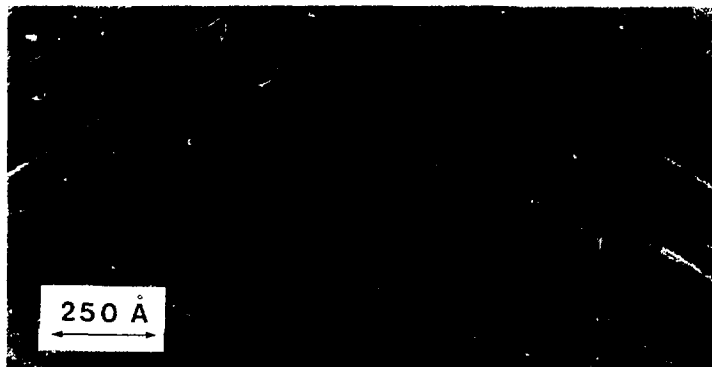


Fig.5. Intervariant interface between two Type I internally twinned variants.



Fig.6. Enlargement from Fig.4. The 010 and 001 martensite reflections only have been used to form the image which makes the relationship between the twinned variants readily apparent.

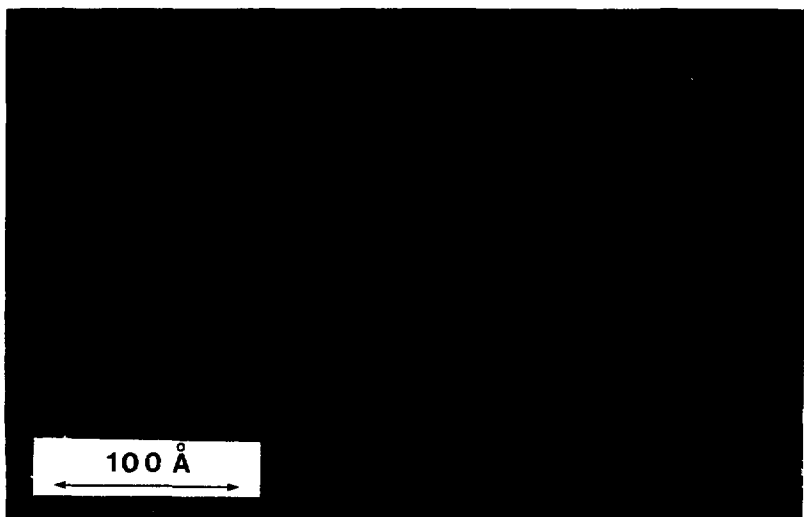


Fig.7. Enlargement from Fig.5. The interface is clearly disordered on the atomic scale.

HVEM STUDIES OF PRECIPITATE MORPHOLOGY SYMMETRIES

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ABSTRACT

Examples are shown to illustrate the effectiveness of the HVEM in the analysis of microstructural symmetries of precipitates in a cubic matrix. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

The shape, direction and distribution of second phase precipitates in a crystalline matrix reflect the symmetries of the two crystals involved. It has been shown that the particle shape obeys a symmetry which is the intersection group of matrix and precipitate point groups [1], i.e. the set of those symmetry elements that are common to the two crystals. The more elements they have in common, the higher will be the symmetry of the particle shape. Particle distribution on the other hand depends on those symmetry elements of the matrix that are not shared by the precipitate since every such symmetry operation will produce a new variant. In the terminology of group theory, the number of possible variants is the index of the intersection group H in the point group of the matrix crystal. Thus a low-symmetry orientation relationship implies a low-symmetry shape and a large number of different variants. Conversely, if the orientation relationship is simple and of high symmetry, only few different variants are possible. In this case the shape, direction and distribution of precipitates is readily apparent from metallographic observations. For example, a dispersion of small plate shaped precipitates on $\{100\}$ planes of a cubic matrix such as θ' plates in Al-Cu is easily recognized. The tetragonal precipitate and the cubic matrix share a number of symmetry elements leading to a simple shape and only 3 variants. If the common symmetry is lower, as in the case of small plates of hexagonal Ta_2C carbide in Ta, the number of variants is larger to the point of appearing random (see Fig. 1a). However,

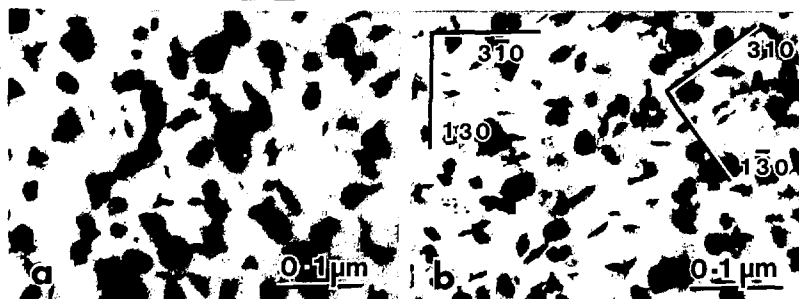


Fig. 1. Distribution of small platelets of hexagonal Ta_2C in a cubic Ta matrix. The appearance is random in a high-index axis (a) but shows symmetry in an $[001]$ zone axis (b) where four sets of $\{310\}$ precipitates are seen edge-on.

when viewed in an $\langle 001 \rangle$ projection (Fig. 1b), the full symmetry of the distribution is displayed. Four of the twelve variants are seen edge-on, and the angles between them show that they lie on $\{310\}$ planes. This type of measurement requires, however, that a sufficient number of different variants are present and that truncation of precipitates in thin foils does not distort the morphology. These problems are overcome by using thicker foils in an HVEM. Fig. 2a shows a thin foil of Fe-Cu (at 100kV) from which Cu precipitates have been dissolved by preferential attack. A thicker section seen at 500kV, shown in Fig. 2b, reveals the true distribution of precipitates along with a network of interconnecting dislocations. Even more so than the $\{310\}$ plate precipitates in Fig. 1, these needle precipitates appear to lie along random directions in the matrix. This may seem surprising since both matrix and precipitate have cubic (bcc and fcc) crystal structures and could have many common symmetry elements. However, the orientation relationship is such that none of the high symmetry axes coincide exactly. Therefore, the common symmetry is low and the number of variants high. In a low-index matrix zone axis the crystallographic nature

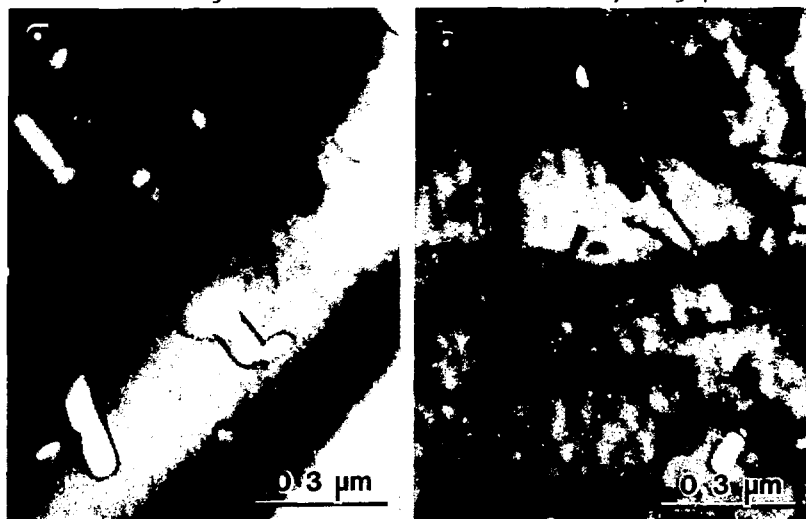


Fig. 2. Needle precipitates of Cu in an Fe-2%Cu alloy. Thin foil transparent at 100kV (a) shows precipitates etched-out by electrochemical thinning. In (b) a thick foil transparent at 500kV shows the true distribution of precipitates and defects.

of the needle directions becomes more apparent. Fig. 3a shows precipitate needles in an Fe-Cu alloy in an $\langle 001 \rangle$ projection. Even though variants in many slightly different orientations, all inclined to the beam direction, are present they clearly cluster near two directions at right angles in this projection. When this is compared to the symmetrically inverted case of bcc (Cr) precipitate needles in an fcc (Cu) matrix in the same $\langle 001 \rangle$ projection (Fig. 3b) an important difference is seen. The Cr needles cluster near four directions at 45° to each other. The precise needle directions may be determined by trace analysis on individual particles or, more accurately and directly, by measuring angles between needle axes in high-symmetry orientations of the matrix crystal. The needle directions so determined are $\langle 776 \rangle$ (clusters around $\langle 111 \rangle$) for Cu in an Fe matrix and $\langle 761 \rangle$ (clusters around $\langle 110 \rangle$) for Cr in a Cu matrix [2].

The reason why these precipitates assume such a low-symmetry orientation relationship with the matrix instead of a cube-cube relation or others is not dependent on crystal symmetry but on the mismatch between the two lattices which can be minimized if the transformation is an invariant line strain. This requires an orientation relationship near the Kurdjumov-Sachs relation which in turn leads to a large number of precipitate variants resulting in a random appearance in their distribution.

It has also been pointed out that any other factors that influence a precipitation process will impose their own symmetry on the final microstructure [1]. This is illustrated in Fig. 4a which shows an Fe-N alloy that was aged under a tensile stress. While crystal symmetry allows three different variants, the superimposed stress lowers the total symmetry, making the one variant perpendicular to the stress direction different from the other two. However, which of these non-equivalent variants form, those parallel or those perpendicular to the stress axis, is not determined by symmetry, but depends on the relative sign of applied stress and transformation strain. In the case of Fe-N shown in Fig. 4a, the tensile stress has aided the formation of the one variant perpendicular to the stress axis [3]. In Al-Cu, θ' is undersize relative to the matrix and the opposite behavior is seen—a tensile stress will oppose the formation of the perpendicular variant, and favor the other two. The same principle applies to any other interaction with the precipitation process such as magnetic fields, temperature gradients, concentration gradients, etc.: the total symmetry is that common to all the factors of influence but the specific microstructure depends on their sign and magnitude.

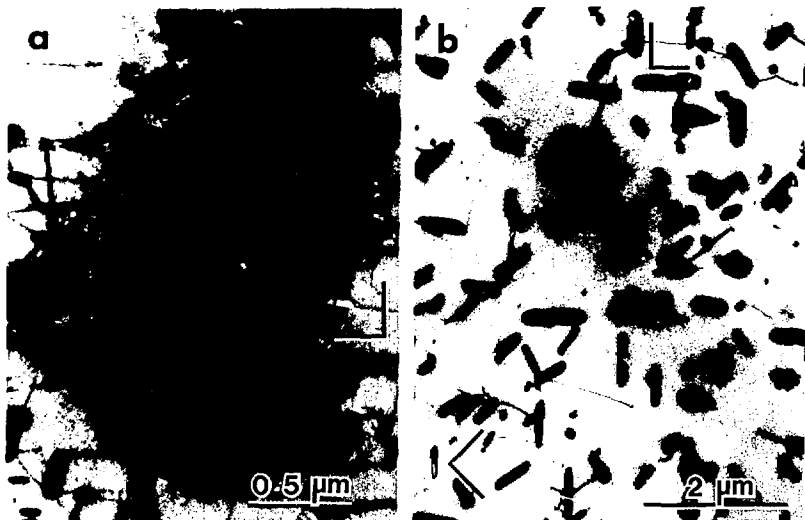


Fig. 3. Comparison of needle precipitate distributions in Fe-Cu (a) and Cu-Cr (b), both seen in an [001] projection. In (a) the Cu needles cluster in two groups at right angles, in (b) the Cr needles cluster in four groups at 45° to each other. The two precipitation systems are structurally inverted, i.e. fcc precipitates in bcc matrix (a) and bcc precipitates in fcc matrix (b) with negligible change in lattice parameter ratio.

These relations can also be used in the converse way. The symmetry of an observed precipitate or defect distribution contains information on the factors involved in their formation. Fig. 4b shows an example of a distribution of γ' precipitates on $\{210\}$ planes in ferrite. Clearly, some variants occur more frequently than others. This distribution was influenced by the free surface of the thin foil because the precipitates were formed by in-situ aging. Even though the shape and orientation of these precipitates are identical to those obtained by bulk aging, their distribution reveals the influence of the free surface.

CONCLUSION

Symmetry relations between the shape, direction and distribution of precipitates in a crystalline matrix can be seen particularly clearly in thick foils used in the HVEM. High-symmetry orientations lead to high-symmetry shapes and easily recognizable variants while low-symmetry orientations result in many precipitate variants easily mistaken for random distributions. Examples have been given which illustrate the increasing complexity of precipitate distributions in a cubic matrix with decreasing composite symmetry of matrix and precipitate using examples of precipitates characterized by $h00$, $hk0$, hkk and hkl indices. The symmetry of external factors influences the total distribution of precipitates but a quantitative assessment of such influences cannot be made from symmetry arguments alone. Symmetry requirements provide a framework within which precipitate morphologies develop but the specific microstructures are determined by the transformation stresses, strains and mechanisms.

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Fig. 4. Influence of external factors on precipitate distributions. In (a) an applied stress has suppressed two of the three α'' variants in a stress-aged Fe-N alloy. In (b) the preference for some variants of the bulk $\{210\}$ γ' precipitates in Fe-N indicates the influence of the foil surfaces during in-situ aging.

HVEM IN-SITU STUDIES OF PRECIPITATE COARSENING AND DISSOLUTION IN A Pt-C ALLOY

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ABSTRACT

The dissolution of thin {001} carbide precipitates in Pt during in-situ annealing in a high voltage electron microscope was found to proceed at a constant rate which was markedly different for α and α' precipitates. At the same time, the beginning of the transition from the α to the α' stage of precipitation was observed in thick foil sections corresponding to established bulk behavior. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

INTRODUCTION

The advantages of the high voltage electron microscope for in-situ studies of phase transformations are well-recognized [1]. Not only does the greater available specimen chamber space make stage construction easier, but with flexibility in the selection of the accelerating voltage, foils of various thicknesses can be studied above or below the damage threshold. This is particularly important in investigations of precipitate growth, transition, or dissolution. In certain alloy systems the observed behavior is found to be markedly dependent on thickness, and superimposed radiation effects can be significant. There are several ways in which the behavior is influenced by the proximity of the foil surfaces. In some alloy systems, e.g., Al-Cu, in-situ dissolution of an intermediate phase occurs because a concentration gradient of solute atoms to the surface is maintained by the surface formation of the equilibrium θ phase. In other alloys, e.g. Fe-N, the solute gradient to the surface is maintained because the interstitial solute atoms diffusing to the surface are evaporated (as N_2) into the microscope vacuum. Platinum-carbon typifies a class of alloy in which formation, growth, transition and dissolution of a carbide phase occurs by a vacancy mechanism. In this case, dissolution is observed in thin regions of the foil because the surfaces are good sinks for vacancies. Preliminary results of an in-situ investigation of annealing behavior in a Pt-0.08 at % C alloy are presented in this paper.

In Pt-C the formation of a Pt_7C_3 intermediate metastable (α') carbide is preceded by a semi-coherent "GP1" zone stage (α) [2]. The purpose of this study is to explore to what extent the course of the precipitation reaction, including the transitions, can be followed in-situ, and to compare the relative stability of the zone and precipitate phases. Fig. 1 is a schematic diagram depicting the predicted behavior in a wedge-shaped foil. Below a critical thickness t_c , which will depend on the annealing temperature and the precipitate size and spacing, the surfaces are the dominant sink for vacancies and only dissolution is observed. When $t > t_c$ the diffusion zones of the precipitates overlap in the foil interior and the possibility of observing the transition and coarsening stage exists. Thus by varying the foil thickness, information on dissolution and coarsening can be obtained separately.

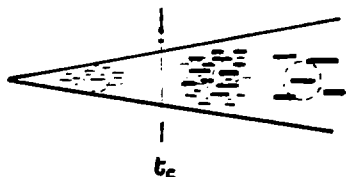


Fig. 1. Schematic representation of the effect of foil thickness on annealing behavior. The large and smaller broken circles represent the diffusion field at temperatures T_2 and T_1 ($T_1 < T_2$) respectively.

EXPERIMENTAL

Foils of the as-received Pt containing 0.08 at% C were quenched from the melting point in ultra-high vacuum and aged at various temperatures in the range 25-500°C to form precipitate structures at different stages in the sequence. Thin foils for microscopy were prepared by standard methods. The in-situ annealing runs were performed in the Kratos EM1500 HVEM at several temperatures and accelerating voltages. Dynamic sequences recorded on video tape using a Betamax 1/2" tape system were periodically interrupted to record a conventional film exposure for increasing the accuracy of subsequent data analysis.

RESULTS

A typical sequence illustrating the dissolution of the GP zone type precipitates during isothermal annealing at 725K (452°C) is shown in Fig. 2. It is apparent that the precipitates, regardless of their location in the foil, shrink in a regular and uniform manner. This is confirmed from the shrinkage data for representative precipitates also given in Fig. 2. In all cases, the plots are linear and an average shrinkage rate of 0.01nm sec⁻¹ was obtained. The effects of foil thickness were strikingly apparent in this experiment. Following the dissolution of all the precipitates in the thin edges of the foil, an examination of the thicker interior regions revealed that virtually no changes in microstructure had occurred there, Fig. 3. Subsequent experiments were designed to observe the transition from the GP zone stage to the true precipitate (Pt₂C) stage by concentrating on the thick regions of the foil. However, some problems were encountered. A deterioration in transmission through the foil was observed at the annealing temperature making direct observation difficult, and the need to avoid radiation damage limited the maximum usable voltage [3].

Nevertheless, examination of the foils following cooling to ambient temperatures showed evidence of the transition in progress (Fig. 4a). For comparison the same stage observed in a bulk-aged and subsequently thinned specimen is shown in Fig. 4b. In both micrographs the contrast difference between the inner disc and outer annulus of the precipitate plate is consistent with that expected for the $\alpha \rightarrow \alpha'$ transition [2].

To compare the stability of the α and α' precipitates, isothermal annealing sequences were performed on α' plates formed during prior bulk-aging. An abbreviated sequence of micrographs is shown in Fig. 5 and the corresponding precipitate radius versus time plot in Fig. 5e. In order to obtain shrinkage rates comparable to those found for the α precipitates (Figs. 2,3) an increase in annealing temperature of 60°C was necessary. This is consistent with the increased stability of the α' Pt₂C precipitates relative to the α GP zones. Preliminary results indicate the α'' precipitates which follow α' in the sequence are even more stable and do not dissolve readily at temperatures as high as 600°C.

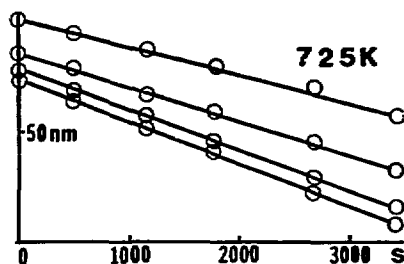
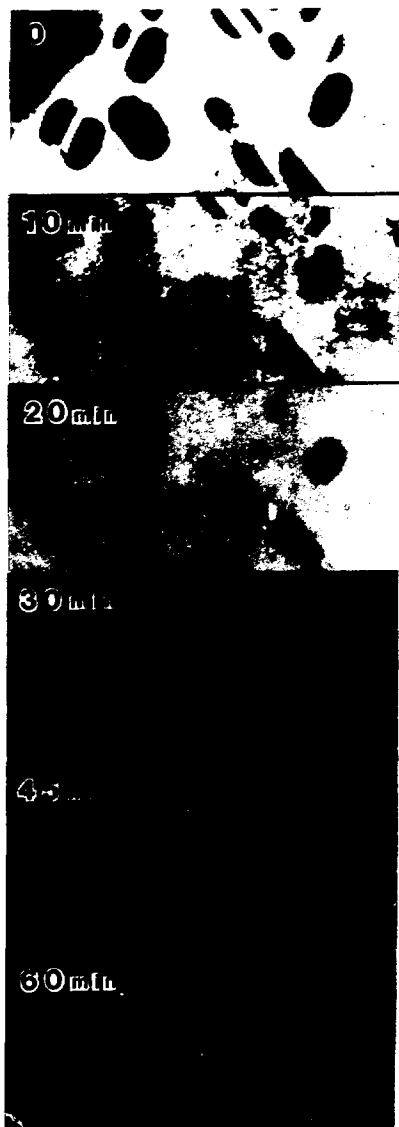


Fig. 2. Isothermal annealing sequence showing dissolution of α precipitate plates at 725K. The uniform, regular shrinkage behavior is reflected in the linear radius versus annealing time plot.



Fig. 3. Micrograph showing unchanged microstructure in thicker regions of foil following in-situ annealing at 725K.

SUMMARY AND CONCLUSIONS

Precipitate structures in thin and thick regions of a foil exhibit markedly different behavior during in-situ isothermal annealing. Studies in the thin regions allow the relative stability of different metastable phases to be assessed. Higher temperature annealing studies of thicker foil sections indicate the possibility of directly following metastable phase transitions and coarsening phenomena.

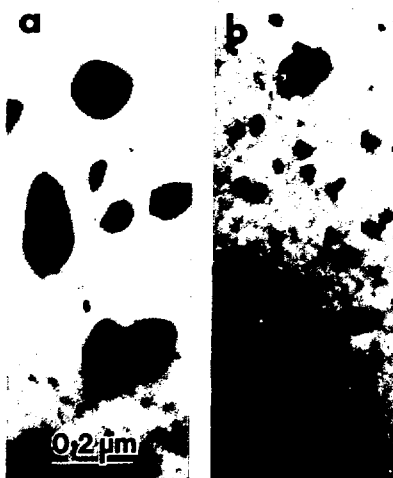


Fig. 4. The transition from $\alpha \rightarrow \alpha'$ observed for some precipitates in thick regions of the foil during in-situ annealing (a); similar examples in bulk annealed and subsequently thinned foil (b).

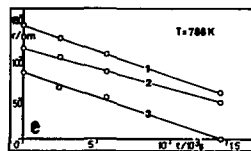
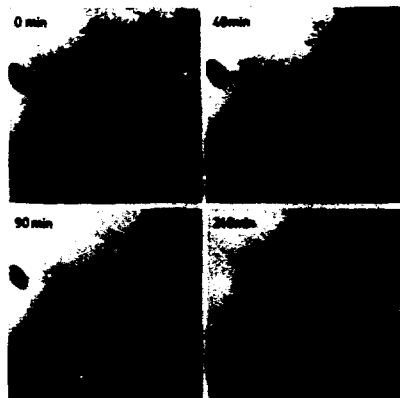


Fig. 5. Isothermal annealing sequence (a-d) of α' precipitates at 788K (515°C) and corresponding graph in (e).

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STRUCTURE OF ELECTRODEPOSITED CHROMIUM

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ABSTRACT

The effect of plating conditions on the columnar grain structure of electrodeposited chromium, the nature of the residual stresses, and the distribution of entrapped plating solution (H_2CrO_4) have been studied using high voltage and scanning electron microscopy and electron and ion beam microanalytical techniques. A low temperature and/or low current density result in the formation of very small grain diameters ($\sim 0.1 \mu m$), a strong $\langle 111 \rangle$ fiber texture, large internal stresses ($\sim 1\%$), and up to 2% trapped electrolyte. This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 and the Department of the Army (ARRADCOM), Watervliet Arsenal.

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INTRODUCTION

Chromium coatings, 5-100 μm in thickness, are widely used to improve corrosion and wear resistance. Plating conditions, i.e., both temperature and current density, determine the appearance and hardness of the electrodeposit, e.g., with 30 amps/ Dm^2 at 55°C it is hard (1150 KHN) and bright, whereas with 120 amps/ Dm^2 at 85°C it is somewhat softer (550 KHN) and dull. Electrodeposited chromium is also characterized by (1) the occurrence of large tensile stresses in the exposed surface side that often result in extensive cracking and peeling from the bumper or whatever else it was intended to protect, and (2) a substantial amount of entrapped plating solution [1,2,3,4].

EXPERIMENTAL RESULTS

A representative 1000 KV transmission electron micrograph of a stripped and ion-thinned sample of hard, bright chromium plating is shown in Figure 1. The 0.1 μm diameter grains (in cross section) exhibit a strong $\langle 111 \rangle$ fiber texture along their columnar axis and contain a dislocation density of about $2 \times 10^{11}/cm^2$. The grains in soft, dull chrome plate are 15 to 25 times larger, exhibit a much weaker texture and contain about 3×10^9 dislocations per cm^2 .

Various methods of chemical analysis reveal that fine-grain chromium coatings contain about 2% chromium hydrate, whereas this amount is reduced by about a factor of 20 in coarse-grain samples. Heating electrodeposited chromium at 800 to 900°C results in recrystallization, 1 to 2% shrinkage of the film, the relief of tensile stresses through the formation of numerous cracks, the evolution of hydrogen and the formation of Cr_2O_3 particles, as illustrated in Figure 2. It appears that the void space in the unequilibrated intercolumnar grain boundaries contains oxygen and hydrogen (possibly as adsorbed H_2O), resulting in a tendency for the film to shrink as the hydrogen is absorbed by the highly dislocated metal lattice.

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0.2 μm

Fig. 1. Dark field TEM (1000 KV) showing cross section of columnar grains in hard, bright electrodeposited chromium.

Fig. 2. Bright field TEM illustrating formation of coarse grains and Cr_2O_3 particles during heating at 875°C.

IN SITU OBSERVATION OF THE COLLECTIVE MOVEMENT OF PARTIAL DISLOCATIONS (MICROTWINNING)

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ABSTRACT : From dynamic recording of partial dislocations propagating on superposed glide planes some characteristics of the microtwinning process are analyzed : the propagation, intersection and characterization of the observed microtwins are discussed, correlation with the macroscopic behaviour of the sample is attempted.

In order to understand the microscopic origin of the instabilities observed during plastic deformation of numerous copper-base alloys, with a low stacking fault energy (γ), in situ straining experiments have been undertaken at a temperature $\sim 480\text{K}$ ($\approx 0.5 T_m$) on a Cu-6.5 at% Si alloy ($\gamma \approx 15 \text{ mJ/m}^2$). In these conditions the microscopic stress-strain curves present serrated yielding for a large scale of deformation rates ($0.28 \cdot 10^{-4} \text{ s}^{-1} < \dot{\epsilon} < 5.56 \cdot 10^{-4} \text{ s}^{-1}$) while the micrographs of the same samples show that deformation proceeds by partial dislocations on superposed glide planes. This deformation mode is generally called "the microtwinning mode" even though we are far from true crystallographic microtwins (MT) (1)(2). We have tried to examine in more details this effect, frequently observed in alloys, using "in situ" deformation experiments in a HVEM (accelerating voltage 800 kV).

The deformation dynamics was recorded in two contrast conditions for a wide area of the microsample ($100 \mu\text{m}$)³. The deformation elementary mechanisms were isolated and evaluation of their contribution to the whole deformation yields the following result : 98% of the deformation is due to microtwinning concentrated in 3% of the volume sample (expressing a great inhomogeneity), while individual displacements of partial dislocations are of little importance (these appear on the contrary rather homogeneous) (3). On the four micrographs of fig. 1 we may observe in detail how deformation proceeds in a, b, c, we have three successive states of the same area ($\vec{g} = [11\bar{1}]$), d presents the final state ($\vec{g} = [200]$). The observed microtwin A belongs to $(11\bar{1})$ glide plane, the different partials 1, 2, etc... which make it up, are observed to propagate during straining : for example partials 4 and 5 or 7, 8 and 9 are superposed in 1-a while they are pulled away in 1-b. This microtwin A is cut along $[10\bar{1}](11\bar{1})$ (in JL, I) by other partial dislocations, as can be seen on fig. 1-d. Their Burgers vector is probably lying near the foil plane $\vec{b} = \pm \frac{1}{6} [21\bar{1}] = \pm (A\gamma)$, otherwise we would observe a breaking of the microsample, since, from the measured step in K fig. 1-c, ~ 840 partials have crossed there. During this intersection new partials are emitted in the first microtwin A (in M fig. 1b, in N fig. 1c), which acts as the obstacle. We have already analyzed in detail (4) this intersection mechanism where the first partials of the incident MT are used to create "a window" in the MT obstacle.

Now, comparing the shear step observed in D with the measured thickness d (fig. 2-a,b) we may try to give an argument in the discussion between the supporters of ordered microtwins (5) and of disordered ones (1,2). Fig. 2-a shows, at a high magnification, the shearing step sketched fig. 2-b ; the thickness d and the shearing amplitude D were measured on the micrograph. The corresponding ratio is $D/d = 0.8$. Then we calculated the theoretical value D/d when the constitutive partials of the MT are followed by intrinsic faults (i) or extrinsic ones (e), creating either a perfect MT or a thin plate of hexagonal compact phase ; we obtain :

$$D = n_i b \cos \alpha \quad \text{and} \quad d = n_i d_{111} \quad \text{if we have intrinsic faults}$$

$$D = n_e b \cos \alpha \quad \text{and} \quad d = 2n_e d_{111} \quad \text{if the faults are extrinsic ones}$$

$$\text{so } \left(\frac{D}{d}\right)_i^{\text{MM}} = \frac{b \cos \alpha}{d_{111}} = 2 \left(\frac{D}{d}\right)_e^{\text{MM}} = 2 \left(\frac{D}{d}\right)_e^{\text{h.c.}}$$

TABLE 1

$\frac{D}{d}$	faults	
	intrinsic	extrinsic
ordered MT	0.7	0.35
h.c thin plate	0.35	//////
experience	0.8	

Table 1 summarizes the results.

From the obtained experimental value the observed MT seems to be rather perfect and the constitutive defects are intrinsic ones. The same result is obtained when using the FS/RH convention (fig. 2-d)

So, in this alloy, the flow stress instabilities appear to be connected to the collective movement of hundreds of partial dislocations propagating on superposed glide planes and pulling intrinsic faults. At this temperature the wide spreading of the defects seems to be premonitory of the f.c.c. $\rightarrow$ h.c.p. phase transformation while a pronounced Suzuki effect which was previously evidenced (6) favours it.

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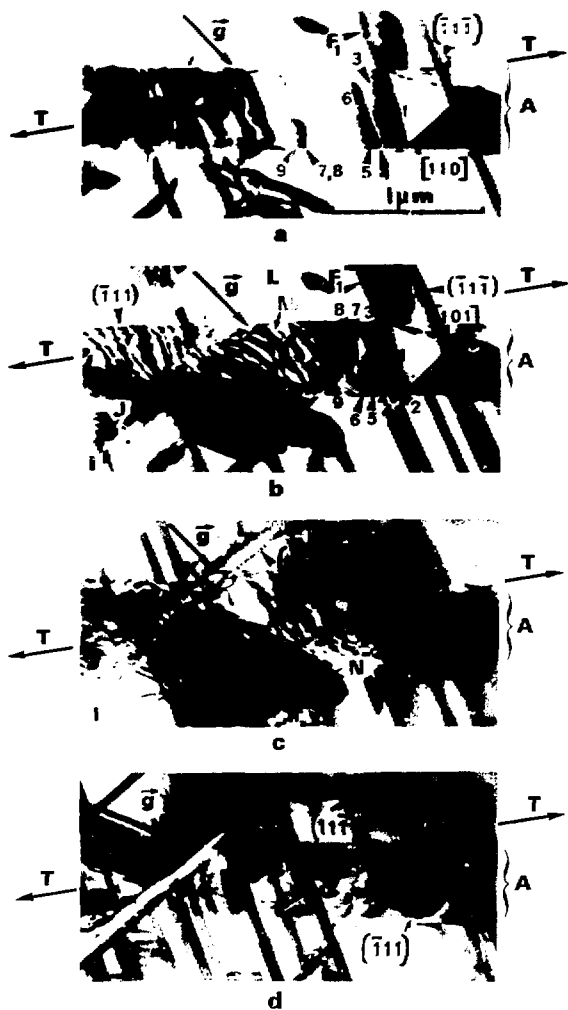


Fig. 1 - Cu 6.5 at% Si - $T = 480$ K

Dynamic sequence of collective movement of partial dislocations in a microtwin A. a, b, c, three successive deformation states. d, final state, the whole deformation is around 4% ($\epsilon = |\bar{2}00|$)

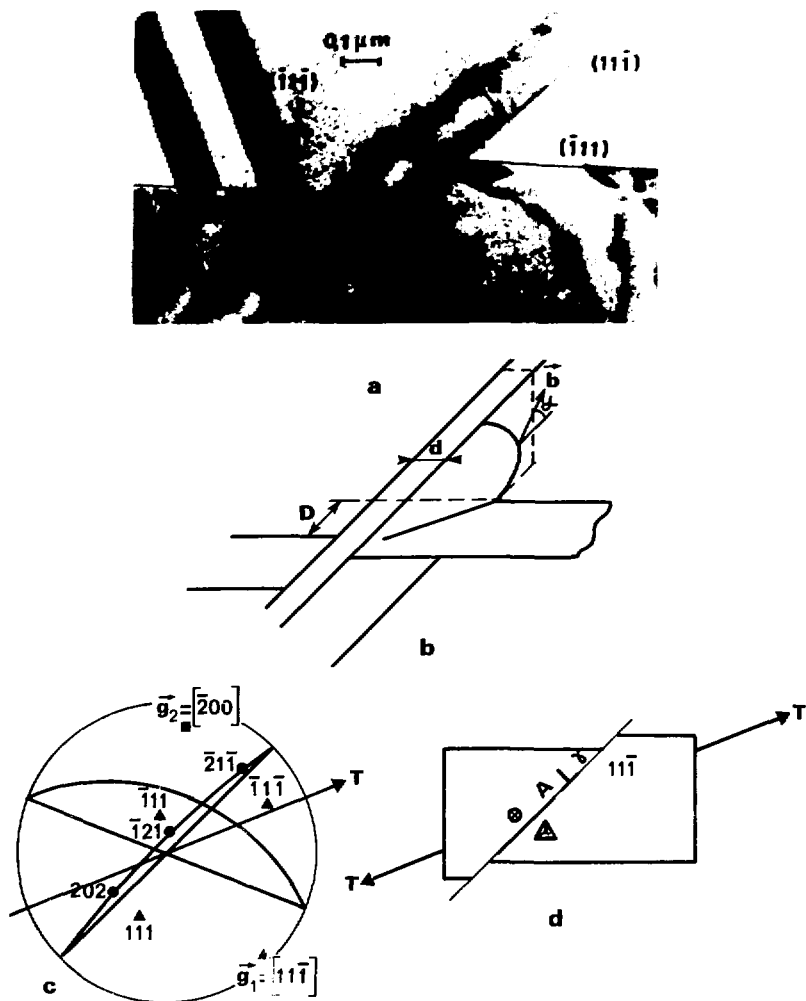


Fig. 2 - Cu 6.5 at % Si - $T = 480$ K

This micrograph provides a comparison between the thickness d and the shearing step D of a microtwin created during "in situ" deformation. a) magnification of the sheared area ; b) sketch of the same area ; c) corresponding stereographic projection ; d) the FS/RH convention is used to determine the nature of the stacking faults involved in the microtwin.

HVEM STUDY OF Nb_3Sn MULTIFILAMENTARY SUPERCONDUCTING WIRES

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ABSTRACT

The HVEM has been used to investigate the microstructure of Nb_3Sn multifilamentary superconducting wires using both transverse and longitudinal sections. Complete Nb_3Sn and bronze grains and the $\text{Nb}/\text{Nb}_3\text{Sn}$ and $\text{Nb}_3\text{Sn}/\text{Cu-Sn}$ interfaces have been viewed at the same time. The effects of different heat treatments have been studied and the resulting microstructures found to be significantly different from previous descriptions.

INTRODUCTION

Compounds of the Al_5 type, with their high critical parameters, have been the leading superconducting materials for the last two decades. Multifilamentary Al_5 superconductors produced by the 'bronze route' [1, 2] or other methods such as in-situ and powder methods [3], have been the subject of intensive research in many laboratories, and have been strong candidates for fusion, high energy physics and many other applications. In the 'bronze route' Nb rods are reduced to final filament sizes desired in a Sn -bronze matrix and then heat treated to form the superconducting $\text{Al}_5 \text{Nb}_3\text{Sn}$ compound. The superconducting properties of this material are very dependent upon the metallurgical properties of the compound [4, 5]. There have been many attempts to improve the critical parameters, especially the critical current density J_c , by altering the processing conditions and/or heat treatment conditions [6, 7]. Therefore the microstructure of this compound must be well characterised through representative sections and the mechanism by which the microstructure is produced understood, in order to adopt appropriate alteration in the processing to achieve even higher critical parameters. We describe, in what follows, the microstructural results obtained by using HVEM.

EXPERIMENTAL

Short lengths of Nb_3Sn wires, produced at Harwell [8] by the bronze route, containing 5143 filaments ($\sim 6\mu\text{m}$ in diameter) were encapsulated in quartz tubing and heat treated for varying times and temperature under atmospheric argon pressure. Transverse and longitudinal TEM specimens were prepared using a set of techniques, applicable also to other composite materials, described elsewhere [9]. There has been considerable microstructural work on this material by other workers, unfortunately based on only longitudinal sections and some incorrect results have been obtained [10]. Since the Nb_3Sn layer is grown by a radial diffusion process around each niobium filament at the $\text{Nb}/\text{Cu-Sn}$ interface, the microstructure is likely to vary along this direction. Longitudinal sections alone are therefore quite likely to produce misleading

results. For a true picture to be built up complementary use must be made of both transverse and longitudinal sections. In all of the samples transverse or longitudinal examined in HVEM there were several filaments penetrable by 1MeV electrons including both of the interfaces, Nb/Nb₃Sn and Nb₃Sn/(Cu-Sn) - see figs. 1, 2, 4(a) and (b).

RESULTS AND DISCUSSION

In the unreacted wires there is a very thin layer of very fine grained Nb₃Sn which is thought to have formed during wire drawing anneals [11, 12]. (See also fig. 1). During the usual formation heat treatments (~700°C for a few days) these preformed fine grains grow abnormally at some parts of the filaments and can decrease the critical current density of the wire. If hot extrusion is employed during wire production thicker layers can form, which break during later reductions and cause problems.

At normal heat treatment temperatures (~700°C) the grain structure of the layer is as follows:-

1. The Nb/Nb₃Sn interface is somewhat diffuse during the early stages of reaction and sharpens up after a day or so. Nb₃Sn grains are usually small and equiaxed at this interface, occasionally elongated in the radial direction, and sometimes intruding into the Nb core;
2. There is usually some elongation of grains in the middle of the Nb₃Sn layer along the radial, or rather Sn flux, direction (see also fig. 2); these grains are larger than those at the inner interface.
3. The grains closer to the Nb₃Sn/(Cu-Sn) interface are even larger and equiaxed. These equiaxed large grains are not uniform around the outer periphery of the Nb₃Sn layer. Their occurrence is found to be dependent upon the shape of the filaments. It is quite likely that these large grains are those which were preformed during process annealings (~550°C for a few hours) [8] for workability, growing abnormally large during the final heat treatment [12]. It seems that not all of the preformed Nb₃Sn grains can grow; while those at the protuberances are inhibited from growth, those at the indentations grow abnormally (see figure 3). This might be due to the stress fields set up by the diffusion and volume expansion taking place during the formation of Nb₃Sn.

Electron microprobe investigations have shown that there is a minimum residual Sn concentration left in the matrix after very long reaction time at a given reaction temperature. Therefore there is a maximum full reaction attainable for a given reaction temperature and a given Nb to bronze ratio, and this residual Sn concentration in the matrix is inversely proportional to the reaction temperature [13].

At lower reaction temperatures (~650°C) the overall morphology of the grains is similar to what has been described above but elongation of the grains is not significant, and, of course, the average grain size is smaller (see fig. 4(a)). At higher reaction temperatures (~850°C) all the grains are equiaxed and elongation has disappeared (see fig. 4(b)). To achieve the full reaction described above at the lower end of the reaction temperature one needs days, and at the higher end a few hours.

An attempt was made to observe the migration of the interfaces and grain growth 'in-situ' by using the hot stage in HVEM without much success, due to

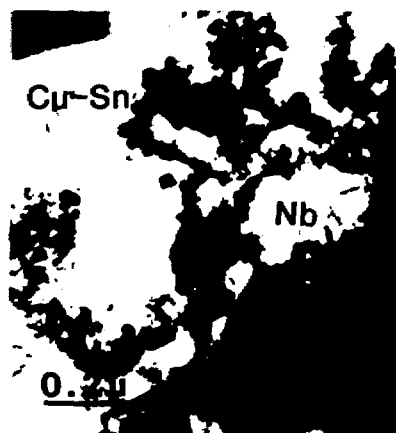


Fig. 1 TEM (HVEM) micrograph of a transverse section of an unreacted wire. Some fine grained Nb_3Sn layer is present and must have been formed during process annealings (1MeV).



Fig. 2 HVEM micrograph of the same wire as in figure 1, taken from a transverse section after reaction of 3 days at 700°C . The elongation of the grains in the middle of the layer is evident along Sn flux direction (1MeV).



Fig. 3 HVEM micrograph of the same wire as above taken from a transverse section after a reaction of 4 days at 700°C . The finer grains at A indicate inhibited growth at a protuberance. Abnormally large grains are present at an indentation B (1MeV).

maybe oxidation and surface diffusion and evaporation of Sn.

Parallel sets of critical current measurements have been made and will be published elsewhere [7].

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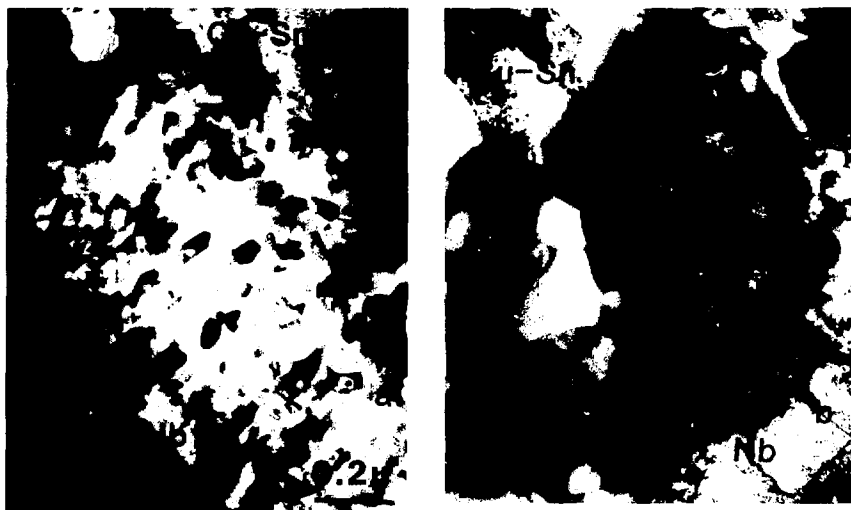


Fig. 4 HVEM micrograph of the same wire taken from a transverse section after a reaction of a) 6 days at 650°C, b) 6 hours at 850°C (1MeV).

A STUDY OF DISLOCATIONS WITH A VERY LARGE MEAN FREE PATH

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ABSTRACT

The mean free path of dislocations in crystals becomes larger than the maximum observable thickness with HVEM under serious conditions. Wide regions of the order of 1mm^2 can be observed with HVEM when the specimen thickness is controlled to be slightly larger than the critical one which is sufficient to observe the same density and distribution of dislocations as in bulk specimens. In the present experiment, this method has been applied to study the work hardening process of Cu-Al alloys, and self-hardening and self-recovery processes of the slip bands have been found out. Based on these results, the cause of fracture under various conditions such as plastic, fatigue and creep deformations are discussed.

INTRODUCTION

In situ experiments on the behavior of dislocations in metals and alloys have been carried out under various conditions[1,2]. The results obtained show that the specimen thickness must be larger than the mean free path of dislocations in order to observe the same behavior as in bulk specimens. When the stacking fault energy is not so small, the processes of deformation, such as the yield and the work hardening phenomena, have widely been clarified under various deformation conditions[1]. The mean free path of dislocations, however, increases more than the maximum observable thickness with HVEM under the following conditions: a) At very early stages of deformation. b) Deformation under very low stress levels as in the fatigue and creep ones. c) When the stacking fault energy is very low. These conditions become more serious at low accelerating voltages of HVEM.

It has been shown that the mechanical properties of materials are determined by the heterogeneity of deformation [3]. The cause of various sorts of fracture such as ductile, fatigue and creep ones is also closely related to the heterogeneity of deformation, especially to the difference of dislocation structures in individual slip bands which are determined by the dislocation behavior at the very early stage of deformation. Therefore, it is very important to study the details of dislocation behavior under the conditions mentioned above.

The observable thickness remarkably increases with increasing accelerating voltage, and thus wide regions of the order of 1mm^2 in the specimens can be observed at the same time with HVEM[2] when the specimen thickness is controlled to be slightly larger than the critical one which is sufficient to observe the same density and distribution of dislocations as in bulk specimens. Since the critical thicknesses for the static observation mentioned above is always smaller than those for the in situ experiments[4], this advantage of HVEM make for a lack of the maximum observable thickness. In this method, in situ experiments should be used for characterization of the dislocations and dislocation structures after the specimens were deformed in order to decrease the mean free path of dislocations.

In the present experiment, the observation of wide regions has been carried out on the work-hardening process in crystals with low stacking fault energies with a Hitachi HU-3000 type 3MV electron microscope, and the cause of

localized deformation is discussed.

EXPERIMENTAL RESULTS

Cu-10at%Al single crystals were stretched up to fracture, about 170% strain, and the observation of both slip bands and the corresponding dislocation structures were carried out by both optical and electron microscopies, and electron microscopy, respectively. Figure 1 is a part of an electron micrograph showing the dislocation structures in a specimen deformed to 10% strain.

The deformation process obtained in the present experiment is illustrated schematically in Fig.2[6] in which the crystal orientation (left), distribution of the slip bands (middle), and distribution of the dislocations (right) are shown at each strain. Furthermore, elongated ellipsoids show the planar dislocation tangles.

[A] Reaction between the Primary and the Conjugate Dislocations

When the density of primary dislocations increases, the reaction between the primary and the conjugate dislocations markedly occurs, and the hexagonal networks of dislocations are frequently formed, as seen in Fig.3. In this case, each conjugate dislocation intersects many primary dislocations on the primary slip plane. The newly formed dislocation segment of the three-fold node of dislocations is arranged nearly along the $\langle 110 \rangle$ intersection, and the primary dislocation segments are shifted along the $\langle 110 \rangle$ intersection, as seen in Fig.3. The Lomer-Cottrell sessile type dislocation arrangement, $\frac{1}{2}a_1 + \frac{1}{2}a_2$, is hardly observed at any strain.

Self-Hardening of the Slip Bands

When the screw dislocations pile up against the obstacles such as the hexagonal network of dislocations and the planar dislocation tangles, the leading dislocation of the pile-up ones make cross slip[5] into fresh regions where the dislocation density is very low. This process is repeated in both sides of the pre-existing slip band and causes the widening of the slip band.

The dislocations on the new slip band interact with those on the original slip band and form the condensed dislocation multipoles, as seen in Fig.1. The dislocation multipoles are mechanically stabilized by the reaction with the conjugate dislocations, and planar dislocation tangles, Figs. 1 and 3, are frequently formed. Namely, the slip bands are self-hardened by this process.

[C] Dislocation Interaction due to Relative Shift of the Slip Bands Induced by Slip of a Different Family

In Figs.4 and 5, secondary slip plane(s) run across primary slip bands ($p_1, p_2, \dots$) successively at points $a_1, b_1, \dots$, and the secondary dislocations are dispersed on primary slip bands. This process is one of the most effective process of the work-hardening of primary slip bands, because many conjugate dislocations hit the primary dislocations in a wide range, b_1-b_2 in Fig.4, on each individual primary slip band. On the other hand, the stress concentration due to the pile-up conjugate dislocations does not occur against primary slip bands when primary slip system is markedly activated. The latent hardening of the secondary slip results from this process.

[D] Self-Softening of the Slip Bands

When primary slip bands are effectively work hardened, the conjugate dislocations pile up against these sterile primary slip bands, and then finally they can move through the latter, as seen in Fig.4, when the number of pile-up conjugate dislocations reaches the critical one. This is the beginning of long path of the conjugate dislocations. In this case, the following two processes occur, as seen in Fig.6: a) Sterile slip band S_1-p_1 is reactivated so that the primary dislocations can easily move to the left side, Fig.6(b),

when the right side crystal bounded with the secondary slip band(s) is shifted upwards. b) Unlike dislocation groups, which ride on slip bands S_1 -p, and S_2 -p, respectively, are rapidly annihilated when the right side crystal is shifted downwards to coincide the level of both slip planes with each other, as shown in Fig.6(c). The following shear strain(γ) is caused on slip band S_1 - S_2 by this process in a very short time; $\gamma = nLb$, where L , n and b are the distance between two dislocation sources on the slip band, the number of annihilated dislocations of each sign, and the Burgers vector of the dislocations. Namely, the work-hardened primary slip bands are self-softened by this process, and the long path of conjugate dislocations is promoted, as shown in Fig.2(e).

[E] Enhancement of Local Deformation

As mentioned above, the work-hardened slip bands are reactivated at the later stages of deformation. In this case, other slip bands in the surrounding matrix are still work-hardened and the stress level is generally very high. Therefore, the local deformation is markedly promoted in the reactivated slip bands, and finally the fracture takes place. Furthermore, the slip bands formed at the very early stage of deformation have simple dislocation structures consisting of the unlike primary dislocations, because the secondary slips are not activated sufficiently. This is a reason why, the self-softening of slip bands preferentially occurs on such slip bands. The self-softening process also occurs in crystals with high stacking fault energies in which the obstacle barriers in the slip bands become small at the beginning of deformation[1]. Therefore, the fracture in fatigue and creep deformation originates in the slip bands formed at the beginning of deformation[7].

Observation of wide regions with HVEM should effectively and widely be used more and more for studying dislocation behavior under serious conditions, as shown in the present experiment.

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Fig.1 Distribution of dislocations in a Cu-10at%Al single crystal deformed to 10% strain.

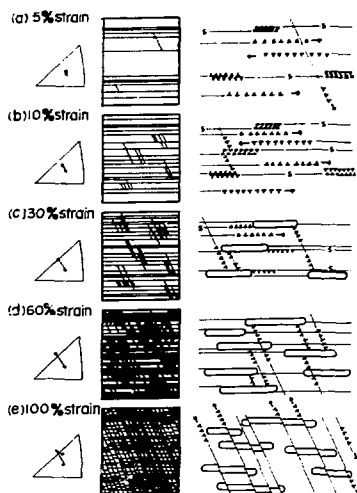


Fig.2 Deformation process at various strains. In the figures, crystal orientation(left side), distribution of the slip bands(middle) and distribution of dislocations(right side) are shown at each strain.

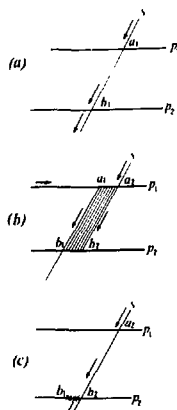


Fig.4 Effect of the primary slip on distribution of the secondary dislocations.

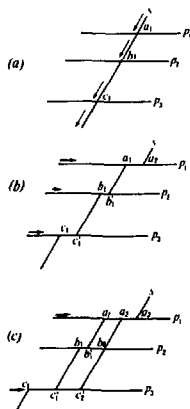


Fig.5 Effect of the primary slip on distribution of the secondary slip bands.



Fig.3 Formation of hexagonal networks of dislocations at 10% strain. At the left side(↑) in micrograph(b), the conjugate dislocations begin to move through the primary slip band which has many hexagonal networks of dislocations.

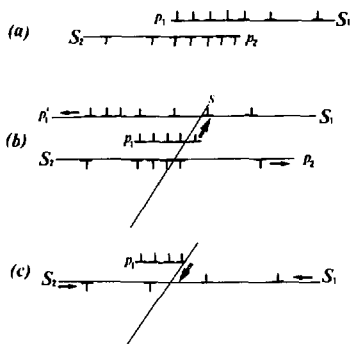


Fig.6 Reactivation process of the sterile slip bands induced by slip of different family. Deformation quickly proceeds by annihilation between unlike dislocations in figure(c).

USE OF HVEM FOR HIGH RESOLUTION BIOLOGICAL STUDIES

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ABSTRACT

Though the usefulness of HVEM for the study of biological thick sections and whole-mounts is widely recognized, the instrument has not been utilized to obtain high resolution ($<1.5\text{nm}$) images from biological samples. Soon after radiation damage was recognized as the prime limiting factor in high resolution biological EM [1], Howitt et al investigated the possibility that the problem might be less severe at higher voltages. Although results from electron diffraction pattern fading studies were encouraging [2], various practical difficulties prevented any concerted effort to pursue this possibility until recently:

- 1) Normal electron microscope films were relatively less efficient at the higher voltages, and this tended to nullify any possible advantage gained during the specimen-beam interaction.
- 2) The instruments available to biologists were not optimized for routine high resolution operation, particularly on cold samples.
- 3) The image available from the viewing screen lacked contrast and was difficult to focus at low magnification.
- 4) Facilities to implement minimal exposure techniques were not available. Recent efforts at the Madison HVEM Facility to overcome these problems are described below.

A FILM FOR LOW-DOSE HIGH RESOLUTION HVEM

Low-dose high resolution microscopy of periodic biological objects places great demands on the sensitivity and resolution of the recording emulsion and this is particularly so at high beam voltages where all emulsions exhibit reduced sensitivities.

The single thickness $20\mu\text{m}$ NTB-3 emulsion described here was recently evaluated at 100kV by Downing and Grano [3]. It was found to be very fast and, unlike x-ray films, very fine grained but the resolution was poor because of lateral scattering of the 100kV electrons in the thick, dense emulsion. At 1MeV, this scattering could be expected to be less. Using only the small scraps of film from an experimental $20\mu\text{m}$ thick production run and larger quantities of the more readily available $10\mu\text{m}$ thick emulsion, we have used optical diffractograms of images of thin carbon films to confirm that:

- 1) The resolution of the $20\mu\text{m}$ thin material is at least sufficient to record $.5\text{nm}$ information at 50kx (2x on film). As this performance equals our best performance by any film at this magnification, the ultimate performance may be even better.
- 2) The film speed bears the same relation to that of other emulsions at 1MeV which Downing and Grano found at 100kV (i.e. about 6x Kodak #4463) and as a result it is basically as good at 1MeV as other films are at 100kV. This film is expected to be produced commercially in the

near future and, when available, it will be the emulsion of choice for low-dose studies at 1MeV.

HIGH RESOLUTION OPERATION

Though the EM-7 was carefully designed, and could on occasion see graphite fringes, this was hardly a routine procedure. To improve this situation we have improved the stability of the high voltage and the objective lens current regulation and control and we have reduced the effect of stray field and vibration.

High voltage instability at 1MeV originally amounted to 5V, p-p at mains frequency and about 10V, p-p in the range DC - 10Hz. The former was reduced by better balancing of the power tubes, frequent tuning of the generator operating frequency and the AC gain and by the rerouting of sensitive wires. The latter has been improved by modifying the frequency response of the error amplifier. We now have about 2V p-p ripple and 6V p-p instability. We hope to produce a further improvement in the ripple by feeding an error-correction voltage to the HV terminal using a newly acquired capacitor and by replacing the present tube-type oscillator-modulator with an integrated circuit type such as is used in the Haefely supply for the Phillips 430.

The lens current regulation was originally about 3 ppm (DC - 10Hz) and this was improved to 1 ppm by replacing the reference supply with an LM-399 temperature-controlled zener diode. To realize this improvement during actual use, it was necessary to replace the analog Medium, Fine and Vernier focusing controls with a 16 bit DAC run by a rotary encoder and having a numeric readout of step number [4]. Mains frequency ripple was still a potential problem. It measured 30mV p-p out of 68V across the coil, while a current transformer inside several μ -metal shields showed about 30uA p-p out of 7.2A, but it was not clear how much of this current was being capacitatively transmitted vertically through the coil or dissipated as eddy current losses and how much would be producing a magnetic field at the gap. We settled on a 2100 μ F, 500V capacitor across the coil. This did not produce noticeable overshoot and it reduced the ripple to 1.5mV, a level comparable to the found on the Cambridge HREM, which uses the same lens coil.

Stray magnetic fields as small as .5m gauss RMS at the column between the objective lens and P_1 were found to reduce performance. To reduce this problem, we added several concentric layers of magnetic shielding material in this section, we shielded the transformer and scan coils of the television monitor, we became very sensitive to ground loops in associated equipment and all AC fans and solenoid-operated valves were switched to DC.

Vibration is probably the major environmental constraint at present, even though the microscope is mounted on a 60 ton block which is suspended on air bags having a 1 Hz resonant frequency. Initial efforts focused on reducing mechanical contact between the block and its surroundings. Although isolation, as measured by 8Hz geophones was improved about 3x, no marked improvement in performance was noted until recently, when we decoupled the upper platform and the column by replacing its semi-rigid vacuum coupling to the accelerator tube, with a long, welded-metal bellows and also began to use a new detachable tip stage rod. Using this stage we readily imaged the .204nm Au lattice using axial illumination and the optical diffractogram

shows spots at $.14 \text{ nm}$ in both directions. To help maintain optimum performance, a 6-channel chart recorder now monitors RMS magnetic field (x and y), vibration, lens current stability, and HV ripple and stability.

Any serious attempt to obtain high resolution results from biological samples must attempt to take advantage of the reduction in radiation sensitivity found when samples are kept near LN_2 temperature [5]. Consequently, a new high resolution cold stage rod is now nearing completion.

EM cold stages are usually cooled with boiling liquid nitrogen and it is therefore necessary to decouple the specimen from the vibration produced by this boiling and this is particularly troublesome in the case of side-entry stage rods which cannot be massively attached to the lens pole pieces. To reduce boiling to a minimum in the present design, great attention was paid to keeping heat leaks to the sample block to a minimum using four plastic point-contacts to mount it in the semi-detachable tip shell. The sample block is connected to the LN_2 by a short copper braid and a longer super-insulated copper rod which passes down the center of the outer rod to a permanently evacuated dewar at the outer end. The tip shell is connected to the heavy-metal outer rod by a bellows and, when in use, it is snapped into the inner ring of the microscope stage assembly [6]. This arrangement effectively shields the sample and the locating cone is filled with metal at approximately room temp.

The vacuum space of the dewar extends almost to the braid and is sealed on the inner end by a thin stainless tube between the outer rod and the copper conductor. After loading the sample, it is protected by two spring-loaded cold blades, above and below the sample. They can be pushed out of the way, using the axial pin in the cone, after the stage has reached equilibrium in the microscope vacuum. This stage is expected to have better than $.5 \text{ nm}$ resolution and $\pm 45^\circ$ tilt. To avoid contamination problems on cold samples, the chamber vacuum has been improved to 2×10^{-7} torr and two new anti-contaminators have been installed. The new units have a permanent dewar vacuum, and bring LN_2 into the column to within a few cm of the sample to ensure very low temperatures on the trapping surfaces above and below it.

FOCUSING ABILITY

We have made the microscope more easy to focus by adding a low light level TV interface and by improving the gun brightness. The lens-coupled TV system with attached frame-store and PDP-11/23 computer has been described before [7]. We have recently added a SKY array processor which reduces the time required for a 256×256 FFT to about 30 seconds and this has been used to correct astigmatism at high magnification. More recently, we fitted a similar TV camera to a 2:1 fiber-optic taper having 10 mg/cm^2 P-22 on its larger surface. Though 10 times more sensitive, this system had low contrast apparently caused by electron scattering in the phosphor and the substrate. We are about to use a 40 mm dia. $\times 75 \mu\text{m}$ single crystal of YAG: Ce (kindly provided by Dr. Autrata [8]) held a few μm above the fiber-optic plate.

At conventional voltages it is common to increase source brightness by increasing total beam current. Beam currents above $10\text{--}15 \mu\text{A}$ are inconvenient at 1 MeV because the apertures overheat and the radiation levels go up. Instead we have used EBTEC Type SG pointed filaments and directly heated LaB_6 from various sources. The former produce about 4x the brightness of a standard

hairpin with a lifetime of about 10 hours. The LaB_6 has produced 12 A/cm² at the sample for 25 hours without failure. We are also experimenting with conical wehnelt geometries.

As a result, we can see a good TV image at 1Mx (microscope magnification) without image averaging using the lens-coupled TV camera and we can compensate astigmatism almost perfectly using this image. At 20Kx we can focus to $\pm .2\mu\text{m}$ using the image averaging in the frame-store to amplify the slight contrast of Fresnel fringe of the edge of a hole.

MINIMAL EXPOSURE SYSTEM

A minimum exposure system employing compensating deflections of the illumination above the sample and of the image below the sample and permitting a deflection of up to $20\mu\text{m}$ in any of eight directions for focusing or photography has been installed [9]. To this we have recently added a multiple preset magnification system which permits the push-button selection of four preset magnifications and five preset settings of C_2 . This allows rapid changes between various preset dose rates and it meshes well with the beam deflection system to provide a flexible minimal exposure system. The system has been checked using carbon film samples and only very small shifts in focus and astigmatism are noticeable even for quite large deflections, presumably because of the relatively long objective lens focal length (8.5mm).

DISCUSSION

In an early paper, Howitt et al [1] suggest a possible 2x improvement in the resolution obtainable, with a given degree of spatial averaging, by going to 1MeV on the basis of reduced radiation damage as measured by electron diffraction pattern fading [1]. Other possible advantages include thicker permissible samples, greater depth of focus, and higher instrumental contrast transfer function. Our preliminary electron diffraction pattern fading studies of glucose-embedded catalase [10] and of fatty acid monolayers, prepared after Downing and Glaeser [11], show a 3x reduction in critical dose between 100kV and 1MeV and a further 3x improvement by going to -150°C. When the new cold stage and the 20 μm NTB-3 film become available, we hope to evaluate the full potential of this approach to high resolution biological imaging.

This work was supported by grant #RR00570 from the NIH Division of Research Resources to the Madison HVEM Facility. This Facility is, at present, available for use by qualified investigators without charge.

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MINERALS AND CERAMICS



THE SIGNIFICANCE OF MINERALOGIES AND MICROSTRUCTURES
IN C2M CARBONACEOUS CHONDRITES

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ABSTRACT

Observations of microstructures in several C2M-group carbonaceous chondrite meteorites are presented and discussed. The study of samples of these friable and complex materials is facilitated by use of IMV electron microscopy (supported by 200kV TEM/STEM/EDS) coupled with special polishing and ion-thinning techniques.

The results indicate that the matrix of C2M meteorites contains incompletely-altered 'high temperature' minerals, in addition to serpentine-group phyllosilicates which are believed to have formed in an aqueous CO₂-bearing regolith. Such minerals appear to represent stages in the gentle accretion, formation and consolidation of the regolith. Evidence is also presented for the effects of grain impacts on the regolith, which are deduced to have occurred at very low velocities. The occurrence of liquid- and gas-filled voids in some 'high temperature' minerals is attributed to their formation at depth in a minor planetary body.

Support from the NERC (grant no.GR3/1668) and access to the SERC-funded IMV microscope at Imperial College are gratefully acknowledged.

INTRODUCTION

Meteorites are relics of materials and bodies formed very early in the history of the Solar System. Because most meteorites were aggregated late, at low temperatures, without prolonged subsequent heating, they hold clues to the conditions and processes pertaining to that time. Carbonaceous chondrites (CCs), carbon- and chondrule-bearing stony meteorites, have long held particular interests for planetary scientists and cosmochemists because

of their apparently primitive nature and the close correlation of their bulk chemistry with solar abundances. The C2M sub-group is the best-characterized group of CCs possessing a phyllosilicate matrix, but many questions remain concerning the history of the meteoritic components. In recent papers MacDougall [1] and others have shown that Murchison and other C2M specimens contain high temperature condensates similar to those in the Allende (C3V) meteorite [2], while Bunch and Chang [3] have shown that the matrix minerals are not truly primitive (although they cannot have been heated to above $\sim 150^{\circ}\text{C}$) because they are apparently the products of aqueous alteration, thus answering questions about a condensation or alteration origin [4,5]. TEM methods have enabled the very fine-scale microstructures and mineralogies of meteorites to be analysed [6,7], resolving [8,9] some of the earlier uncertainties about the nature of the matrix [10] and demonstrating the presence of complex phases and intergrowths [11,12]. Nevertheless, important problems remain which may only be solved by means of methods with high spatial resolution, such as TEM/STEM/EDS. For example, it is still not established where the alteration processes which produced the matrix took place, although the regolith of a minor planet is a generally favoured site. Furthermore, there is yet no generally accepted identification of minerals and enigmatic phases such as Q [13], which host high concentrations of noble gas fractions in meteorites [14], nor of grains responsible for isotopic anomalies.

MATERIALS AND METHODS

Specimens were made by ion-thinning of polished thin sections, taken from five C2M meteorites: Cold Bokkeveld, Cochabamba, Nawapali, Nogoya and Murchison. Ultrathin sections [15] were used on occasions to facilitate optical-HVEM comparisons, or when it was important to achieve large electron transparent areas. The advantage of HVEM for meteorite work is that it enables one to study contacts and transition zones between phases possessing very different ion-thinning rates. Use of ultrathin sections also helps, but it has the disadvantages that impregnation with epoxy resin must be employed with friable materials, such as meteorites, and that the methods are laborious.

Most of the observations were made using the IMV EM7 microscope at Imperial College, London. Particular problems were also studied with a JEOL 200CX TEM/STEM/EDS and, in one case, the Cambridge 600kV HREM.

RESULTS

Evidence for Incomplete or Late-Stage Alteration

Extensive searching has shown that there exists a small population of grains in the matrix which, although altered or partially altered, retain their original external form and sometimes evidence of their parent mineralogy. Figure 1 shows part of an object with an approximately rhombohedral outline, which consists of numerous sub-parallel fibres of Mg,Fe serpentine. The fibres have not separated very much, suggesting that the original grain remained relatively undisturbed during alteration, prior to consolidation in the matrix. The region of strong contrast appears to be relic olivine, to judge from the electron diffraction data. Other similar examples have been found, so that the aqueous regolith (if this was the alteration environment) was not vigorously stirred by impacts. Figure 2 shows a grain at an early stage of alteration, in which regions have developed lamellar, cleaved structures (e.g. at P). Adjacent to the grain

there are smaller clasts, some of which may have been part of it, since the grain may well have been injected late into the matrix precursors.

Carbonates, principally Fe-bearing calcite [9], although themselves likely to be alteration products, are interesting because they frequently exhibit signs of attack (corrosion). This suggests that carbonates were not formed late in the alteration processes and it is conceivable that some of them originate from earlier stages in the creation of the metecritic components. There is incipient alteration along twins and dislocations in some of the calcites in all the meteorites examined. Figure 3 shows part of a calcite in Cold Bokkeveld, with a corroded periphery and signs of attack along dislocations. Clearly, alteration continued after this carbonate formed or was emplaced. There is already evidence from the work of Armstrong et al [16] on the hibonite- and calcite-bearing Blue Angel inclusion in Murchison that carbonates can be emplaced within the matrix and do not necessarily all originate during undisturbed alteration in a regolith. Recent work by Swart et al [17,18] shows that different forms of carbon in meteorites are distinguishable and this development stimulates interest in the carbonates.

Nuclei of serpentinite alteration products occur along fractures in other wise pristine non-phyllitic minerals, as illustrated in Fig.4. Such examples probably result from the final stages of matrix formation, when active fluids were becoming scarce and only limited alteration could occur on recently emplaced minerals.

Evidence for Fracture of Grains by the Emplacement Process

A regolith model for the formation of CCs seems to require that the regolith, before consolidation, had the properties of a wet slurry to provide a soft landing for accreting and impacting grains and condensates. This idea is supported by TEM evidence for unaltered or incipiently-altered 'high temperature' minerals (mainly olivine and pyroxenes) which have been fractured but not dispersed, apparently by impact rather than by settling or by shear in the regolith. Figure 5 shows a good example where an oval-shaped grain has broken in two pieces which still lie adjacent. The end of the smaller fragment is altered and matrix material has entered a void in the larger fragment. The surrounding matrix, mostly a spongy Mg-rich phyllosilicate, has been pushed away and slightly compacted by the impact of the grain. Along the line XY was the regolith surface when grain was emplaced and that material to the south east of XY was accreted later. The penetration depth of this grain ($\sim 2\mu\text{m}$) implies a very low velocity of impact ($\sim 1\text{m sec}^{-1}$, depending on the properties assumed for the regolith). The integrity of the impacting and accreting mineral is in marked contrast with the brecciated microstructure of gas-rich meteorites, where the clastic minerals result from impacts on a dry dusty regolith.

Evidence for the complicated nature of the aggregation and emplacement processes of bodies into the matrix comes from the discovery that some of them appear to have been composed of phyllosilicates at the time of emplacement. One striking example was an optically-opaque oval grain $\sim 0.5\text{mm}$ long which HVEM showed to consist mainly of 'books' of phyllosilicate platelets (principally Mg,Fe serpentine), but with a few olivine grains. The centre of this body was slightly porous, as shown by Fig.6 but most of it was dense and it had a smooth periphery. One concludes that this body became

rounded either by i) a stage when the aqueous regolith allowed grains to be rolled about and smoothed by abrasion or ii) its existence floating free outside the regolith, subject to erosion by the prevailing flux of radiation, particles and dust.

Voids, Fluids and Phyllosilicates in 'High Temperature' Minerals

Optical and electron microscopy reveals that unaltered inclusions and grains often possess internal voids, fluids, gases, and phases apparently precipitated from the fluids and gases. Although these materials originated as condensates in a low-pressure, high-temperature environment, many of the grains have spent part of their lives at considerable depths within minor planetary bodies. Analysis of the contents of these minerals could therefore provide information about the conditions and sizes of the parent bodies, a matter of great importance.

Figure 7 illustrates an olivine grain with three cavities, each with a different content. A and B contain particulates: partly phyllosilicates in case B (identity unknown) but apparently not phyllosilicates in case A. Both these cavities were connected to the grain surface and hence, indirectly, the surrounding matrix. Infilling of cavities by matrix minerals is common. Cavity C, remained internal to the grain even after ion-thinning and contained a fluid and bubble. This grain must surely have come from considerable depth in a planetary body.

Figure 8 shows another curious object, in which a fine-grained mixture of sulphur-bearing phyllosilicate has a mantle of high temperature material. Such a configuration could result from infilling of a void. But the rounded phyllosilicate periphery, the mimicry of the internal form by the mantle, the incipient mantle-rim alteration and different external phyllosilicate mineralogy all could indicate that the mantle condensed upon the phyllosilicate interior.

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Fig.1 Almost complete alteration of olivine to fibrous serpentine, with original grain outline still discernible.



Fig.2 Cleavage (P) and incipient alteration of Murchison grain, surrounded by clastic material and matrix phyllosilicates.



Fig.3 Corrosion of surface and dislocation in a calcite grain in the Cold Bokkeveld meteorite (200kV micrograph).



Fig.4 Spherulitic nuclei of Povlen-type [9] chrysotile formed along a fracture in small olivine chondrule from Murchison.



Fig.5 Fractured oval olivine grain (attributed to emplacement) in Murchison. XY was probably the position of the regolith surface at time of emplacement.

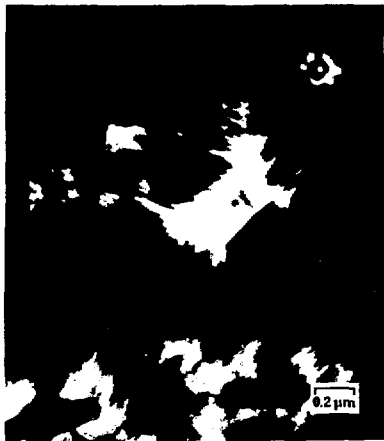


Fig.6 Internal microstructure (books of platelike phyllosilicate) near centre of oval-shaped sub-millimetre inclusion in Murchison.



Fig.7 Solid and fluid contents of internal cavities A, B and C, in olivine grain in Murchison. C also contains a gas bubble.



Fig.8 Rounded spongy phyllosilicate encased by slightly-altered Mg,Fe silicate mantle, adjacent to matrix minerals in Cold Bokkeveld.

ARAGONITE-CALCITE AND CALCITE-LIME TRANSFORMATIONS OBSERVED
IN SITU IN THE HIGH VOLTAGE TRANSMISSION ELECTRON MICROSCOPE

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ABSTRACT

Aragonite and calcite thin foils are heated under vacuum in a high voltage TEM to document the temperatures and orientation relations for the aragonite-to-calcite polymorphic phase transformation and the calcite-to-lime and CO_2 decomposition reaction. Aragonite transforms between 480° and 520°C , and calcite begins to decompose above 500°C . Topotactic relations observed include (001) aragonite and (0001) calcite, (010) aragonite and (1010) calcite, and (0001) calcite and (111) lime. Transformation mechanisms may involve rotation and arrangement into layers of CO_3^{2-} groups with increasing temperature, followed by decomposition into CaO and CO_2 , all within a cation framework which preserves crystallographic directions despite collapse of the lattice.

INTRODUCTION

At room temperature and atmospheric pressure the stable form of CaCO_3 is calcite. Calcite transforms into its polymorph, aragonite, at high pressures and into lime and CO_2 at high temperatures. The structures of the three mineral phases are related. Lime (CaO) is cubic and has the NaCl structure. Calcite is a rhombohedral variation of the NaCl structure with CO_3^{2-} groups whose apices point in opposite directions on alternate basal planes. Calcite is a derivative of the cubic close-packed structure, while aragonite corresponds to the hexagonal close-packed analog. Transformations between the phases have been investigated from both a geologic (e.g. Brown, et al. [1]; Vance [2]; and Carlson and Rosenfeld [3]) and a ceramic materials perspective (e.g. Powell and Searcy [4]).

The aragonite-calcite transition involves a coordination change of calcium atoms by oxygen atoms from nine-fold to six-fold. Buerger [5] classified this as a typical reconstructive transformation. Others have proposed a martensitic mechanism through movement of dislocations in the crystal lattice (e.g. Gillet and Madon [6]). Topotactic relationships have been proposed by several investigators (e.g. Brown, et al. [1]; Dasgupta [7]; and Hiragi, et al. [8]).

The thermodynamics and kinetics of calcium carbonate decomposition have been studied by Powell and Searcy [4,9], who concluded that the slowest chemical step in the decomposition process may be rate limiting under conditions of low background CO₂ pressure. The calcite-lime transformation appears to preserve an orientation relationship (Burrage and Pitkethly [10]). In situ observation of the above phase transformations has been previously performed using beam heating in the TEM at a 100 kV accelerating voltage (Burrage and Pitkethly [10]).

MATERIALS AND METHODS

The present study has the advantage of a quantitative heating stage in a high voltage electron microscope, which reduces the effects of radiation damage to carbonate samples (e.g. Barber and Wenk [11]). Starting materials include ion-thinned foils of calcite single crystals from Chihuahua, Mexico, cut normal to [11 $\bar{2}$ 0] and aragonite from Eugui, Spain, cut normal to [010] and [001]. A Swann double-tilt side-entry heating stage with a tungsten heating element is used on the Kratos EM 1500 electron microscope at the National Center for Electron Microscopy at the Lawrence Berkeley Laboratory. Operating voltages are 600 kV and 1.2 MeV, as available. Observations in both image and selected area diffraction modes are recorded on both film and videotape.

RESULTS

No changes are observed in heating single crystals of aragonite up to 400°C. Above this temperature the foil begins to shift and vibrate, vitiating attempts to photograph the images. Contrast conditions change rapidly with the buckling of the foil. Thicker foils appear to be more stable but yield good diffraction information only at higher accelerating voltages. Between approximately 480° and 520°C the aragonite-calcite transformation occurs with a boundary rapidly sweeping across a region of the foil and erasing twin and dislocation microstructures in the initial aragonite crystal (Figure 1). This is followed at higher temperature by decomposition of calcite, forming lime and CO₂ (Figure 2). Inconsistencies in the measured temperatures of transformation are observed, ranging from 480° to 800°C. The lower temperatures are probably correct, in agreement with previous studies (e.g. Brown, et al. [1]), with higher temperatures indicating poor contact between the sample and the conducting nickel grid or difficulties in maintaining constant temperature across a relatively large sample surface.

Preliminary analyses of diffraction patterns document an orientation relationship with (001) aragonite parallel to (0001) calcite and (010) aragonite nearly parallel to ($\bar{1}$ 012) calcite, which is close to ($\bar{1}$ 010) calcite. Corresponding crystallographic directions in calcite and aragonite are similar, although the coincidence is not perfect.

The transformation is comparable to massive phase transformations observed in metal alloys (e.g. Massalski [12]). A volume change of 7-10% accompanies the transformation, which results in the formation of microfractures throughout the thin foil. A videotape recording documents the advance of phase boundaries as aragonite is converted into single-crystal calcite, culminating in the complete engulfment by calcite.

The onset of calcite decomposition is signalled by the development of rings in the diffraction pattern upon heating above 500°C. Rings with diffraction spots persist as the conversion to polycrystalline material is incomplete, and rings show heterogeneous density indicating preferred orientation of precipitating lime (Figure 2a). This again suggests structural similarities between the phases. Rings sharpen and homogenize gradually, and their appearance and intensification occur over a broad range of temperature, which may represent a gradual loss of CO₂ within a relatively rigid Ca⁺⁺ framework. Lattice parameters in the calcite structure do not appear to change during transformation, but porosity develops locally (Figure 2b), slowly becoming more pervasive with temperature and time. A molar volume reduction of 17% has been reported for calcite decomposition (Dai [13]). Porosity tends to align roughly parallel to (0001) in calcite as it coarsens (Burrage and Pitkethly [10] and this study (videotape)). This is comparable to planar structures observed in carbonates, which may have undergone decomposition reactions during their geologic history (Figure 2c).

DISCUSSION

Preliminary experiments suggest that the aragonite-calcite transformation occurs between approximately 480° and 520°C under dry conditions and involves the migration of phase boundaries. Boundaries may be moving in crystallographically preferred directions, although more data is needed. An orientation relationship between initial and final phases shows an approximate correlation between (001) and (0001), (010) and (1010) in aragonite and calcite respectively, and between (111) and (0001) in lime and calcite respectively. Decomposition of calcite takes place above 500°C with porosity coarsening and aligning in basal planes of calcite as temperature increases. The transformations may involve a relatively simple rearrangement of CO₃⁻ groups followed by a driving off of CO₂.

Due to the structural similarities and coincidence of minimum transformation temperatures among calcite, aragonite, and lime, some overlapping reactions may occur. Above 500°C aragonite may transform directly into lime and CO₂. Future in situ experiments involving real-time videotaping should provide kinetic information, and high resolution microscopy may establish the mechanism for the studied phase transformations.

ACKNOWLEDGMENTS

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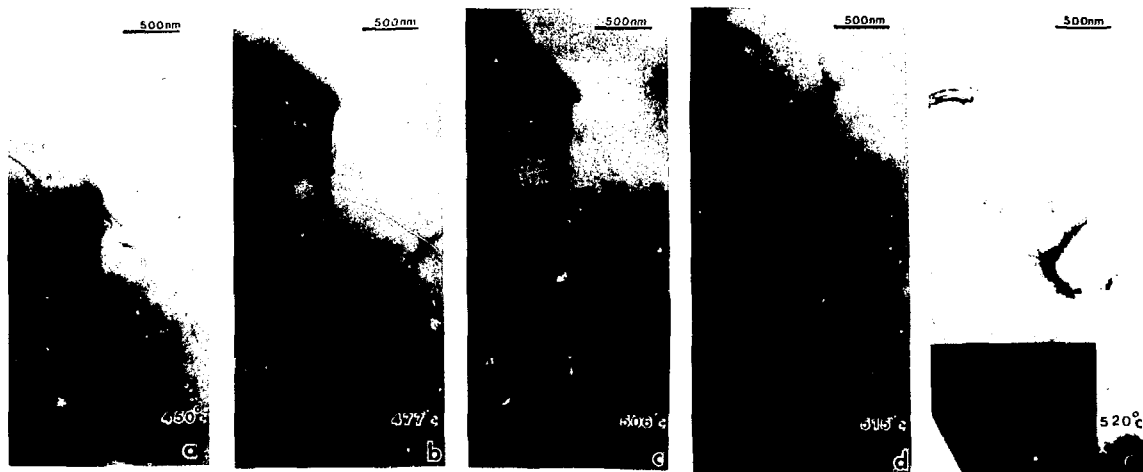


Figure 1. In situ heating experiment: (a-d) Wedge-shaped aragonite grain engulfed as phase boundaries move inward. (e) Aragonite is completely transformed into calcite.

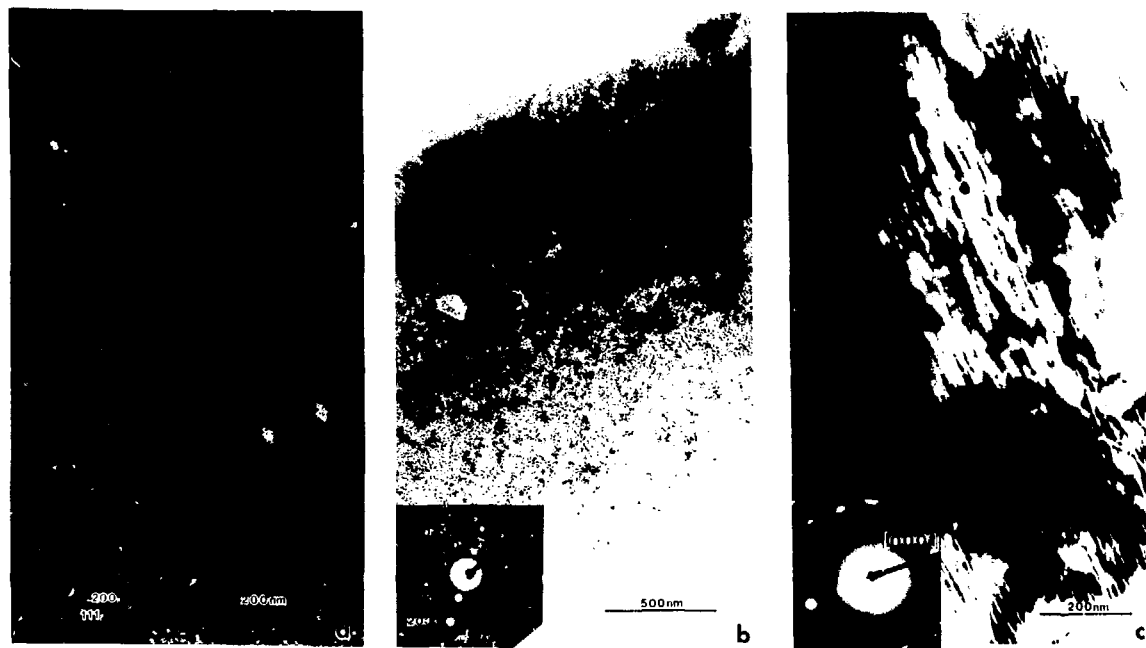


Figure 2. (a,b) Decomposition of calcite. (c) Alignment of planar porosity features in natural carbonatite in (0001) basal planes of calcite.

MICROSTRUCTURE OF PLASTICALLY DEFORMED SANIDINE (K-FELDSPAR)

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ABSTRACT

Typical microstructure features of K-feldspar natural single crystals deformed in compression under hydrostatic pressure are analysed in a high-voltage electron microscope. A large number of glide systems is observed to be available. As judged from the dislocation distribution, the glide mechanisms differ considerably in these systems. Dislocation glide in various dominant systems leads to the formation of large stacking-fault like defects having a shift vector of approximately 0.7λ . The energy of one type of (010) stacking faults is estimated to be $(3 \pm 2) \cdot 10^{-2} \text{ J} \cdot \text{m}^{-2}$.

INTRODUCTION

Feldspars (i.e. aluminosilicates of potassium, sodium, and calcium) are the most abundant constituents of earth's crust. Therefore knowledge of their mechanical behaviour is desirable. As a prerequisite for an understanding of the plastic behaviour, glide elements and typical dislocation features should be evaluated, which can be performed already by laboratory scale experiments. Sanidine offers relatively simple experimental conditions. This feldspar is monoclinic and deforms plastically by dislocation motion only. Mechanical twinning, which is typical of triclinic plagioclases [1,2] and which would impede the study of dislocation structures, does not occur. Also, sanidine is free of segregations into K- and Na-rich domains ('exsolutions'), which otherwise would complicate the interpretation of dislocation features.

This paper bases on earlier work [3-5] on glide geometry and dislocation structure in sanidine single crystals that were plastically deformed. It extends electron microscope studies at an accelerating voltage U of 100 kV. These suffered from excitation radiation damage and the small, necessarily thin transmittable areas of the specimens. Only limited conclusions on defect types and glide modes could be obtained. The reduced ionization cross-section in a high voltage electron microscope leads to a greatly improved lifetime of the specimens permitting detailed analysis of dislocations. Stacking-fault like planar defects could be studied more reliably from fringe contrast using the thick specimens. In this case a sufficient number of fringes occurred also with reflections that are associated with a rather long extinction distance ξ_g (typ. 300 nm). (The relevant quantity t/ξ_g , t : specimen thickness, increases approx. with $\sqrt{U}$).

CRYSTALS AND EXPERIMENTAL PROCEDURES

The investigated crystals (6mm in diameter, 12 mm long) were taken from a

batch of sanidine single crystals collected in the Eifel (Germany). The crystals contained subgrains several mm in diameter and microcracks. The dislocation density was $\rho < 10^{10} \text{ m}^{-2}$, the chemical composition was $\text{K}_{0.8}\text{Na}_{0.2}\text{AlSi}_3\text{O}_8$ /6/. The crystals were deformed in compression in a Griggs apparatus along three orientations (e.g. Table 1) under hydrostatic pressure ($p = 16 \text{ kbar}$) at $T = 700^\circ\text{C}$ with a strain rate $\dot{\epsilon} = 1.2 \cdot 10^{-6} \text{ s}^{-1}$ /6/. After deformation (for deformation curves see /6/) discs were cut and ion-milled, that had orientations considered appropriate for the identification of the glide elements from contrast analysis.

Although an extended observation time was available, care had to be taken in the contrast analysis because of possible artifacts due to radiation damage. This damage started always at the dislocation lines and consisted of an increasing amorphization of the dislocation core regions (cf. Fig. 1). Such a change of defect 'nature' might affect the dislocation contrast under the various selected diffraction conditions.

OBSERVATIONS AND RESULTS

General dislocation arrangement

Table 1 summarizes the information on the glide geometry as determined by previous and the present investigations. Each of the three crystal orientations is associated with the activation of one specific predominant glide system. Although these predominant systems are all different, the dislocation distribution in the crystals has several features in common. Generally glide bands are observed having a thickness of up to several micrometers and a typical extension of several tens of micrometers. The dislocation density in the centre is $\rho > 10^{13} \text{ m}^{-2}$; therefore the detailed analysis of the dislocations was performed at the rims of these bands. It should be noted that the systems $(12\bar{1})$ $[10\bar{1}]$ in addition developed much less concentrated bands and sometimes filled a crystal region quasi-homogeneously indicating easy dislocation multiplication and glide (e.g. next section).

The glide bands were frequently observed to emanate from microcrack tips and subgrain boundaries suggesting these defects to be a major dislocation source in the initial stage of deformation. As a further characteristic common feature, each dislocation of the predominant systems produces during glide a planar defect that gives rise to weak fringes at best (Figs. 2,3) /3/. For the faults in the systems $(12\bar{1})$ $[10\bar{1}]$, the direction of the shift vector $\mathbf{R}$ could be shown to lie in the plane of the fault parallel to $[10\bar{1}]$ and $[00\bar{1}]$ respectively (determined in each case by two independent fringe extinction conditions). The length of $\mathbf{R}$ could be estimated for the $(12\bar{1})$ fault. Fig. 2 shows two partly overlapping faults, one extinction distance apart. Therefore, the fringe intensity in the overlapping region is essentially determined by twice the phase shift α of one fault ($\alpha = 2\pi \mathbf{g} \cdot \mathbf{R}$). Since the intensity is (in thick foils) proportional to the sine of the phase shift /7/, and since it is enhanced in the overlapping region, we get $\sin 2\alpha > \sin \alpha$. Thus, $\alpha < \pi/3$, which gives an upper limit for $R < 1/12$ $[10\bar{1}]$, i.e. $0.7\bar{2}$. The contrast behaviours indicate similar values for the faults on the planes (010) .

Dislocation structure and glide modes

In the following selected details of the dislocation structure will be

discussed that are thought to be typical of the glide processes in the various glide systems.

(121) [101]. Glide in this system leads to a rather 'conventional' dislocation arrangement (Fig. 3). Essentially edge dislocations are observed, which frequently form dipoles and multipoles. Screw dislocations are practically absent which indicates easy cross-slip, presumably on (010) (see following paragraph). Some of the dislocation segments are of mixed type and -as seen from their straight line- lie in a Peierls valley. The whole dislocation distribution resembles that typical of 'easy glide', which causes comparatively low work-hardening rates in many crystal structures. Correspondingly the predominant activation of this glide system is associated with a reduced work-hardening, as can be deduced from the work-hardening curves in /6/.

(010) [101]. Only a few observations could be made. Typical dislocations are shown in Fig. 4. The screw segments of the expanded loops are much shorter than the other segments (formed by 60°-dislocations in this case). This observation suggests that the screw dislocations have a relatively high mobility.

(010) [001]. Fig. 5 shows part of a glide band, which lies inclined in the foil. The most interesting detail is the occurrence of stable screw dislocation dipoles (arrows). Such dipoles can exist only, if cross-slip is strongly impeded. In fact, there seems to be no cross-slip plane available, at least under the present deformation conditions, since no other glide system with the same Burgers vector [001] was observed (Table 1). The screw dislocation dipoles can be formed either at immobile jogs in gliding edge dislocations (e.g. /8/) or by mutual trapping of screw dislocations with opposite Burgers vector. At a higher applied stress, of course, the screw dislocations of a dipole may bow out and glide again to form a single ended dislocation source (indicated at A in Fig. 5).

(001) [201]. This glide system, which does not belong to the predominant ones, is interesting because the dislocations are visibly dissociated. The Burgers vector [201] could be established from contrast experiments at dislocation triple nodes, one of which is identified in Fig. 6 a-c. All of the dislocations in Fig. 6 lie in the foil plane (010) as corroborated by stereomicrographs. The invisibility criterion yields Burgers vectors $b(\alpha) = [100]$ (Fig. 6b) and $b(\beta) = [101]$ (Fig. 6c). The perfect Burgers vector of dislocation γ would thus be either [001] or [201]. [001] can be ruled out on grounds of energy and contrast considerations. Dislocation γ is therefore dissociated into partials with $b = 1/2 [201]$, which remain visible in all three imaging conditions of Fig. 6. The separation of the partials yields an estimate for the stacking fault energy on (010) of $\gamma = (3 \pm 2) \cdot 10^{-2} \text{ Jm}^{-2}$. The stacking fault is not visible in Fig. 6. It was, however, observed earlier (Fig. 5 in ref. /4/), but the dislocations were not identified then.

CONCLUDING REMARKS

The present observations show that the plastic flow of sanidine crystals is governed by many different glide systems already at deformation temperatures that are relatively low in the case of covalent crystals ($0.7 T_m$). Moreover, the glide mechanisms in these systems differ considerably from each other as shown by the discussed dislocation structure. In view of this glide behaviour, an assessment of the deformation experiments performed in the la-

boratory (e.g. /6/) in terms of dislocation processes, or an evaluation of the dislocation structure observed in naturally deformed feldspars (e.g. /9/) in terms of deformation history needs more of this basic work. The system $(12\bar{1})$ [101] can obviously be activated in profuse glide. Experiments, in which sanidine deforms by single glide in this system, would be favourable, since relatively easy to interpret, for relating macroscopic and microscopic plastic behaviour.

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Table 1

Glide elements as observed in sanidine at 700°C

Orientation crystal normal	Nr. /6/	Glide systems		Reference
		x:predominant d: dissociation	$ b $ (Å)	
$[2\bar{1}0]$	1	$(12\bar{1})$ $[101]$ x (010) ?	8.43	/4/, text /4/
$[212]$	4	(010) $[101]$ x (001) $1/2$ $[110]$	8.43 7.78	/3/, text /3/
$[012]$	2	(010) $[001]$ x (001) $1/2$ $[1\bar{1}0]$ (010) $[201]$ d	7.19 7.78 15.39	/5/, text /5/ see text

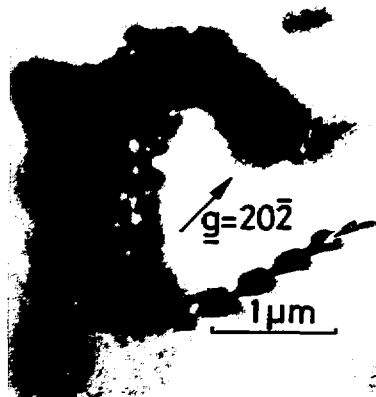


Fig. 1. Electron irradiation damage. Amorphization starts at dislocation cores. g : diffraction vector



Fig. 2. Overlapping planar defects lying on $(12\bar{1})$.

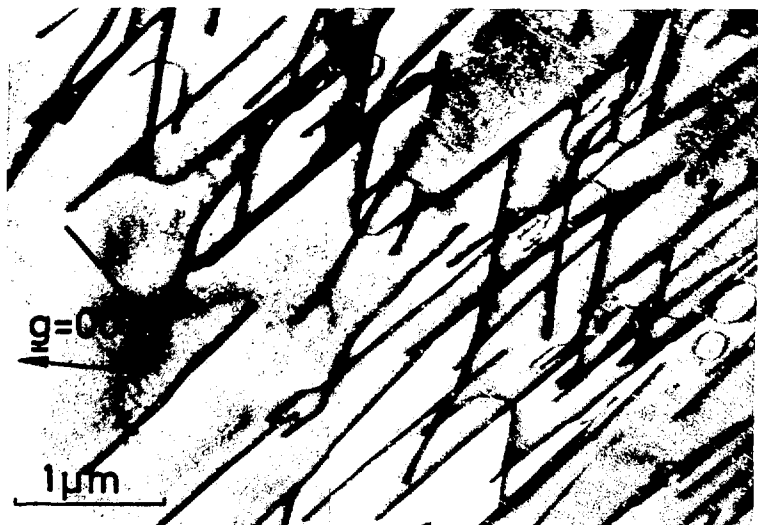


Fig. 3. Typical dislocation arrangement in glide system $(12\bar{1})$ $[101]$. Section oblique to glide plane. Weak fringes arise from planar defects that are created during dislocation glide. b : direction of Burgers vector.

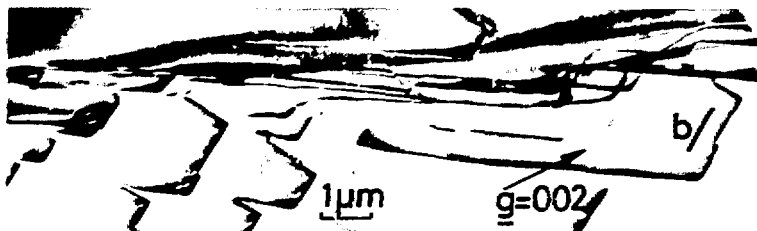


Fig. 4. Dislocation arrangement in glide system (010) [101].



Fig. 5. Dislocation arrangement in glide system (010) [011].
Arrows: Screw dislocation dipoles.
A: Dislocation source.



Fig. 6. Dissociated dislocations in glide system (010) [201]. Contrast experiment.

IN-SITU STRAINING EXPERIMENTS OF ZIRCONIA-CONTAINING CERAMICS

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ABSTRACT

The stress-induced, tetragonal $\rightarrow$ monoclinic martensitic transformation in zirconia particles confined in different ceramic matrices was studied by in-situ experiments in an HVEM using a straining stage. Crack propagation in the specimen could readily be observed and tetragonal ZrO_2 particles close to the crack tip transformed to monoclinic symmetry. The size and shape of the transformation zone obtained for thin foils, which are close to a plane stress configuration, have to be evaluated carefully for their applicability to bulk specimens. This is possible if all deformation but the martensitic transformation is elastic.

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INTRODUCTION

In-situ straining experiments have generally been performed in metals and alloys for the understanding of the mechanisms which occur during plastic deformation - dislocation glide, reactions of dislocations, multiplication of dislocations, and dislocation dynamics (see e.g. Imura /1/). Those in-situ observations generally revealed processes which were expected from other experiments on plastic deformation and from the theory of dislocations. Ohr and Narayan /2/ demonstrated that the creation and mobility of dislocations in front of a crack tip in bcc metals could also be studied by in-situ observations. HVEM is not essential for all those studies (Kubin and Veyssi re /3/), as all processes can be studied using conventional electron microscopes (operating voltage ≤ 200 kV).

Limited in-situ straining experiments have been performed on brittle materials (e.g. ceramics), where plastic deformation due to dislocation processes is difficult or entirely absent. These experiments are very difficult as the brittle materials often cleave without any plastic deformation, although plastic deformation studies of MgO have been successful. Recently, in-situ straining experiments of zirconia (ZrO_2)-containing ceramics became particularly attractive for (i) understanding the mechanisms leading to "transformation toughening" and (ii) determining the important parameters necessary for theoretical evaluation of the improved toughness of these new ceramics.

The tetragonal (t) to monoclinic (m) martensitic transformation of confined zirconia particles (diameter $\leq 2 \mu\text{m}$) embedded in a ceramic matrix can be utilized for toughening ceramics (Evans and Heuer /4/). The concentration of t-ZrO₂ particles or precipitates is usually $\leq 20 \text{ vol.}\%$. The M_s temperature of bulk ZrO₂ is $\sim 1200 \text{ K}$, whereas M_s is substantially less for confined particles. For example, M_s is below room temperature for faceted t-ZrO₂ particles embedded in an Al₂O₃ matrix, if the diameter is $\leq 0.6 \mu\text{m}$ (Heuer et al. /5/), and below 20 K for some spherical particles in the same matrix. The transformation of confined particles can be induced by the stresses in front of a crack tip ("stress-induced transformation"), and the volume and shape change connected with the t $\rightarrow$ m transformation alters the stress distribution at the crack tip; this hinders the crack from further propagation (McMeeking and Evans /6/, Budiansky et al. /7/). In this paper, we report the transformation of confined t-ZrO₂ particles during crack propagation induced by in-situ straining experiments.

EXPERIMENTAL DETAILS

Specimens of Al₂O₃-ZrO₂ dispersion ceramics (zirconia-toughened alumina or ZTA) and of MgO-partially stabilized zirconia (Mg-PSZ) were studied. The ZTA specimens contained 15 vol.% ZrO₂, all ZrO₂ particles possessing tetragonal symmetry prior to straining. The sizes and size distribution of the Al₂O₃ grains, as well as of the t-ZrO₂ particles were determined by standard techniques of quantitative stereology (Rühle and Kraus /8/). The mean diameter of the Al₂O₃ matrix grains was $d_g = 0.44 \mu\text{m}$ and of the t-ZrO₂ particles $0.21 \mu\text{m}$. The diameter of the t-ZrO₂ particles ranged between $0.06 \mu\text{m}$ and $0.5 \mu\text{m}$.

The t-ZrO₂ particles in Mg-PSZ are formed by precipitation in a cubic matrix (Porter and Heuer /9/) and are homogeneously distributed. It is assumed that the precipitates are coherent with the matrix.

Specimens suitable for straining experiments, and with a cross section of $3 \times 5 \text{ mm}^2$, were mechanically polished carefully to a thickness of $50\text{--}80 \mu\text{m}$. The specimens were ion-thinned using a special technique so that 2 slightly elongated holes were formed (Fig. 1). The specimen was transparent for 1 MeV electrons nearly in the entire region of the ridge (R) between the two holes. The Mg-PSZ specimen possessed a porosity of $\sim 5 \%$, in the form of many small pores (Fig. 2). The specimens were used in deformation holders which were inserted in the deformation stage and subsequently deformed in the double tilting straining stage described by Loretto and Brooks /10/. The relative velocity of the specimen holders against one other was variable, between $1 \cdot 10^{-6}$ and $1 \cdot 10^{-4} \text{ mm/s}$, which results in a straining rate of $\sim 4 \cdot 10^{-6} \text{ s}^{-1}$ to $\sim 4 \cdot 10^{-4} \text{ s}^{-1}$. Specimens were usually strained with a constant straining rate of $3 \cdot 10^{-6} \text{ s}^{-1}$. The stresses applied to the specimen could not be measured.

EXPERIMENTAL RESULTS

Micrographs of the unstrained specimens were taken of the entire transparent part of the ridge. No m-ZrO₂ particles or precipitates could be observed in either type of specimen. The beginning of elastic deformation of the specimens could be observed by the movement of bend contours in different grains. In ZTA, some t-ZrO₂ particles transformed to m-ZrO₂ before a crack propagated. Usually, however, a crack started to propagate from the regions of highest stress concentrations at the thinnest area of one hole. In ZTA, the t-ZrO₂ particles transformed in front of the crack tip, the distance of the transforming particles from the crack tip depending on the size of the particle, the depth of the particle inside the foil, and on the foil thickness. The

transformed $m\text{-ZrO}_2$ particles could easily be identified by the presence of mechanical twins inside the particles. Fig. 3 shows examples of ZTA (containing intercrystalline $t\text{-ZrO}_2$ particles) before and after a crack was introduced and clearly shows the transformation during loading and near the crack tip. Similar observations are obtained for intracrystalline $t\text{-ZrO}_2$ particles (Fig. 4), which are completely included in an Al_2O_3 grain.

Fig. 5 shows the complete surrounding of a crack introduced in the fine-grained ZTA containing exclusively intercrystalline $t\text{-ZrO}_2$ particles. All ZrO_2 particles were identified as either $m\text{-ZrO}_2$ or $t\text{-ZrO}_2$ and are represented in Fig. 6. A well-defined transformation zone exists, in that all $t\text{-ZrO}_2$ particles close to the crack transformed. In front of the crack tip, all $t\text{-ZrO}_2$ particles within $4\text{ }\mu\text{m}$ had transformed, and the fraction of transformed particles decreased with increasing distance perpendicular to the crack. The evaluation of Fig. 5 and 6 is shown in Fig. 7.

During the *in-situ* straining experiments for Mg-PSZ, the crack jumped from pore to pore within the thinned area. It has not yet been possible to map out the transformation zone in a crack which has been arrested in the cubic matrix. However, a well-defined transformation zone does exist, and Fig. 8 shows that all $t\text{-ZrO}_2$ precipitates within $0.5\text{ }\mu\text{m}$ of the crack transformed.

INTERPRETATION AND DISCUSSION

The *in-situ* straining experiments show that $t\text{-ZrO}_2$ particles or precipitates indeed transform in front of a crack tip and allow determination of the width of the transformation zone. However, caution is mandated in applying the results obtained in a thin foil to bulk ceramics. At best, a thin foil can be described by a plane stress situation, whereas the transformation zone in the bulk can best be represented by plane strain. It is well known from fracture mechanics and plasticity theory that the plastic zone sizes are different for plane strain and plane stress (Fig. 9) and the relative zone size in each case has been calculated. Insofar as the transformation zone ahead of a crack tip contains matter that has been deformed during the course of the martensitic transformation, a similar result for transformation zones might be expected. However, the $t\text{-ZrO}_2$ particles in PSZ and ZTA present different geometries to the far-field (applied) stress, which need to be taken into account.

Consider PSZ first. In a $\langle 100 \rangle$ zone axis foil orientation, two of the three precipitate variants (those with c-axes in the foil plane) extend throughout the foil, intersecting both foil surfaces. These particles are then subject to actual plane-stress loading. For this case, it is possible to use the plane-stress solutions and to show that the size of the transformation zone ahead of the crack is about 5x larger than for the plane strain case a_0 ; for the transformation zone normal to the crack, it is $w_0/w_c \approx 1.52$ (Poisson ratio $\nu = 0.25$, McClintock and Irwin [11]). Fortunately, the width w_0 of the transformation "wake" is the parameter needed for existing theories of transformation toughening in two-phases ceramics, and the *in-situ* result should be quite appropriate.

The third variant, whose c-axis is normal to the foil plane, is different. Coherency stresses are undoubtedly present due to precipitation, but will be modified by stresses arising from thermal expansion mismatch between particle and matrix (c and $t\text{-ZrO}_2$) during cooling from the precipitation temperatures. The residual stresses in both particle and matrix will be relaxed during foil preparation, the effect being greater the closer the particle is to the foil surface. It is possible that particles far removed from the foil surface do

approximate to plane strain loading during in-situ deformation; as far as matrix constraints are concerned, therefore, the situation is similar to bulk material. However, it is also possible that a loading situation intermediate between plane stress and plane strain exists for this case, which would prevent any closed form solution. Thus, real caution is required to evaluate the zone dimensions for this orientation of particle.

Two types of particles also have to be considered in ZTA, intragranular, which are spherical or quasi-spherical, and intergranular, which must of necessity be faceted. (Because ZrO_2 particles are under such a large tensile strain in ZTA due to thermal expansion mismatch, most particles that intersect a free surface will transform. We thus only consider particles completely enclosed in the foil.) For the former type, the situation with respect to plane stress and plane strain will be similar to the in-plane precipitate variant in PSZ. Even if plane strain conditions can be assumed, certain problems remain. Prior to loading, the stresses in particle and matrix arising from thermal expansion mismatch can readily be calculated using an Eshelby-type approach. The relaxation in these stresses in thin foils as a function of distance from the foil surface has been considered by Mura /12/ and Mader /13/. However, an analytical solution does not exist for the case where particle and matrix with different elastic moduli are under residual stresses and are subject to far-field loading. Thus, caution in using zone dimensions from in-situ experiments for understanding bulk behavior is mandatory.

The situation with respect to faceted ZrO_2 particles in ZTA also demands caution. Rühle and Kriven /14/ have argued convincingly that in most cases, the applied stress permits the nucleation barrier for the martensitic transformation to be overcome, and that the sharp facet edges are particularly important because they can act as effective stress concentrators. A closed form solution appropriate for bulk material has been considered, that of cuboids. However, the modification to the half-space geometry suitable for thin foils has not been treated, nor are cuboids a good model morphology for intergranular ZrO_2 particles in ZTA.

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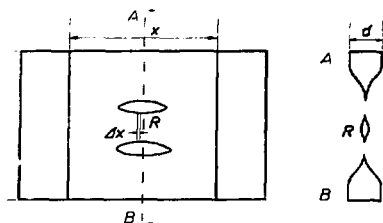


Fig. 1. Geometry of specimen suitable for in-situ straining experiments.

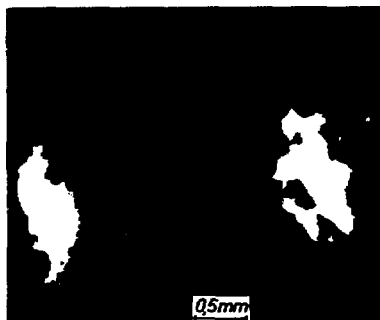


Fig. 2. Specimen of Mg-PSZ for straining experiments. Many small pores are visible besides the two ion thinned holes.

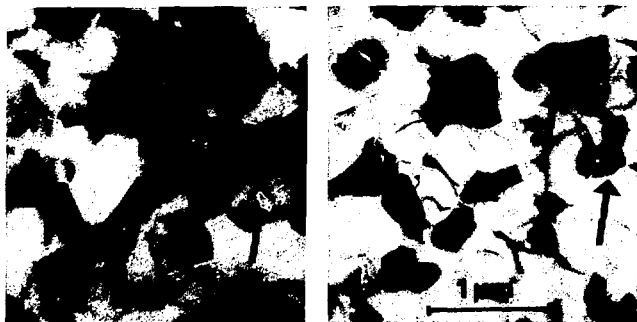


Fig. 3. Stress-induced martensitic transformation of confined intercrystalline, faceted $t\text{-ZrO}_2$ particles, (a) $t\text{-ZrO}_2$ particles (arrowed) prior to the straining experiment; (b) transformed $m\text{-ZrO}_2$ particles.

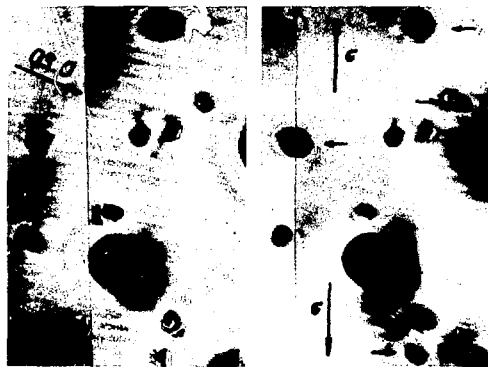


Fig. 4. Stress-induced martensitic transformation of confined intracrystalline, spherical $t\text{-ZrO}_2$ particles; (a) prior and (b) after straining.

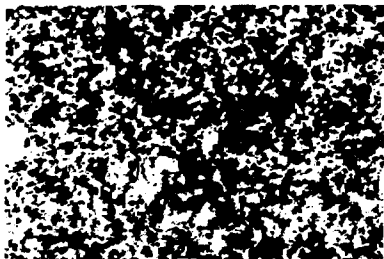


Fig. 5. Micrograph of Al_2O_3 specimen containing intercrystalline ZrO_2 particles. A crack moved into and was arrested in the specimen.

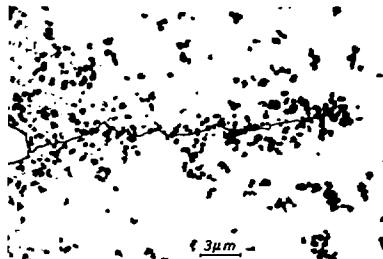


Fig. 6. Evaluation of Fig. 5. All ZrO_2 particles and the crack are marked. Dark areas: projection of transformed $m\text{-ZrO}_2$ particles, grey areas: $t\text{-ZrO}_2$ particles.

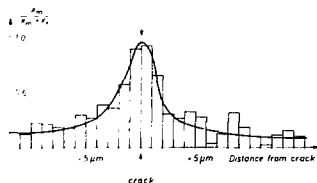


Fig. 7. The fraction of $m\text{-ZrO}_2$ particles as a function of distance perpendicular to the crack. Prior to the crack propagation, no $m\text{-ZrO}_2$ particles were present.

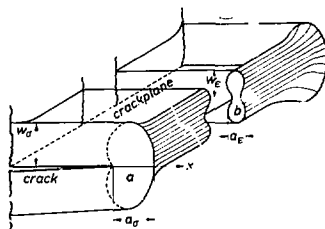


Fig. 9. Plastic zone around a crack for (a) plane stress and (b) plan strain configurations.

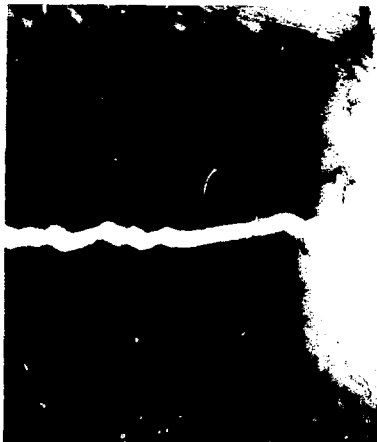


Fig. 8. Stress-induced transformation of $t\text{-ZrO}_2$ precipitates embedded in the cubic matrix of Mg-PSZ . The crack jumped from pore to pore (see Fig. 2).

EFFECT OF VOLTAGE ON THE ORIENTATION DEPENDENCE OF ELECTRON INDUCED CHARACTERISTIC X-RAY EMISSIONS

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ABSTRACT

The dependence of electron induced characteristic x-ray emissions on both the orientation and the acceleration voltage for MgAl_2O_4 have been calculated. A non uniform voltage dependence, characterized by an 'inversion' voltage is predicted. The characteristics of this 'inversion' voltage is shown to be different from the conventional critical voltage effect.

INTRODUCTION

As a result of dynamical scattering of an incident plane wave of electrons, a standing wave pattern is set up within the crystal unit cell. For a given crystal, depending on the orientation, this intensity modulation will be a maximum on certain crystallographic sites. Hence, the intensities of highly localized scattering events such as inner shell excitations, show a strong orientation dependence [1,2]. Under favourable conditions, this orientation dependence of characteristic x-ray emissions can be exploited to obtain crystallographic information, particularly with respect to the determination of the specific site occupancy of the constituent elements [4,5,6]. In this paper, the influence of the acceleration voltage is discussed as an independent parameter on this orientation dependence, based on calculations.

THEORETICAL FORMULATION

This theory assumes that the characteristic x-ray emission of element x at the coordinate $\vec{p}$ in the unit cell is proportional to (a) the intensity of the electron standing wave at $\vec{p}$ and (b) the probability of the localization of the scattering event at $\vec{p}$, i.e., $P(\vec{p})$. For the approximation that $P(\vec{p})$ is highly localized, i.e., a delta function at the mean atomic positions, for a crystal of thickness 't':

$$N_x = \sum_{\text{RSI}} \int_0^t \phi^* \phi \, dz \quad (1)$$

where N_x is the intensity of the characteristic x-ray emission of element x and the summation is over the relevant crystallographic sites of interest. Here ϕ is the scattered wave amplitude at any depth z expressed as a linear combination of Bloch waves, for the case of an incident plane wave, in the conventional dynamical theory formulation [7].

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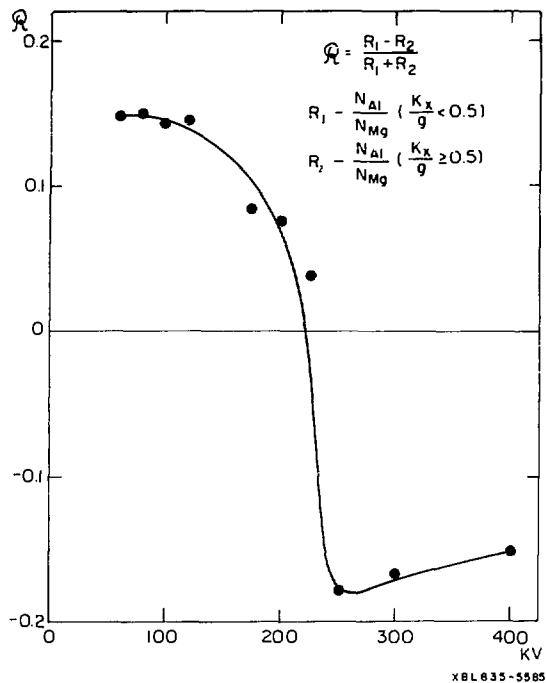


Fig. 1. Variation of the electron induced characteristic x-ray emissions with both orientation and acceleration voltage. Calculations were performed for 15 beams, systematic excitation condition ($\bar{g} = 400$).

On carrying out the integration and rearranging the various terms, one can express the characteristic x-ray intensity/unit thickness as:

$$N_z = \frac{\bar{z}}{RSI} \left[\sum_{\vec{g}} \bar{h} \exp(\bar{h} - \bar{g}) \cdot \bar{x} \right] \left\{ \sum_{j=1}^{\infty} C_o^{(j)*} C_g^{(j)*} C_o^{(1)} C_h^{(1)} \right. \\ \left. + \sum_{j>1}^{\infty} C_o^{(j)*} C_g^{(j)*} C_o^{(1)} C_h^{(1)} \frac{\sin[(k_z^{(j)} - k_z^{(1)})t]}{(k_z^{(j)} - k_z^{(1)})t} \right\} \quad (2)$$

where $C_h^{(j)}$ are the Bloch wave coefficients and $k_z^{(j)}$ are components of the wave vector for the electrons in the crystal. (A more detailed exposition of the theoretical formulation is given elsewhere [8].)

RESULTS AND DISCUSSIONS

Using the above expression (2), electron induced characteristic x-ray emission intensities were computed for $MgAl_2O_4$. This compound has a spinel structure, which in the (100) projection can be separated into alternate planes of Aluminium atoms (octahedral coordination) and magnesium atoms (tetrahedral coordination). Calculations were done for a 15 beam ($g=400$) systematic excitation condition, over a range of orientations $\{0 \leq k_x/g \leq 1.0\}$ and acceleration voltages (60-400kV). Figure 1 describes the variation of the intensities of the characteristic x-ray emissions as a function of both orientation and acceleration voltage. The ordinate R is a normalized measure of the orientation dependence and is defined as $R = (R_1 - R_2)/(R_1 + R_2)$ where R_i is the ratio N_{Al}/N_{Mg} at their corresponding positions of extrema and i takes the value 1 or 2 for orientations with $k_x/g < 0.5$ and $k_x/g \geq 0.5$ respectively. A positive value of R signifies a maxima of the characteristic x-ray intensity of Mg (N_{Mg}) for some orientation with $k_x/g \geq 0.5$ and a minima for $k_x/g < 0.5$. It also signifies an exactly opposite behavior for N_{Al} . The prediction of the orientation dependence at 100 kV is in agreement with experimental results [6]. However, it can be seen, that at higher acceleration voltages, this orientation dependence though not particularly enhanced in magnitude, exhibits an interesting reversal in character, i.e., above some 'inversion' voltage the orientation dependence of N_{Al} and N_{Mg} are interchanged, and in Fig. 1, this is represented by R taking negative values. Moreover, the orientation of a minimum or maximum also varies slightly with the acceleration voltage.

In order to isolate the role of the acceleration voltage alone, the variation of the ratios of the characteristic x-ray intensities as a function of the acceleration voltage were calculated for a number of different orientations. These were normalized in the same manner as done earlier (with $R_1 = N_{Al}/N_{Mg}$ at the orientation of interest, k_x/g and $R_2 = N_{Al}/N_{Mg}$ at a non-channelling symmetric orientation) and plotted (Fig. 2). From this plot, one can infer that at the 'inversion' voltage, these normalized ratios of intensities do indeed undergo a reversal in character (sign) at all orientations, though the effect is more pronounced as k_x/g increases. This suggests that one can use this voltage dependence to determine qualitatively, site occupations of elements in crystals provided that this 'inversion' voltage is known in advance.

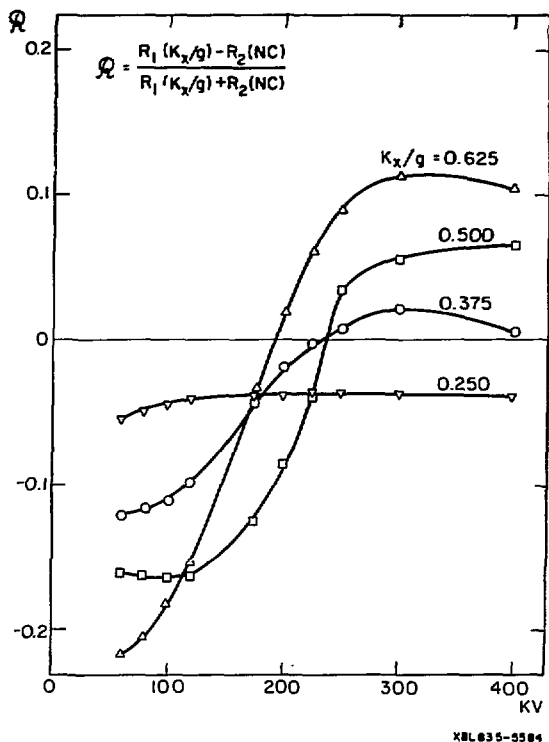


Fig. 2. Variation of the electron induced characteristic x-ray emissions as a function of the acceleration voltage for fixed excitation errors. Normalization is done with respect to a non channelling (NC) symmetric orientation.

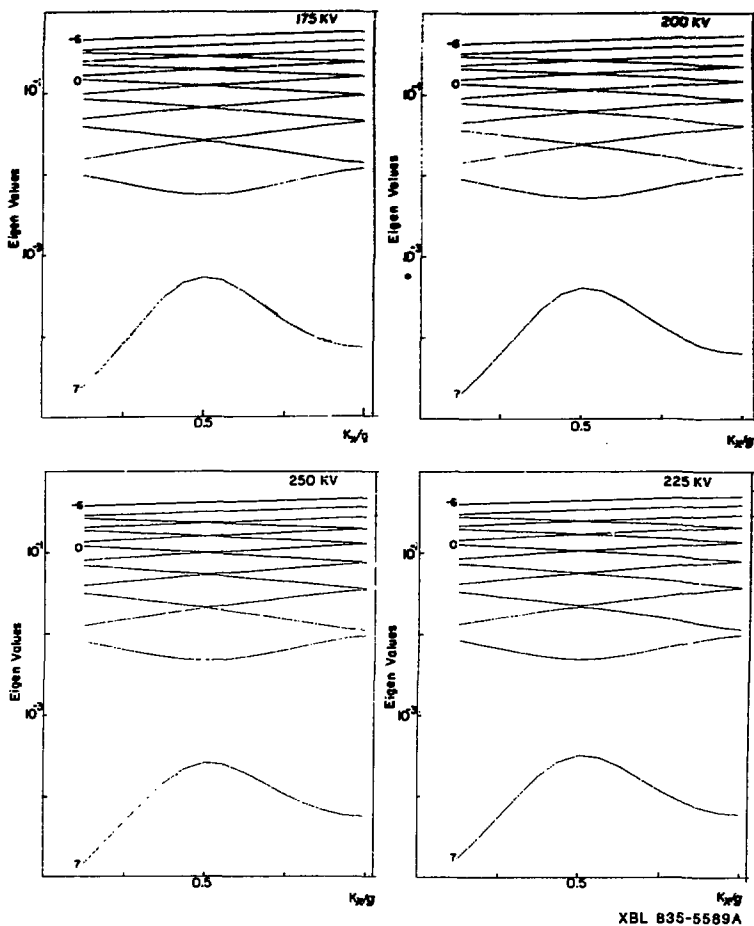


Fig. 3. Dispersion surfaces [Eigen values of the Bloch waves vs. orientation (k_x/g)] for different acceleration voltages.

According to Lally, et al. [9], for a centrosymmetric crystal set at the symmetric Laue position for the reflection $2\bar{1}$, a change in the symmetries and excitation amplitudes of the Bloch waves is observed, at a particular critical voltage characteristic of the crystal. An alternative way of interpreting this is that at the critical voltage, the eigenvalues of the Bloch waves become degenerate. In Fig. 3, the dispersion surfaces have been plotted, calculated at 25 kV intervals over the voltage range of interest with the thickness, t modified at each voltage such that λt is a constant. These dispersion surfaces indicate that for this particular case of the crystal oriented at the reflection $1\bar{1}$, exact or with positive or negative excitation errors, no observable degeneracy in the eigenvalues of the Bloch waves are present. This indicates that the nature of this sensitivity of the electron induced characteristic x-ray emissions to the acceleration voltage which we term as the 'inversion' voltage is different from the conventional critical voltage effect. However, a change in orientation or voltage should have similar effects in so far as they independently change the diagonal elements of the dynamical scattering matrix. Further calculations and experiments are in progress to understand this anomaly.

CONCLUSION

It has been shown that the electron induced characteristic x-ray emissions, apart from being orientation dependent are also voltage dependent. This voltage dependence is not uniform but exhibits an 'inversion' behavior, which for MgAl_2O_4 is predicted to be between 175-250 kV. It appears that this sensitivity to voltage can be used to determine qualitatively site occupations of elements in crystals as an alternative to the orientation dependence. The exact nature of this 'inversion' voltage seems to be anomalous for it exhibits characteristics different from the conventional 'critical' voltage effect.

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IN SITU EXPERIMENTS OF REFRACTORY MATERIALS AT VERY-HIGH TEMPERATURES

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ABSTRACT

A new type of very-high temperature stage for a 3MV electron microscope has been developed, with which the specimens can be tilted up to $\pm 8^\circ$ around any axis and stretched up to fracture in a wide temperature range up to 2300K. In situ heating and stretching experiments have been carried out with this stage on annealing phenomena of Al_2O_3 powders and martensitic transformation of ZrO_2 crystals. Detailed processes of sintering, boundary migration, void disappearance, and the effect of other oxides such as MgO and ZrO_2 on the annealing phenomena of Al_2O_3 have been investigated.

INTRODUCTION

In order to study the properties of refractory materials with HVEM, the specimens are necessary to be heated and deformed at very-high temperatures under a necessary reflecting condition. The authors have previously reported a very-high temperature stage using an electron beam heating system and its applications to materials science[1,2].

In the present experiment, a new type of very-high temperature stage with both a universal tilting and a stretching systems has been developed. Using this stage, annealing and mechanical phenomena of various refractory materials have been widely studied in a wide temperature range up to 2300K with a 3MV electron microscope.

CONSTRUCTION AND FEATURES OF A NEW HEATING STAGE

Figure 1 shows an outside view of the newly-developed heating stage with which the specimens can be tilted up to $\pm 8^\circ$ around any axis[2] and stretched up to fracture in a wide temperature range from room temperature to 2300K. This stage was designed for use with a 3MV Hitachi HU-3000 type electron microscope so as to utilize the advantages* of HVEM. The tilting system consists of a sliding stage with a spherical surface, a supporter-ring, two driving wheels and a balancing weight. The specimen is set on the tip of a Ta-cylinder at a position corresponding to the center of curvature of the spherical surface. The Ta-cylinder is cut into two pieces which are relatively moved with a motor(M). The electron beam strikes the Ta-cylinder so that the specimen being controlled by the voltage supplied between the Ta-cylinder and a loop filament of 0.15mm ϕ W-wire, in the range 100~600V. The tilting mechanism can be used under stressing condition for the continuous observation of lattice defects in various materials even at high temperatures around 2300K. The electron microscope used was of Hitachi HU-3000 type and micrographs were taken at 2MV using a TV-VTR system.

* Simultaneous excitation of many reflections is important in observing lattice defects in different grains or powders at the same time.

EXPERIMENTAL RESULTS

[A] Stretching Experiments on the Dislocation Movement in α -Al₂O₃ at High Temperatures

Figure 2 shows successive stages of dislocation movement in a single crystal of α -Al₂O₃ in deformation at 1300K. Recording time of each micrograph is indicated at the lower side in a sequence of hour, minute, second and sub-second. Two dislocations in Fig.2 interact with each other during movement, but their own shapes do not change so much even at 1300K. The dislocations frequently change to helical ones when the same specimen was heated from room temperature to 1600K without stressing.

[B] Thickness Effect on Annealing Phenomena in α -Al₂O₃ Powders

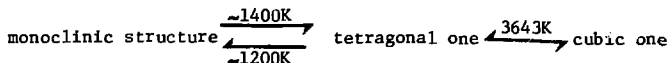
Figure 3 shows the effect of thickness on the annealing of α -Al₂O₃ powders. Micrographs (a) and (b) were taken after (a) a foil specimen of about 5 μ m thick and (b) a bulk specimen of 0.5 mm thick were annealed at 1800K for 1.8 ks respectively. The thickness of the bulk specimen was reduced to about 5 μ m after the annealing. From a comparison of these two micrographs, it is concluded that the effect of thickness on annealing phenomena such as sintering and grain growth is scarcely observed when the specimen thickness is about 5 μ m. Therefore, the following in-situ experiments were carried out using foil specimens of about 5 μ m thick.

[C] The Effect of MgO Addition on Annealing Phenomena of α -Al₂O₃ Powders

In-situ annealing has been carried out on sintering of α -Al₂O₃ powders without and with 0.1wt% MgO powders, respectively. Recrystallization occurs preferentially around small powders at the beginning of sintering so that the orientation of adjacent powders coincides with those of the small ones[2,3], and then mutual diffusion among the powders is enhanced. After that, vacant gaps among the powders gradually change to voids during sintering. During these processes, grain growth more rapidly occurs in α -Al₂O₃ without MgO[2]. This is due to the preferential disappearance of high-energy boundaries in the specimen. On the other hand, additional MgO powders preferentially coagulate on high-energy boundaries so that the energies of individual boundaries are homogenized. Therefore, the boundary reaction occurs rather homogeneously around all three-fold nodes of boundaries in sintered α -Al₂O₃ polycrystal with MgO and the average grain size does not increase so much compared with that in α -Al₂O₃ without MgO. Furthermore, the high-energy boundaries are almost completely shrunk in the later stages of grain growth in both the specimens, and thus the boundary energies depending on the boundary structures are also homogenized. As a result of these facts, the boundary reaction occurs homogeneously around individual three-fold nodes of boundaries.

[D] Phase Transformation in ZrO₂ by Cyclic Heating

ZrO₂ crystals show various functional characteristics. One of them is phase transformation and it has been used for increasing toughness of oxide-ceramics. It is known that the phase transformation occurs by thermal treatments as follows[5,6];



In the processes, very fine martensite crystals are formed by tetragonal



Fig.1 Outside view of a new type of high temperature stretching stage.

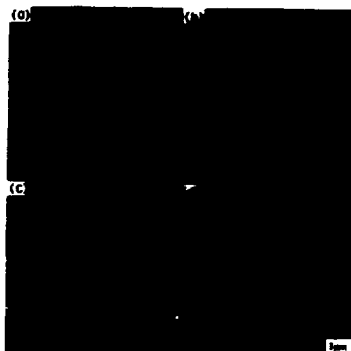


Fig.2 Dislocation movement in Al_2O_3 single crystal at 1300K.



Fig.3 Thickness effect on annealing phenomena of Al_2O_3 .

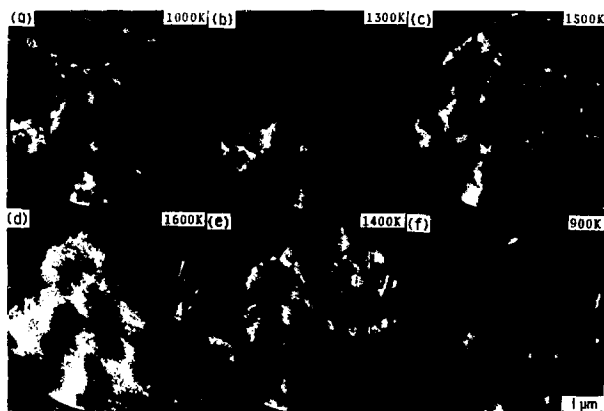


Fig.4 Phase transformation in ZrO_2 crystal by cyclic heating.

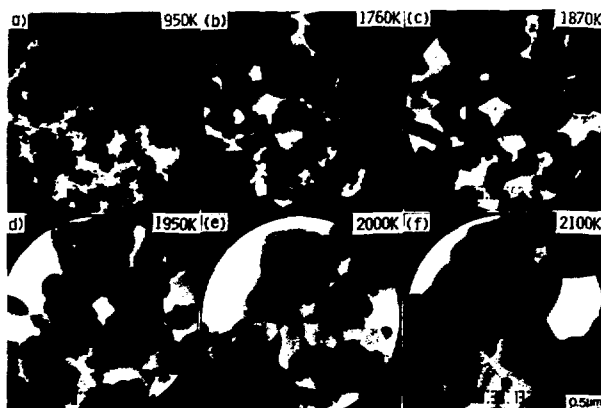


Fig.5 Sintering and successive grain growth of Al_2O_3 powders with 15vol.% ZrO_2 powders (VTR).

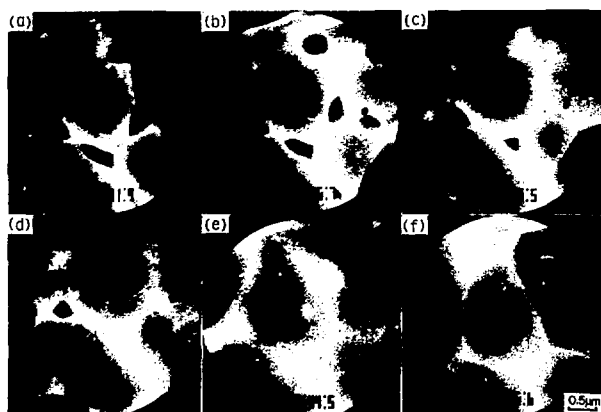


Fig.6 Interaction between Al_2O_3 grains and ZrO_2 grains (black contrast) at 2230K (VTR).

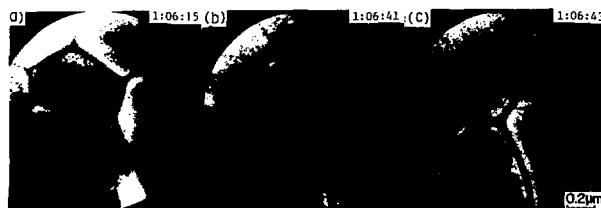


Fig.7 Boundary reaction in sintered Al_2O_3 with 0.1wt.% MgO . Grains A and B disappear at the same time with rapid migration of their boundaries at 2300K (VTR).

→ monoclinic transformation. Figure 4 is an example showing reproducibility of the martensitic transformation in ZrO_2 by cyclic heating. In Fig.4, fine monoclinic martensite plates in the matrix of tetragonal structure, micrograph (a), are gradually transformed to the tetragonal structure when the specimen temperature increases more than about 1300K, and the transformation is almost finished at about 1600K, (d). The monoclinic martensite plates begin to appear again at about 1400K by cooling, (e), and the matrix is completely covered with fine martensite plates at about 900K. In this process, each individual martensite plate is rapidly formed by cooling at the corresponding former position in micrograph(a). Namely, the martensite plates are reproduced almost exactly at the same positions by every cyclic cooling in the temperature range from room temperature to 1600K, and a considerably wide temperature range is necessary to finish the transformation in spite of rapid formation of each individual martensite plate, i.e., 1300 ~1600K for monoclinic → tetragonal and 1400 ~900K for the reverse process, respectively.

Furthermore, M_s temperature of monoclinic martensite decreases with increasing applied stress, as expected from the stress-induced martensitic transformation of other crystals.

[E] The Effect of ZrO_2 Addition on Annealing Phenomena of $\alpha-Al_2O_3$ Powders

Figure 5 shows sintering and successive grain growth of $\alpha-Al_2O_3$ powders with 15 Vol.% ZrO_2 powders which appear as very fine blocks in micrograph(a). When the powders are annealed, sintering successively occurs among $\alpha-Al_2O_3$ powders and also among ZrO_2 powders, respectively, as seen in (b). In this process, ZrO_2 powders coagulate to form some grains, which show black contrast in Fig.5, separately in $\alpha-Al_2O_3$ grains.

Furthermore, it is noted that the speed of grain growth decreases by ZrO_2 addition, but the voids are hardly formed in sintered regions. The latter is due to not only the enhancement of sintering around very fine ZrO_2 powders[3], but also a good affinity between $\alpha-Al_2O_3$ and ZrO_2 . The former results from the retardation of boundary migration with ZrO_2 grains, so that ZrO_2 grains are distributed at the three-fold nodes of $\alpha-Al_2O_3$ grains, as seen in Fig.6. The ZrO_2 grains are gradually absorbed into $\alpha-Al_2O_3$ grains along the boundaries by isothermal annealing at about 2000K, and then the growth speed of $\alpha-Al_2O_3$ grains rapidly increases when the ZrO_2 grains are completely absorbed, as seen in Figs. 6(e) and (f).

The toughness of sintered $\alpha-Al_2O_3$ powders markedly increases when the small ZrO_2 grains are distributed at every three-fold node of boundaries, as seen in Figs.6(a) ~ (c), because the stress concentration at the three-fold nodes is easily relieved by stress-induced martensitic transformation in small ZrO_2 grains, whose M_s temperature is about room temperature, even at low temperatures. On the other hand, when the specimens are kept for a long time at high temperatures larger than 2000K, the chemical composition is homogenized but the grain growth rapidly occurs, as seen in Fig.6(f). Furthermore, increase of the toughness due to the stress-induced martensitic transformation can not be expected in this case.

[F] Disappearance of Voids and Boundary Migration

When the temperature of Al_2O_3 crystals is increases to about 2300K, marked grain growth occurs, as seen in Fig.7. In Fig.7 grains A and B are rapidly eliminated by the boundary reaction around individual three-fold nodes of boundaries. The migration speed of the boundaries is estimated to be about 0.4 m/s. Here it is noted that voids are quickly absorbed into the grain bound-

daries which hit the voids[2,4]. Figure 8 shows the detailed process of the disappearance of a void into a three-fold node of boundaries. Micrographs (a)-(h) were taken in about one second. When a three-fold node of boundaries hits the void, the lower part of the void is first absorbed into the lower boundaries, as seen in (b) and (c), and then the upper part of the void is also absorbed into the boundaries. Finally, the residual part of the void is absorbed very rapidly into the three-fold node of boundaries in less than a thirtieth of a second, as seen in micrographs(f)-(h).

The voids also migrate during heating, as seen in Fig.9, depending on the specimen temperature. The migration speed of voids increases with increasing temperature and decreasing size of the voids, and it is quite small in general even at 2300K[2]. Thus, even when the voids migrate towards the specimen surface, the tendency of the voids to escape from the surface is very low because of their small driving force, as seen in Fig.9. Namely, disappearance of voids is mainly controlled by the migration speed of boundaries. This phenomenon can be effectively used for eliminating voids which were formed by any process such as sintering and irradiation damage in materials.

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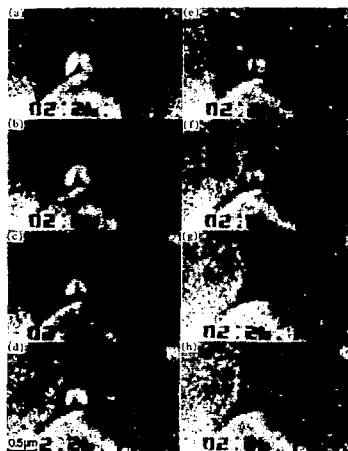


Fig.8 Absorption of a void into a migrated three-fold node in sintered Al_2O_3 with MgO at 2300K (VTR).

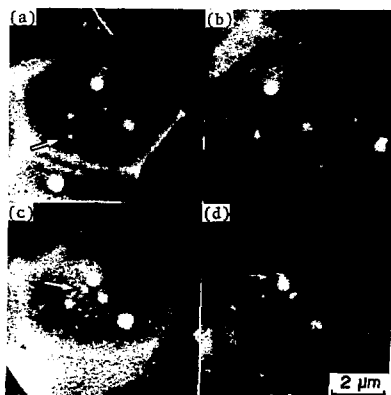


Fig.9 Movement of voids in sintered Al_2O_3 with MgO at 2300K. A small void (↑) moves towards the upper side, but interaction with neighboring voids is not so large (VTR).

HIGH-RESOLUTION STUDIES OF DEFECTS IN NATURAL DOLOMITES

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ABSTRACT

Modulation microstructure and other defects in various sedimentary, low-temperature dolomites have been investigated using lattice imaging techniques at 500kV. In general, lattice planes are observed to be continuous across the modulations but show local bending or changes of interplanar spacing, suggestive of compositional variations. Evidence for widespread disorder or ApBs is uncommon. Multi-slice image calculations indicate that lattice images only provide information about cation positions.

INTRODUCTION

Interest in structural defects in dolomite, $\text{CaMg}(\text{CO}_3)_2$, has been stimulated by the recent TEM observations of Reeder and Wenk [1-3] of sedimentary dolomites which revealed diffuse modulated microstructures. Reeder [3] has associated such microstructures with non-stoichiometry ($\text{Ca/Mg} > 1.0$), but Gunderson and Wenk [4] have observed similar effects in fairly pure oolitic calcites which suggests that the origins of the microstructures might be complex. It is important to understand the origins and significance of these features since the processes whereby well-ordered dolomites evolve from disordered precursors are not well understood. Moreover, superficially-similar microstructures have now been found in uncommon sedimentary 'saddle' dolomites [5] and high temperature dolomite carbonatites. In this paper, we describe observations of microstructures and crystal defects in dolomite using the Cambridge University 600kV high resolution electron microscope (HREM) [6] operated at 500kV, as well as lower resolution studies using AEI EM-7 and JEOL 200CX instruments. The 600kV HREM has a point-to-point resolution of better than 0.20nm and is thus well-suited to the lattice imaging of dolomites since major lattice spacings are typically $\sim 0.2\text{--}0.3\text{nm}$. Although most carbonates suffer radiation damage at 100kV, the damage rate decreases substantially at higher voltage so that high voltage electron microscopes have featured strongly in earlier carbonate work, e.g. [7,8]. Indeed, we have found it possible to image under high beam current conditions at high magnifications without resort to minimum exposure techniques [9].

RESULTS AND DISCUSSION

Dolomite (symmetry $R\bar{3}$) possesses an ordered layering of Ca^{2+} and Mg^{2+} ions, interleaved by layers containing CO_3^{2-} groups, with the normal to the layers corresponding to the z -axis (hexagonal axes $c=1.598\text{nm}$, $a=0.480\text{nm}$). Figure 1 is an example of the modulated microstructure in specimen #102-429. Two modulations with different wave-lengths are visible, approximately orthogonal to each other and corresponding to the trace of $\{10\bar{1}4\}$ planes. Lattice images from several specimens of different geological age have shown similar features.

For example, Figure 2 shows modulations in specimen 124-9, bulk composition $\text{Ca}_{1.1}\text{Mg}_{0.88}(\text{CO}_3)_2$, but close examination does not yield much information about their nature. The lattice planes are continuous across the lamellae (i.e. there are no offsets which might correspond to APB's, etc.) and the diffraction contrast is seen to result from slight local tilting of the lattice away from the ideal imaging condition. The imaging planes are wavy where they cross the lamellae and the interplanar spacing is varied.

A geologically young (Holocene) dolomite shows much more varied microstructures and no well-defined lamellae. In this case, much of the lattice is continuous and undistorted, but regions exist where lattice twists and discontinuities occur, as exemplified by fig.3a. This particular region appears to consist of several small subgrains adjacent to an amorphous region, and yet APBs are not apparent in the crystalline fraction. Figure 3b shows another part of the same specimen in which dark striations (perhaps diffuse lamellae) are visible. The striations correspond to regions where the definition of the lattice image is degraded, presumably showing that some of the atoms are situated at non-ideal positions, and are indicative of either impurity atoms or disorder.

Well-defined, almost planar faults are present in a young Mississippian dolomite DC-FL, as shown in the lattice image of Fig.4a. Offsets in the lattice planes can be found along the lengths of the faults, (approximately parallel to the $\{0001\}$ planes). We believe that the faults shown here are not thermal APBs, which in dolomite are strongly curved and not crystallographic (see Reeder and Nakajima [10]), but faults in the stacking of cations, possibly a result of nonstoichiometry. Many of the faults extend over several $\{0006\}$ interplanar spacings, as also noted for basal faults generated in dolomite by slip [12]. APBs do exist in the Mississippian material, as illustrated in fig.4b. In fact, of the sedimentary dolomites examined by HVHREM, this specimen, DC-FL, is most similar in characteristics to dolomite disordered at high temperatures [10], and later examined by us, shown in fig.5. In this material there are numerous curved APBs and planar faults parallel to $\{0001\}$ which are mistakes in the regular alternation of Ca and Mg layers.

The evidence presented here is insufficient, without better compositional data than is currently available, to establish the nature of modulated structures in sedimentary dolomites. A further complication is the possibility of carbonate group rotational disorder [4], an idea given some support by the recent work of Barber et al [11]. Unfortunately, however, multi-slice image simulations indicate that only the cation sublattice is resolvable in current microscopes; substantial improvements are required before the positions of the atoms comprising the CO_3 group can be determined. Fig.6 shows idealised Weak-Phase-Object simulations [12] over the resolution range from $4\text{\AA}$ to $1\text{\AA}$. At $2.7\text{\AA}$ WPO resolution the Ca and Mg sites are indistinguishable and, although contrast differences become more apparent as resolution improves, it is not until resolutions approaching $1\text{\AA}$ that the orientations of the CO_3 groups become visible.

We acknowledge SERC for continued support for the 600kV HREM and NERC (grant GR3/4324) for supporting research on dolomites. We thank R.J. Reeder and H.R. Wenk for samples and continuing collaboration.

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Fig.1. Modulation microstructure in sedimentary dolomite, 102-429 (Pleistocene) Koobi Ford, East Africa. Two approx. orthogonal modulations are visible.



Fig.2. Lattice image of modulations in Eugene specimen 124-9 (Floridan aquifer), viewed along $\langle 1120 \rangle$ zone axis.

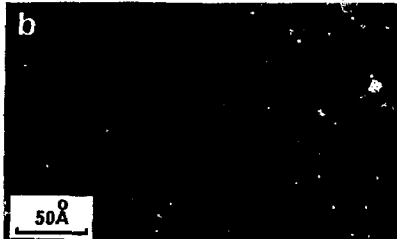
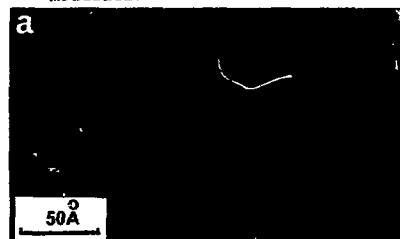


Fig.3. (a) Lattice image illustrating lattice twists and discontinuities in geologically-young (Holocene) dolomite; (b) Lattice image of striated region in Holocene dolomite. Lattice perfection is impaired in the dark striations.

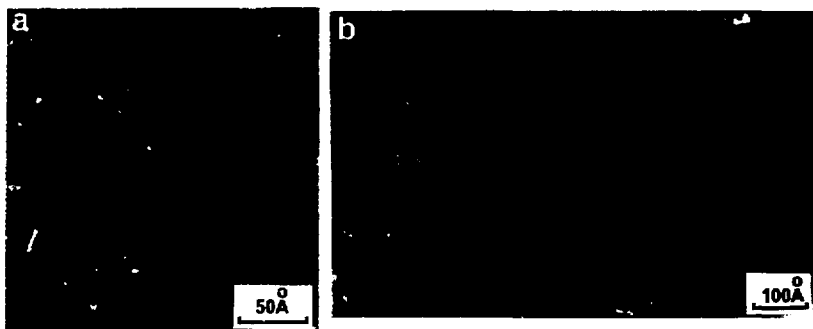


Fig.4. (a) Lattice image of approximately planar $\{0001\}$ cationic stacking faults in nearly stoichiometric Mississippian dolomite, DC-FL. The width of the faults extends over several basal interplanar spacings; (b) Curved APB and adjacent cationic stacking faults in Mississippian dolomite, DC-FL.



Fig.5. Lattice image of curved APB and cationic stacking faults in thermally-disordered Eugui dolomite (after Reeder and Nakajima [10]),

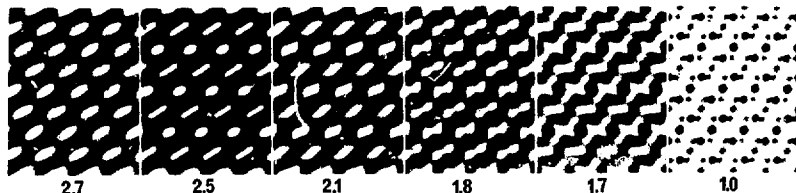


Fig.6. Weak-Phase-Object simulations of dolomite showing change in appearance as image resolution (marked) improves.

HIGH-RESOLUTION IMAGING OF REDUCED AND DEFORMED RUTILES

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ABSTRACT

Structural defects occurring in samples of plastically deformed, non-stoichiometric rutile, TiO_{2-x} ($0 < x < 0.0035$), have been characterised by high resolution electron microscopy. Crystallographic shear planes (CSPs) were observed, although not seen previously in quenched non-deformed materials of this composition range, and these had considerable local disorder in orientation and structure. These observations imply a different precipitation mechanism for these defects in deformed samples. $\{100\}$ platelet defects were also observed both in isolation and "decorating" CSP. Computer image simulations offer a useful guide for interpreting high-resolution images of the CSP and the possibility of semi-quantitative or quantitative confirmation of models.

INTRODUCTION

Recent studies by high resolution electron microscopy (HREM) of undeformed nonstoichiometric rutile, TiO_{2-x} ($0 < x < 0.01$), reduced at 1323K, have confirmed the absence of crystallographic shear planes (CSP) in specimens quenched from 1323K with $x < 0.0035$ [1], and established a number of structural features not revealed by earlier low-resolution studies. These include: *i* the existence of $\{100\}$ platelet defects in rapidly-cooled specimens forming at lower temperatures than CSP and often "decorating" the CSP [2]; *ii* the precipitation of pairs of CSP in slowly-cooled crystals [3] with the longitudinal and lateral order of the CSP fine structure increasing for slower cooling rates [4]; *iii* the presence of "small linear" defects in quenched and rapidly-cooled material [5]. These results have led to the development of new structural models for cation interstitial and anion vacancy defects [6]. In this paper we describe recent 500kV high-resolution studies of nonstoichiometric rutile crystals which have been mechanically deformed and contrast the results with those obtained previously in non-deformed samples.

METHODS

Single crystals were cut as parallelepipeds ($\sim 6 \times 6 \times 2.8 \text{ mm}^3$) and then reduced and deformed, at a strain rate of $5.6 \times 10^{-5} \text{ s}^{-1}$, at 1323K (with composition maintained), and then cooled to room temperature in a dynamic vacuum of 10^{-6} torr to preserve stoichiometry [1,7]: the two samples described below, of compositions $\text{TiO}_{1.9965}$ and $\text{TiO}_{1.9970}$, were cooled to RT in 2 mins and 5 mins respectively. In both cases, mechanical compression was along $[001]$ so that the $\{101\} < 101 \rangle$ slip systems were active [7]. Foils suitable for electron microscopy were prepared by mechanical polishing followed by ion-beam thinning [4]. Examination was with the Cambridge University HREM [8] operated primarily at 500kV, normally with crystals oriented to the $[111]$ projection since the series

of swinging CSP in rutile all contain this axis. Dynamical electron scattering within the crystals was simulated using the multislice formulation [9,10] and then used for image generation.

RESULTS AND DISCUSSION

Low magnification images showing the characteristic microstructure of the two different materials are shown in Figs.1(a) and (b). Families of CSP of equivalent (mean) orientations, often terminated by platelets (T), are visible either inclined (giving fringe contrast) or edge-on. Isolated inclined platelets (P) can also be seen. The traces of the edge-on CSP reveal frequent deviations of the same CSP (up to $\sim 5^\circ$) with respect to the mean orientation {132} and some exhibit splitting or branching (S).

High-resolution images show a number of other structural features which differ from those listed above for non-deformed specimens. Most CSP were observed having mean orientation lying between {132} (as expected from previous studies) and {011} (corresponding to a slip plane). Fig.2, for example shows two widely-separated defects, having mean orientations {143} and {275}, each having lattice fringe displacements consistent with single CSP [11]. Moreover, compared with undeformed samples, there was a relatively high proportion of these isolated planar defects, such as shown in Fig.3, and many changed frequently to pairs of CSP over short distances, as seen in Fig.4, (top left). Note also the line contrast features parallel to {011} in Fig.4, suggesting aggregation and ordering of small defects at the boundary [2,6].

As well as considerable disorder and variations in composition along their length, the CSPs generally produce quite broad contrast despite careful alignment procedures. This suggests disorder along the beam direction, namely [111]. Computer simulations for imaging at 500kV are shown in Fig.5 for a range of CSPs having mean orientations between {011} and {121} in crystals 35.7Å thick at the optimum Scherzer defocus position. All cation positions in the rutile basis structure are clearly resolved as black spots, as are the cations at the antiphase and face-shared octahedral elements within the various boundaries. It was very uncommon for the experimental images of CSPs in the deformed samples examined here to appear as clearly as in the simulations, although the rutile matrix usually did. Image simulations over a wide range of defocus and thickness values for boundaries ordered along [111] were unable to reproduce the broad contrast, thus confirming the lateral and longitudinal disorder [see 4,5].

The various precipitation phenomena observed to occur in slightly-reduced undeformed rutile are consistent with new interstitial cationic defects, based on pairs of face-shared octahedra. In deformed samples, dislocations presumably already exist and the face-shared octahedra in these defects can act as nucleation sites for the formation of single CSPs - our structural interpretation of single CSP terminations, to be described elsewhere [12], confirm an interstitial mechanism for CSP generation.

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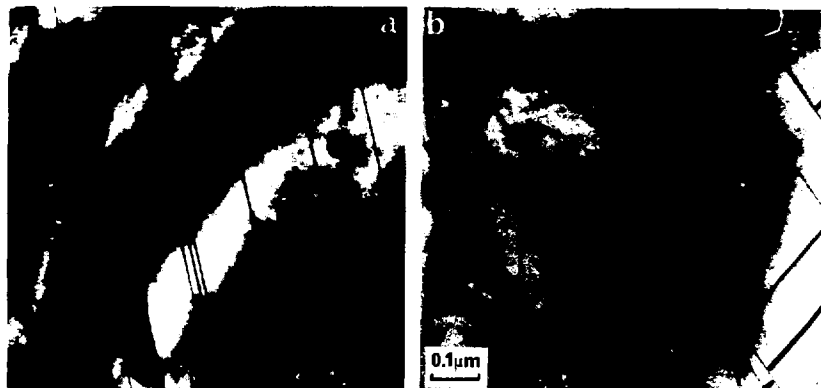


Fig.1. Low magnification images of (a) $\text{TiO}_{1.9965}$, and (b) $\text{TiO}_{1.9970}$ showing typical defect morphology. Note isolated inclined platelets (P), CSPs terminated by platelets (T) and CSP splitting (S).

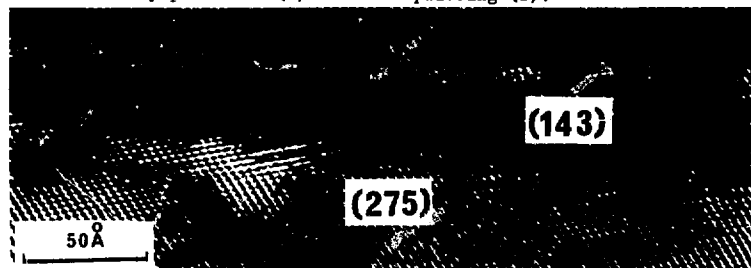


Fig.2. High resolution image showing extended CS defects having mean orientations {143} and {275} as indicated.

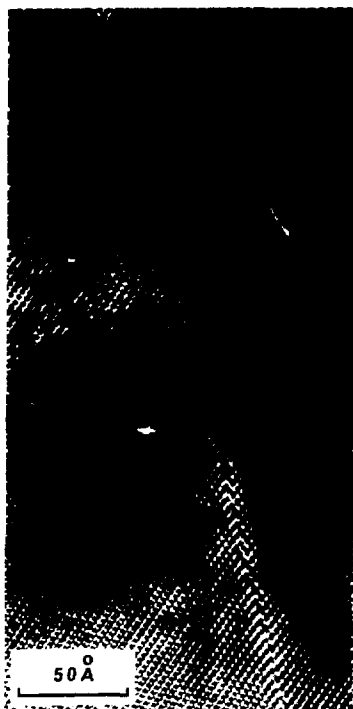


Fig.3. High resolution image of isolated CSP.

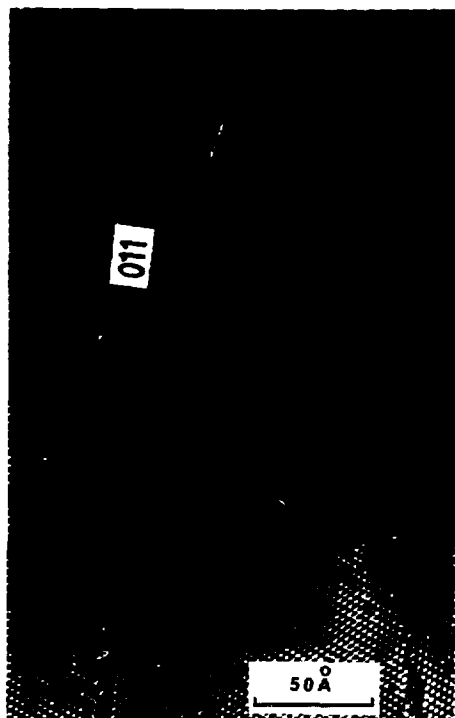


Fig.4. Two extended CS defects with considerable lateral disorder. Note also the (011) line contrast features.

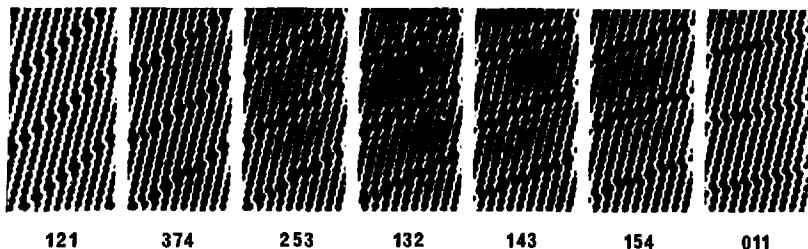


Fig.5. Image simulations for a range of CSPs with orientations marked. 500kV, $C_s = 2.7\text{mm}$, $R = 1.7\text{\AA}$, $\Delta = 160\text{\AA}$, Scherzer defocus ($619\text{\AA}$).

HIGH RESOLUTION STUDIES OF Bi-W-OXIDES

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ABSTRACT

Intergrowth tungsten bronzes of stoichiometry $\text{Bi}_x\text{W}_{1-x}\text{O}_3$ ($x \sim 0.1-0.2$) have been examined by 500kV high-resolution electron microscopy (HREM) before and after annealing in vacuo at 950°C. In untreated samples, the ITB structure has been directly confirmed. After heat-treatment, the material was observed to decompose to a disordered Aurivillius phase, with some reduction of the remaining WO_3 matrix. The conversion clearly took place in a topotactical manner and both lamellar and equidimensional nuclei developed.

INTRODUCTION

Bi and W are known to form a series of "Aurivillius" phases with composition $\text{Bi}_n\text{W}_{1-n}\text{O}_{3n+2}$. Those with $n=1$ and 2 have been observed in well-ordered form [1,2] whilst HREM has indicated a disordered $n=3$ phase [3]. More recently, oxides of composition $\text{Bi}_x\text{W}_{1-x}\text{O}_3$ ($x \sim 0.1-0.2$) have been prepared, comparable to the intergrowth tungsten bronzes (ITB) phases. These latter materials, typified by those containing Rb or Cs [4,5], have been shown to consist of slabs of WO_3 structure separated by single or double strips of hexagonal tungsten bronze (HTB) configuration, with the alkali cations accommodated in the hexagonal tunnels. This type of tunnel structure was not seen in initial HREM studies of the Bi-bronze materials, which gave images more closely resembling those of the PbWO_3 phase [6]. Image-matching at 200kV indicated, however, that the Bi-bronzes did possess the accepted ITB structure, although with all tunnels being filled the similar scattering factors of Bi and W were making structural identification difficult. This study, which will be published elsewhere [7], also indicated a barely sufficient resolution at 200kV, and hence the present higher-resolution 500kV study has been carried out.

EXPERIMENTAL

The samples were prepared in the Indian Institute of Science, Bangalore, by Prof. C.N.R. Rao, and had nominal compositions of $\text{Bi}_{0.1}\text{W}_{0.9}\text{O}_3$ and $\text{Bi}_{0.2}\text{W}_{0.8}\text{O}_3$. Sample preparation was by direct combination of metallic Bi and WO_3 in sealed tubes at 850°C for six days. Further heat-treatment involved annealing at 600°C, and, for one portion of the $\text{Bi}_{0.2}\text{W}_{0.8}\text{O}_3$ sample, annealing at 950°C in vacuo for four days. Crystals of each sample were deposited from suspension onto holey carbon films and examined in the Cambridge University HREM at 500kV [8]. Images were normally recorded at magnifications of ca. 600,000X after correction of astigmatism and beam alignment by observation of the support film granularity.

RESULTS AND DISCUSSION

Initial examination at 500kV confirmed the ITB structure of the Bi-bronzes: a typical micrograph taken along the tunnel axis is shown in Fig.1 together with a schematic representation of the structure. In some regions it appears that electron irradiation creates vacant tunnels which are readily observed, as in the Ba-bronzes [9]. The surface restructuring of this phase is also very clearly revealed. When viewed in a direction perpendicular to the tunnels, as shown in Fig.2, only a slight discontinuity is observed at the positions of the hexagonal tunnels, suggesting that the Bi and W cations all lie in the same plane, unlike the alkali bronzes. Although relatively well ordered on a sub-1000Å scale, the overall spacing of the superlattice varied considerably, averaging one HTB strip in every eight WO_3 layers. No cases of double HTB strips were noted.

No structural re-ordering of the structure was observed after annealing at 600°C, but, after heating in vacuo at 950°C, considerable changes became evident. The overall periodicity of the lattice became more variable, and the presence of free WO_3 and a new layered structure were noted. This latter material, shown in Fig.3 could be identified as the phase $Bi_2W_9O_{29}$, although it was generally found in a more disordered state than that shown in Fig.3. Single unit-cell strips of higher-order numbers were also observed up to a maximum of $n=7$. Fig.4 shows the edge of the most common type of fragment, with $n=2$, $n=3$ and $n=4$ regions visible. Finally, as seen previously [3], in situ reduction to WO_3 often occurred at crystal edges.

Although the resultant Aurivillius phase generally occurred in relatively equidimensional nuclei of greater than 1000Å diameter, these were invariably oriented along one of the principal directions of the WO_3 matrix. In some cases a lamellar-like development of $Bi_2W_9O_{29}$ was observed: one such is shown in Fig. 5, where four $Bi_2O_7^{2+}$ layers have been produced. This type of lamellar growth would be expected to produce minimum strain energy with the WO_3 matrix, and could thus represent the equilibrium assembly. Because the annealing occurred in vacuo, the WO_3 matrix was also disordered and many examples of CS planes were visible as shown in Fig.6. Similar features, though often more disordered, were common to all extensive areas of WO_3 .

We are grateful to Prof. C.N.R. Rao for provision of specimens and S.E.R.C. for financial support.

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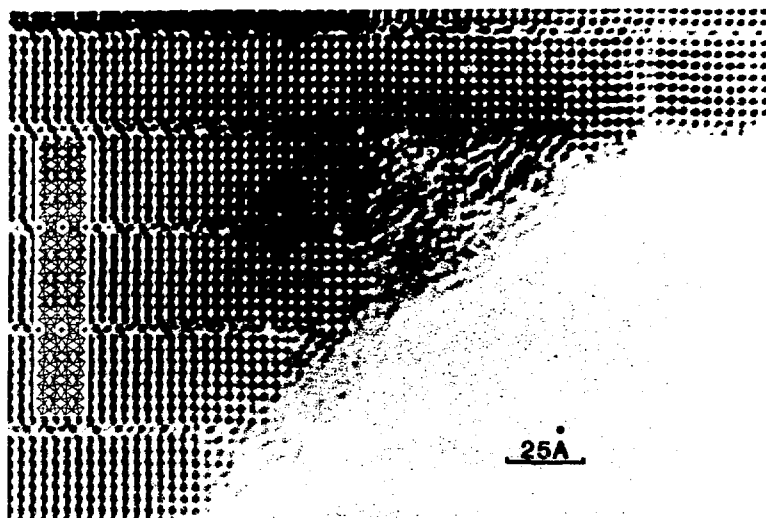


Fig.1. High-resolution structure image of $\text{Bi}_{0.1}\text{WO}_3$ showing ITB structure between WO_3 blocks, with structural schematic inset.



Fig.2. Structure image of $\text{Bi}_{0.1}\text{WO}_3$ perpendicular to tunnel direction.

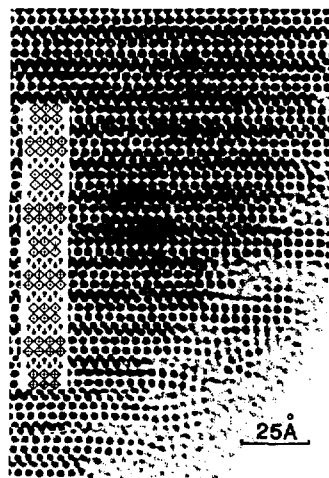


Fig.3. Structure image from a crystal of $\text{Bi}_2\text{W}_2\text{O}_9$, obtained after annealing treatment.

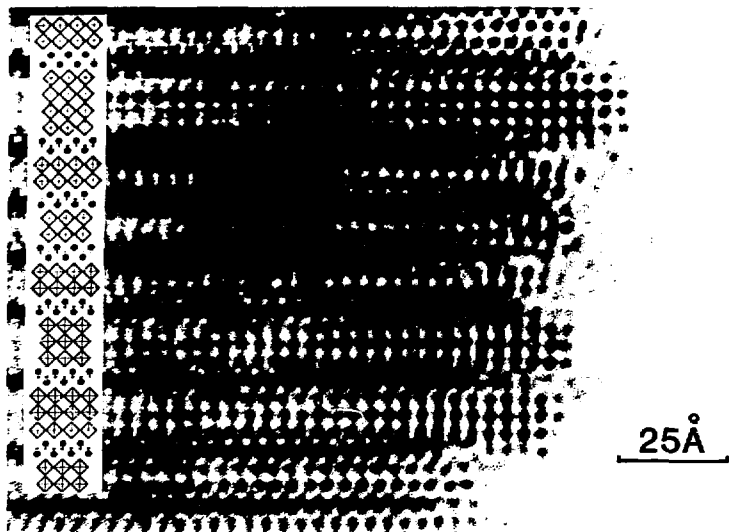


Fig.4. Typical mixed layer structure visible after annealing with schematic structure inset.



Fig.5. Lamellar-like development of $\text{Bi}_2\text{W}_2\text{O}_9$.

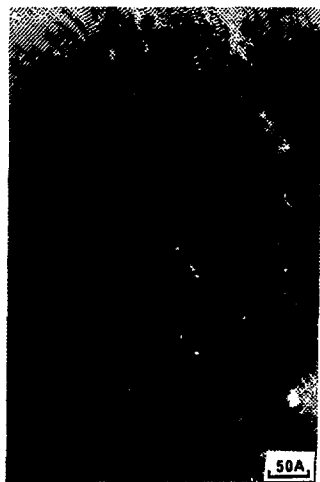


Fig.6. Area of WO_3 matrix showing development of CS planes.

SEMICONDUCTORS AND THIN FILMS



ON THE FORMATION OF LATTICE DEFECTS IN TWO-STEP ANNEALED CZOCHRALSKI SILICON

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ABSTRACT

The defects introduced during a low temperature nitrogen anneal and during a subsequent high temperature oxidation in Czochralski silicon wafers with a high interstitial oxygen content are studied by means of high voltage and high resolution electron microscopy. After the low temperature step the defects can be characterized as rod-like defects, dislocation dipoles and platelike precipitates. Upon high temperature oxidation faulted and perfect dislocation loops and octahedral precipitates are formed. The size and density of these defects are strongly determined by the conditions of the preanneal.

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INTRODUCTION

The increasing interest both in the intrinsic gettering capabilities of lattice defects present in the silicon bulk and in the formation of a defect denuded zone near the wafer surface, has recently led to a large number of investigations concerning the influence of multistep annealing treatments on the reduction of the interstitial oxygen content and the therewith connected formation and growth of lattice defects [1-6].

In a previous report [4], results were discussed on the influence of a low temperature treatment in the range 650°C - 900°C on the defects formed during a subsequent high temperature oxidation. It is seen that the defect density and size are strongly correlated with the conditions of the low temperature treatment and with the interstitial oxygen content of the wafers.

In the present paper the defects which are introduced during a low temperature treatment will be studied and their correlation with the defects generated during the subsequent high temperature step will be discussed.

EXPERIMENTAL PROCEDURE

The experiments are performed on Czochralski grown silicon wafers with a high interstitial oxygen content of $11.5 - 11.7 \cdot 10^{17}$ atoms/cm³ (IR determined following the DIN-norm 50438) and a low carbon concentration of $7.0 \cdot 10^{15}$ atoms/cm³. The crystal is grown in the [001] direction with a diameter of 80mm and wafers are cut out of it both in the [001] and in the [111] orientation. These are chemically etched to a thickness of about 700 µm. The material is p type (boron-doped) with a resistivity of 14 Ωcm.

The low temperature treatments are performed in a nitrogen atmosphere in the temperature range 650°C - 900°C for 3 h to 100 h. The high temperature steps are done in a wet oxygen ambient at 1150°C for times between 10 minutes and 8 hours.

The wafers are studied by means of high voltage electron microscopy (HVEM) in a Jeol 1250 kV microscope operating at 1000 kV. The high voltage is advantageous because of the possibility to investigate relatively thick areas (more than 5 μm), so that a large transparent region is obtained, which is particularly useful in case of a low defect density. The nature of small defects, which cannot unambiguously be determined in the two beam imaging mode, is further investigated with high resolution electron microscopy (HREM) in a Jeol 200 CX instrument. In order to obtain specimens in the $[110]$ orientation, which is the most suitable one for high resolution imaging, a cross section thinning method is developed [7].

Although radiation damage in the high voltage electron microscope is not a severe problem under normal working conditions, small black-white spots appear in the specimens (fig.1a). If these are subsequently investigated with the HREM-technique, small amorphous regions are observed (fig.1b) which are correlated with the radiation damage. This phenomenon was extensively studied by Werner et al [8]. As will be seen further, other amorphous defects are also present in the material. Therefore care is taken not to study specimens with the high voltage electron microscope if these are to be analysed with HREM.

RESULTS AND DISCUSSION

After the low temperature treatments, three different types of defects can be identified [9] : rod-like defects, dislocation dipoles and platelike silicon oxide precipitates.

The rod-like defects are only present at the lowest treatment temperatures (650°C - 750°C). They are elongated in the $\langle 110 \rangle$ directions and show in two beam imaging conditions always weak contrast independent of the diffraction vector. They have therefore no dislocation character. Only for the diffraction vector $g = (220)$ parallel to the line direction, perfect extinction is observed. Their displacement field can be described as $R \propto [001]$. Similar defects are also observed after the anneal of ion implantation damage [10] and after analogous treatments as discussed here by Tempelhoff et al [2] and by Bourret [11], who has identified these defects by means of high resolution electron microscopy as crystalline SiO_2 precipitates with the coesite structure. Possibly the nucleation of these rod-like defects occurs on the intermediate defect complexes (IDC) which are discussed by Tan et al [12] in order to explain the formation of dislocation dipoles during a low temperature anneal or during the anneal of ion implantation damage. These aggregations of point defects (vacancies or interstitials) along $\langle 110 \rangle$ directions have been observed by Föll et al [13] after the anneal of As^+ ion implantation damage. As yet, no evidence is obtained that these IDC's are present in our starting material or are formed during the initial stage of our anneal treatments.

In the same temperature region, also dislocation dipoles are found. These too lie in the $\langle 110 \rangle$ directions. The majority of them are characterized as interstitial type 60° dislocation dipoles; only a minority has an edge type Burgers vector. HREM-imaging shows that the dislocations are usually undissociated and are not or only weakly decorated. The habit plane of the dipole is

close to the $\{113\}$ plane and the separation of the two dislocations is of the order of 30 nm. The dislocation dipoles are connected with the rod-like defects and are aligned along the same $\langle 110 \rangle$ directions. Their widths can increase by the absorption of silicon interstitials which are formed due to the concentration difference of the silicon atoms between the oxide precipitates and the silicon matrix. With increasing temperature the density of the dipoles decreases, so that they are nearly absent above 800°C. Those present at the higher temperatures are usually severely decorated and often dissociated (fig. 2).

Over the whole temperature range small precipitates are observed. At the lowest temperatures (650°C - 750°C), they are seen as small black-white contrast features in the HVEM. For the higher temperatures, they can be characterized as platelike precipitates which are usually associated with perfect dislocation loops. They lie parallel to the different $\{001\}$ planes with their sides in $\langle 110 \rangle$ directions. The surrounding silicon matrix shows a strong strain field. In no case, even for the largest ones in very thin regions, supplementary diffraction spots can be observed. Because the area selected for obtaining the diffraction pattern, always corresponds with a specimen volume which is much larger than the precipitate volume, this observation is insufficient to determine the structure of the precipitates as a noncrystalline phase. However, the structure of these defects can be unambiguously determined with HREM. It is seen that the platelike precipitates consist of amorphous silicon oxide. Until now, the exact composition could not be determined, but parallel measurements with infrared absorption show a decreased interstitial oxygen content after the heat treatments, which indicates the composition to be SiO_x (with x presumably close to 2). The size of the precipitates increases with time and temperature, but their thickness never exceeds 4 nm. Once this thickness is reached the growth can be considered as a two dimensional process at the precipitate edges.

The high temperature wet oxidations are performed after a low temperature treatment of 3 h or 15 h at temperatures between 650°C and 900°C. It was observed [4] that the stacking fault density rapidly increases with the preanneal temperature, reaches a maximum around 800°C - 850°C and then steeply decreases. Without a preanneal in the cited temperature range, nearly no defects are formed. The stacking fault diameter shows an inverse behaviour. The defects are characterized as extrinsic Frank partial dislocation loops with $b = \frac{1}{3}[111]$. They are heterogeneously nucleated in the initial stage of the high temperature treatment on precipitates formed during the low temperature preanneal. This initial precipitate remains in the center of the stacking faults. Normally, no other decoration in the fault plane or on the bordering partial dislocation is observed by HVEM. As the partial dislocation is curved, no end-on structure imaging of the core region, which would clearly reveal any possible decoration, can be performed.

The stacking fault behaviour is studied as a function of the oxidation time for respectively a low (650°C preanneal) and a high (850°C preanneal) defect density. In the first case, the SF-growth goes on till about 1.5 h and multiple faults are formed. The transformation of a double Frank partial into a $\frac{1}{6}[114]$ stacking fault and a perfect dislocation loop is not very often observed, in contrast with some of our previous investigations [14] which were, however, performed on different silicon material.

The defect density remains nearly constant with oxidation time. In the case of the high SF density (fig.3), the defects have reached their final dimensions already after a 10 minutes oxidation. This indicates that all silicon interstitials, which are generated by the oxygen precipitation process, are absorbed by the SF's and by the perfect dislocation loops. No multiple stacking faults are formed under these conditions and again the defect density is independent on the oxidation time.

Perfect dislocations are present together with the faulted loops. Dislocation dipoles, prismatic loops in $\{110\}$ planes and small irregular loops can be distinguished. The dislocation dipoles have a high density in the wafers pretreated between 700°C and 800°C. They have the same Burgers vectors as those observed after the low temperature steps, but their widths are always much larger (about 100 nm). Oxide precipitates decorate these dislocations. The prismatic loops are hexagonal or diamond-shaped with an edge type Burgers vector and are of the interstitial type. They are mainly observed in the wafers which received a low temperature treatment at 850°C - 900°C. Prismatic punching on platelike precipitates only occurs in wafers pretreated at 900°C.

Except after a preanneal at 900°C, the platelike precipitates which are formed during the low temperature step are replaced by truncated octahedral ones after an oxidation of 1.5 h. In the HVEM, these are observed as small (30 nm) black or white, hexagons or squares in specimens with respectively $[111]$ and $[110]$ or $[001]$ orientation (fig.4a). The shape for the different orientations corresponds with the projection of a truncated octahedron. A perfect octahedron should show a diamond-shape in the $[110]$ orientation, which is not observed. The exact structure could be determined by high resolution imaging (fig. 4b). Hexagonal regions with different contrast than the surrounding silicon matrix are observed. The precipitates are usually only partly contained in the thinned specimen. Along the $[110]$ diagonal of the hexagons, where the projected precipitate thickness is the largest, an amorphous contrast can be seen if the thickness of the underlying silicon matrix is small compared with the precipitate thickness. In very thin specimen regions, the amorphous contrast can be observed in nearly the whole hexagon. These precipitates also consist of amorphous silicon oxide like the platelike ones. The edges of the octahedral precipitates are smaller than those of the platelike ones which are present after the low temperature step, so that the volumes are roughly the same. During the high temperature treatment, the platelike precipitates grow out normal to their $\{100\}$ habit plane, while shrinking in the other directions. Due to this rearrangement, the strain is fully resolved and silicon interstitials are ejected, which are absorbed by the faulted or perfect dislocations. Octahedral precipitates have been observed during high temperature treatments by different authors [5, 15, 16]. The truncated structures discussed here, will probably further grow out to perfect octahedra, during the longer treatment times. Maybe the platelike precipitates formed during the 900°C preanneal, are too large to transform to an octahedral shape and in this case the strain is released by the prismatic punching mechanism.

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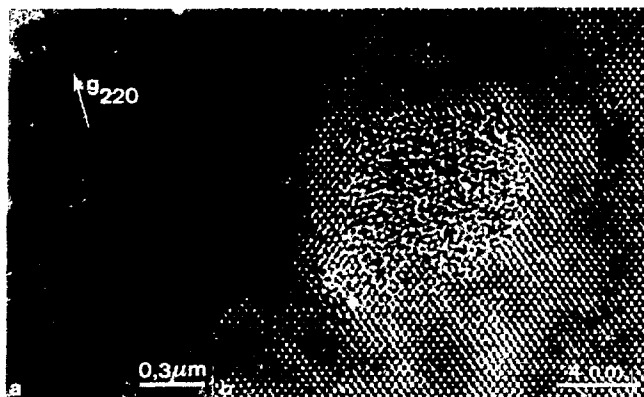


Fig.1. HVEM (a) and HREM (b) images of radiation damage produced in the high voltage electron microscope.

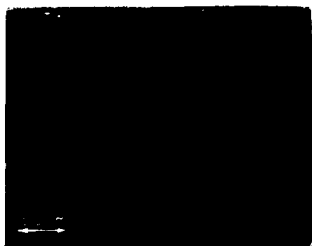


Fig.2. A weak beam image of a dissociated and decorated dislocation dipole (N_2 800°C 50 h).



Fig.3. A high SF-density is observed after a two step anneal : N_2 850°C 3 h + wet O_2 1150°C 1,5h.

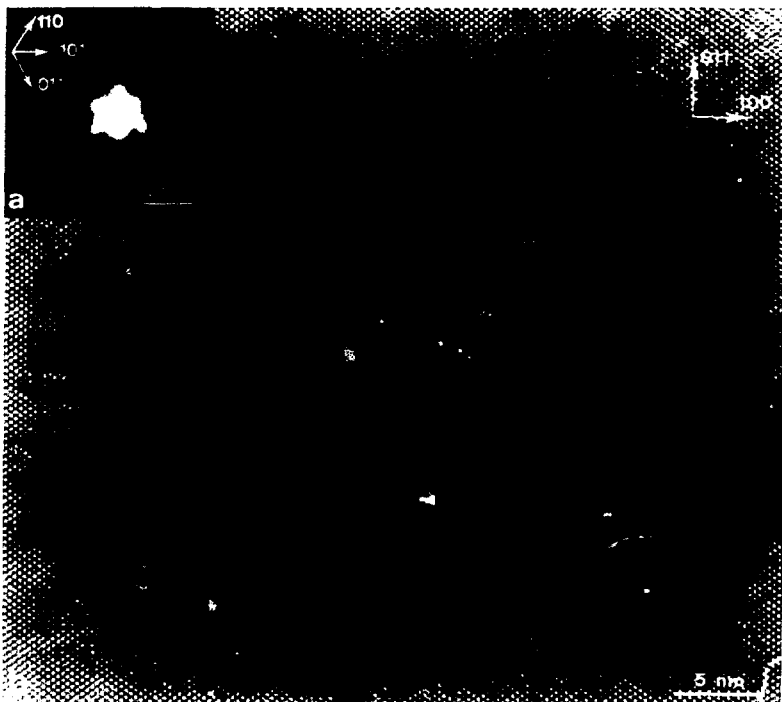


Fig. 4. HVEM (a) and HREM (b) images of a truncated octahedral precipitate for respectively a $[1\bar{1}1]$ and a $[01\bar{1}]$ oriented specimen.

CRITICAL VOLTAGE EFFECT OF SI-GE SOLID SOLUTION

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ABSTRACT

The critical voltages of Si-Ge solid solutions and pure elements were measured as functions of temperature and composition. The atomic mean square displacements were derived from the measured critical voltages for 333 and 440 reflections. The concentration dependence of the Debye temperature and the static mean square displacement were evaluated and compared with the theoretically calculated results. It appeared that Debye's model for lattice vibration can account for the temperature dependence of critical voltages in Si, Ge and Si-Ge solid solution, and that the anharmonicity effect is smaller compared with the one in metal crystals such as Al and Cu. The static mean square displacement of the solid solution changes parabolically with the concentration of Ge in agreement with the theoretical prediction.

INTRODUCTION

The critical voltage effect has been used to determine low angle structure factors in metals and solid solutions [1,2]. The critical voltage V_c of a solid solution depends on composition, temperature and degree of short range or long range order through the average atomic scattering factors [3]. The critical voltage effect in ordering alloys has been studied both theoretically [4] and experimentally [5,6], and static mean square displacements of atoms and Debye temperatures have been estimated. In the previous paper [7] we demonstrated the method to obtain the static mean square displacements and Debye temperatures in Cu-based alloys in which the temperature dependence of the Debye temperatures cannot be ignored. In order to study the variation of V_c 's with composition and temperature in a solid solution it is interesting to choose a system which has a large solubility and has neither short range nor long range order. A silicon-germanium solid solution is one of the suitable examples because the pure solute and solvent are isostructural and it has a complete solid solubility. Furthermore any short range or long range order has not been observed in Si-Ge system. This paper will show an example of our recent application of the critical voltage measurements to Si-Ge solid solutions.

EXPERIMENTAL

Solid solutions were prepared by melting required amount of Si and Ge in an electron beam furnace. Then the solid solutions were annealed for a long duration at 1173 K. The thin specimens for electron microscopy were obtained by an ion-thinning technique. The V_c 's of 333 and 440 reflections were measured for the solid solutions and the pure elements. The measurement was carried out with the high voltage electron microscope JEM-1000, equipped with a hot stage, at HVEM LAB, Kyushu University. The V_c was determined by observing the reversal of asymmetry in contrasts for the first and second order Kikuchi lines as well as the intensity minimum at Bragg position in the convergent beam diffraction pattern. The compositions of the solid solutions were estimated from the

composition dependence of lattice constants [8]. The measurement of lattice constants was carried out by the analysis of Kikuchi pattern [9] which was taken from the same area as was used for the V_C measurement.

ANALYSIS

The critical voltage V_C depends chiefly on the low order atomic scattering factors. The average scattering factor of a solid solution is represented by

$$f = m_A f_A \exp(-B_A s^2) + m_B f_B \exp(-B_B s^2), \quad (1)$$

where B_A is related to the mean square displacement of atoms by

$$B_A = \frac{8}{3} \pi^2 \langle u^2 \rangle_A, \quad (2)$$

and similarly for B_B . In these expressions m_A and f_A are the molar fraction and atomic scattering factor, respectively and $s = \sin\theta/\lambda$, where θ is the Bragg angle and λ the wave length of electrons. According to Shirley and Fisher's treatment [10], $\langle u^2 \rangle_A$ and $\langle u^2 \rangle_B$ are identical for the completely disordered *fcc* or *bcc* solid solution. In the present analysis we assume $\langle u^2 \rangle_A \approx \langle u^2 \rangle_B = \langle u^2 \rangle$. The atomic mean square displacement $\langle u^2 \rangle$ consists of two terms:

$$\langle u^2 \rangle = \langle u^2 \rangle_{th} + \langle u^2 \rangle_{st}, \quad (3)$$

where $\langle u^2 \rangle_{th}$ is the thermal mean square displacement originating from the vibrational motion of atoms and $\langle u^2 \rangle_{st}$ the static mean square displacement arising from the size difference of the component atoms. The $\langle u^2 \rangle_{st}$ is essentially independent of the temperature, whereas $\langle u^2 \rangle_{th}$ depends on temperature with the Debye temperature Θ as a parameter [10]:

$$\langle u^2 \rangle_{th} = \frac{9\hbar^2}{\mu k} \left\{ \frac{T}{\mu \Theta^2} \Phi(\Theta, T) + \frac{1}{4\mu \Theta} \right\}, \quad (4)$$

where μ is the averaged atomic weight for the solid solution. The $\langle u^2 \rangle_{th}$ is proportional to the specimen temperature when $T > \Theta$. It has been pointed out that an accurate value of the atomic scattering factors is necessary for the analysis of the measured V_C of the solid solutions [3,10]. In the present work the values of f_{Si} and f_{Ge} for 111 and 220 reflections were estimated from observed V_C 's, before the analysis of the solid solutions. The results are summarized in Table 1. The V_C 's of the solid solutions were analysed by the 15 or 16 beams dynamical theory with the high order atomic scattering factors given by Doyle and Turner [14] and by Matsushita et al. [15] and Aldred and Hart [16] for 222 reflection.

RESULTS AND DISCUSSION

The V_C 's of pure Si and Ge and the Si-Ge solid solutions decreases approximately in proportion to the temperature as shown in Fig.1 and 2 where the measured V_C 's of 333 and 440 reflections are plotted against the temperature. From these results and the atomic scattering factors estimated above we can determine the $\langle u^2 \rangle$ as a function of temperature. The $\langle u^2 \rangle$ thus determined for pure Si and Ge are shown in Fig.3 and 4, respectively. It is apparent that

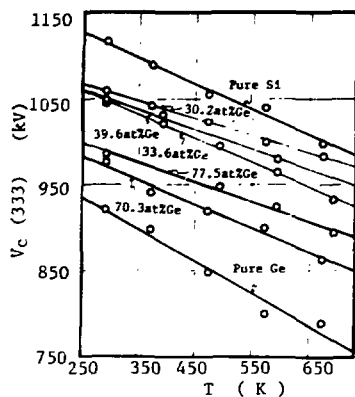


Fig. 1 Temperature dependence of the critical voltage V_C for 333 reflection.

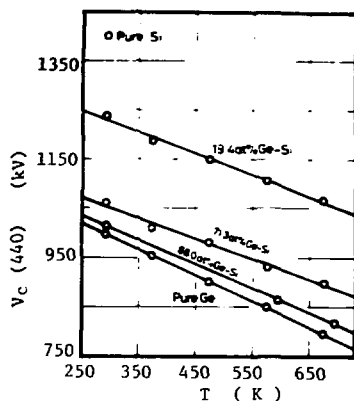


Fig. 2 Temperature dependence of the critical voltage V_C for 440 reflection.

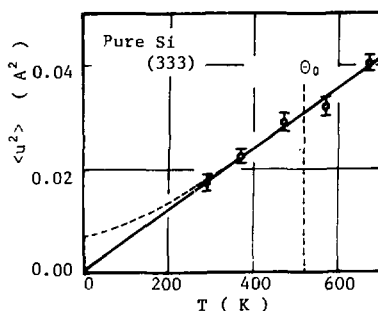


Fig. 3 Mean square displacement for Si as determined from 333 V_C . The broken line is the best fit of eq.(4) to the data.

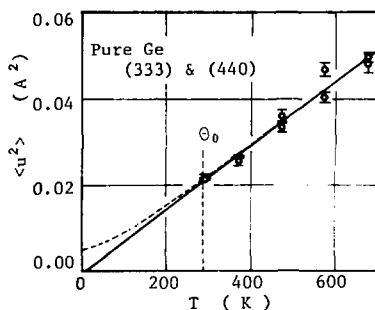


Fig. 4 Mean square displacement for Ge as determined from 333 and 440 V_C . The broken line is the best fit of eq.(4).

the values of $\langle u^2 \rangle$ satisfy a linear relationship with the temperature in accordance with the theoretical prediction of eq. (4) at a high temperature and the straight lines satisfy $\langle u^2 \rangle = 0$ at $T = 0$. The dotted curves in Fig. 3 and 4 are the best fits of eq. (4) to the experimental data. From these fittings we determined the Debye temperatures Θ for Si and Ge. The results are shown in Table 1 where Θ obtained by other investigators [17, 18] are also shown for comparison. The present results are in good agreement with those obtained by other investigators.

The $\langle u^2 \rangle$ for Si-Ge solid solutions are shown in Fig. 5, where the linearity of the data is also satisfactory and we can obtain Θ and $\langle u^2 \rangle_{st}$ from the slope and the intercept of the straight line, respectively. The Θ 's thus obtained are shown in Fig. 6 by triangles. The open circles in Fig. 6 indicate the values obtained by the best fitting of eq. (4). We attempted to compare our data with the theoretical predictions. Shirley and Fisher [10] have derived a formula to express Θ of a solid solution;

$$\mu\Theta^2 = m_A \mu_A \Theta_A^2 + m_B \mu_B \Theta_B^2 + (\tau-1)(1-\alpha) m_A m_B (\mu_A \Theta_A^2 + \mu_B \Theta_B^2), \quad (5)$$

where μ_A and Θ_A are the atomic weight and the Debye temperature of a pure element A, respectively, τ is a dimensionless measure of the force constant between a pair of unlike atoms and α the Cowley-Warren short range order parameter. The dotted line in Fig. 6 was obtained from eq. (5) by assuming τ to be 1.77 and $\alpha = 0$. According to Lindeman's rule [18] Θ is related to the melting point T_m by

$$\mu\Theta^2 = \frac{9\pi^2 T_m}{x_m^2 k r^2}, \quad (6)$$

where x_m is a dimensionless constant which is in the range of 0.2 to 0.25 for most solids and r the mean radius of unit lattice. The Debye temperature calculated from eq. (6) is shown in Fig. 6 by the broken line. In the calculation we assumed T_m to be the average of the liquidus and solidus temperatures [19] and ignored the difference between Θ for diffraction and Θ for specific heat. The present data are adequately described by eq. (5) rather than eq. (6).

The values of $\langle u^2 \rangle_{st}$ evaluated are plotted in Fig. 7 against Ge concentration. It is apparent in Fig. 7 that the composition dependence of $\langle u^2 \rangle_{st}$ is characterized by a parabolic relation which opens downward, and the tendency of our data is approximately reproduced by Shirley and Fisher's formula as indicated by the dotted line in Fig. 7.

As to Θ and $\langle u^2 \rangle_{st}$ for Si-Ge solid solutions, there are no other data to be directly compared with ours. However, the linearity of the temperature dependence of $\langle u^2 \rangle$ and a fairly good agreement between the present results of Θ for pure Si and Ge and those of other investigators [16, 17] imply the adequateness of our treatment. The present analysis shows that the lattice vibration in Si, Ge and Si-Ge crystals can be described well by Debye's model and an effect of anharmonicity is negligibly small in contrast with those in copper and its alloys where the temperature dependence of the Debye temperature evaluated is appreciable [3]. These results are consistent with the conclusion by Soma and Matsuo [20] that the contribution of acoustic modes to the mean square displacement for Si and Ge at high temperatures is predominant as compared with the contribution of optical modes.

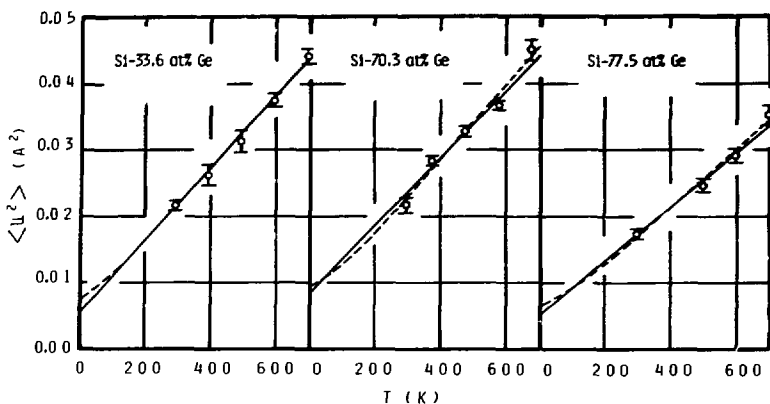


Fig. 5 Mean square displacement for Si-Ge solid solutions. The broken line is the best fit of eq.(3) and (4) to the data.

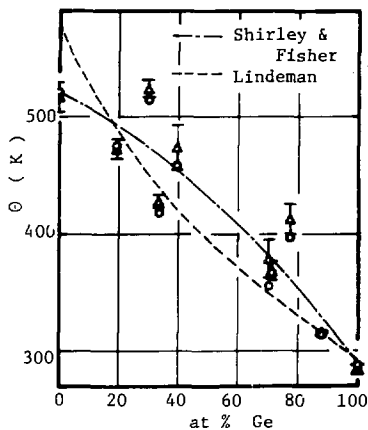


Fig. 6 Composition dependence of the Debye temperature for Si-Ge solid solutions. Δ : from a linear approximation of eq.(3) and (4), $\circ$: from the best fit of eq.(3) and (4).

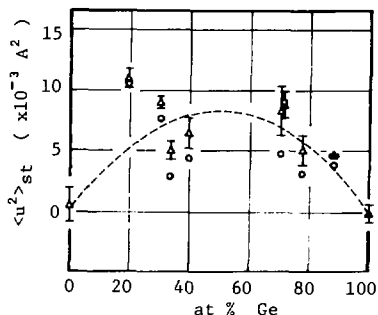


Fig. 7 Static mean square displacement in Si-Ge as a function of composition as determined from the V_c measurement. The broken line is the theoretical prediction from the formula in reference [10].

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Table 1

Critical voltage V_c , atomic scattering factor for electron f^e and Debye temperature Θ of Si and Ge.

	V_c (kV) at 300 K		f^e (A)		Θ (K)
	333	440	111	220	
Si	1116.3 ± 4.5	—	3.060 ± 0.006	—	521 ± 13
			3.096 ± 0.012 (ref.11)		532.5 (ref.16)
			3.064 ± 0.006 (ref.16)		
Ge	921.3 ± 1.0	997.5 ± 3.0	4.531 ± 0.001	3.151 ± 0.003	288 ± 4
			4.553 ± 0.010 (ref.12)		290 (ref.17)
			4.542 ± 0.122 (ref.13)		

INFLUENCE OF MISFIT DISLOCATIONS ON THE STRENGTH OF Ni/Cu/(001)Ni TRIPLE LAYER EVAPORATED FILMS

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INTRODUCTION

In 1970, Koehler [1] proposed the possibility of developing a composite material with a very high strength, taking into account of dislocation image repulsive force. This proposed material has a laminate structure of multiple layer films composed of two kinds of metals. Investigations of such laminate systems showed various degrees of strength enhancement [2-5]. However, the influence of interfacial dislocation structures on the strengthening of the layer films have not been well understood yet.

In this study, Cu/(001)Ni double layer and Ni/Cu/(001)Ni triple layer films were made epitaxially by evaporation, and interfacial structures of these films were observed by a high voltage electron microscope, and tensile tests of these layer films were carried out. From the results of the microscopic observations and of the tensile tests, the influence of interfacial dislocation structures on the strength of multiple layer films is discussed.

EXPERIMENTAL PROCEDURES

Cu-Ni double layer and Ni-Cu-Ni triple layer films were made by evaporation of 99.99 % Ni and 99.99 % Cu in the ultra-high vacuum evaporator at the pressure of less than 1.5×10^{-6} Pa [6]. The substrate was a NaCl single crystal cleaved in air. For the preparation of Cu-Ni double layer film, Ni film was evaporated on (001)NaCl surface at 350 °C, and subsequently Cu film was evaporated on the Ni film at 150 °C, and a Ni-Cu-Ni triple layer was made by evaporating Ni on the double layer film at 150 °C. The evaporation rate was 2.0 nm/s for Ni, and 1.0 nm/s for Cu. The thickness of each layer was controlled by means of a quartz-crystal thickness monitor, and the final thickness was also examined by interference microscope.

Transmission electron microscope investigations of the layer films were carried out using HU-3000 operating at 2 MeV.

Tensile tests were performed with the specially designed tensile testing machine for thin metal films. The details of the testing machine, the shape of a tensile specimen and the procedures of tensile test were described elsewhere [7].

EXPERIMENTAL RESULTS AND DISCUSSIONS

Transmission electron micrographs of Cu-Ni double layer and Ni-Cu-Ni triple layer films are shown in Fig.1 (a) and (b), respectively, where the thickness of each layer is 80 nm. When the thickness of each layer is more than 80 nm, layer specimens are continuous without channels and holes, as

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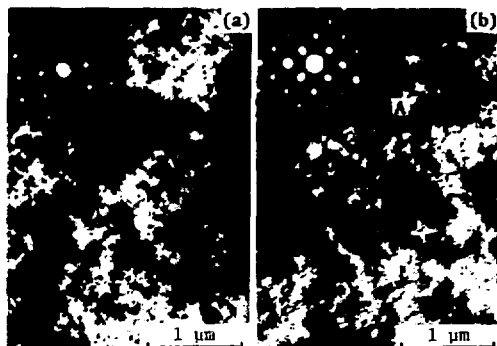


Fig. 1. Transmission electron micrographs of (a) Cu/(001)Ni double layer film and (b) Ni/Cu/(001)Ni triple layer film. Thickness of each layer film is 80 nm.

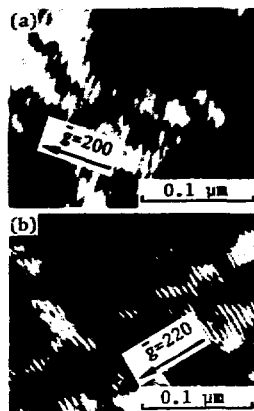


Fig. 2. Moiré fringes appeared in dark field images of Cu/(001)Ni double layer film. Thickness of each layer film is 120 nm.

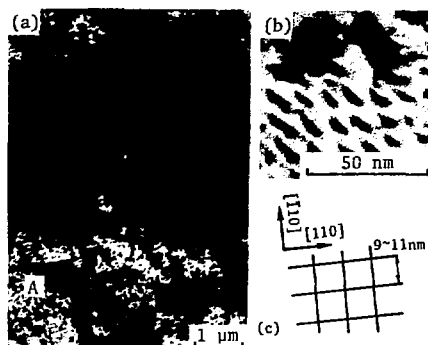


Fig. 3. Misfit dislocation arrays in Cu/(001)Ni double layer film. Thickness of each layer film is 200 nm. The part indicated by A is enlarged in (b) and (c) is the schematic diagram of the dislocation network.

shown in Fig.1. The selected area diffraction images both in (a) and (b) reveal (001) single crystal patterns, meaning that Ni film evaporated on (001)NaCl substrate, and subsequent Cu and/or Ni film grows epitaxially. It is also seen in Fig.1 that the threading dislocations are present in high density all over the films, and that some moiré fringes, as indicated by A, exist close to the bend contour. Thus the interface does not contain any contaminated layers and the constituent metals layers continue coherently.

Interfacial dislocation structures were studied for Cu/(001)Ni double layer films. Fig.2 shows the dark field images by the diffraction of (a) 200 and (b) 220. It can be noticed that most of moiré fringes are perpendicular to the reflection vector, and that the spacings of moiré fringes in 220 reflection are reduced to about $1/\sqrt{2}$ of those in 200. This agrees well with those obtained from electron diffraction theory for moiré patterns [8]. The moiré fringe

spacings in Cu films of various thicknesses were measured on the electron micrographs. As the thickness of Cu film increases, the spacing of moiré fringe decreases, and finally attains to the constant value of 6-8 nm in Cu for films of more than 20 nm in thickness. This may indicate that the lattice misfit between Cu deposit and Ni substrate is accommodated by the introduction of misfit dislocations [9].

Fig.3 is an electron micrograph of misfit dislocations which were observed in Cu/(001)Ni double layer films. Misfit dislocations construct a continuous square network and are lying along the directions of $[110]$ and $[\bar{1}\bar{1}0]$. Average spacing of misfit dislocations is 9.3 nm. Burgers vector analyses showed that the misfit dislocations were of edge type, lying on the deposit-substrate interface [10-12].

Tensile tests along $[100]$ were performed for (001)Cu and (001)Ni films of various thicknesses, and for Cu/(001)Ni double layer and Ni/Cu/(001)Ni triple layer films, having the layer thicknesses ranging from 80 to 600 nm.

Fig.4 shows (a) the scanning and (b) the transmission electron micrographs of the fractured part of Ni/Cu/(001)Ni triple layer film. In (a), the fractured edge segments and many fine slip lines are lying along the crystallographic directions of $[110]$ and $[\bar{1}\bar{1}0]$. Such slip lines were observed only in the fracture region. In Fig.4 (b), long and straight dislocations are seen in this region along the direction of $\langle 110 \rangle$. These dislocations were not present before the tensile test and they are supposed to pile up at the interface, because of the repulsive force due to the stress field of misfit dislocations.

Fig.5 shows the typical stress-strain curves of Ni and Cu single crystal films, and Cu/(001)Ni double layer and Ni/Cu/(001)Ni triple layer films. The tensile properties of Ni/Cu/(001)Ni triple layer films can be summarized as follows : (i) The stress-strain curves are nearly linear up to the fracture stress, and the slope is 182 GPa in average, which is larger than that of Ni single crystal films (120 GPa). (ii) The plastic strain is extremely small. (iii) The yield stresses are 600-700 MPa, independent of the individual layer thickness and about three times of Ni single crystal films and five times of Cu.

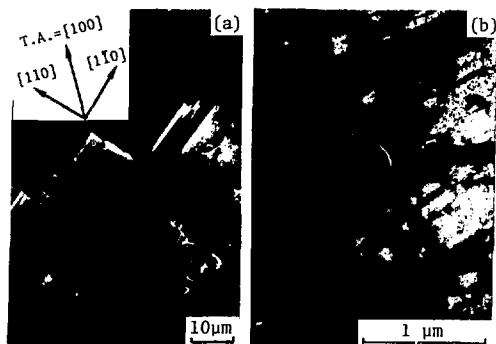


Fig. 4. (a) the scanning electron and (b) the transmission electron micrographs of fractured parts of Ni/Cu/(001)Ni triple layer films.

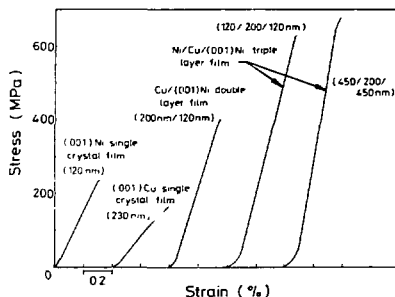


Fig. 5. Typical stress-strain curves of (001)Cu, (001)Ni films, Cu/(001)Ni double and Ni/Cu/(001)Ni triple layer films, elongated along [100].

theoretical values. This might be due to the occurrence of the fracture at the interface caused by the pile-up dislocations, which would lower the strength of layer films. However, it can be mentioned that misfit dislocations contribute to the strengthening of Ni/Cu/(001)Ni films, since the experimental values were larger than those calculated from the mixture rule of individual strength and were independent of layer thickness ranging from 80 to 600 nm.

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In order to clarify the influence of misfit dislocations on the strength of Ni/Cu/(001)Ni triple layer film, the repulsive force due to the stress field of misfit dislocation arrays against a mobile dislocation was calculated, assuming that the mobile dislocation with Burgers vector of $a/2\langle 110 \rangle$ type on (111) plane in Cu film is parallel to the misfit dislocations [13]. The repulsive forces were dependent on the positions of a mobile dislocation, and the yield stresses calculated from the repulsive forces at various positions were 1000-1600 MPa. The yield stresses obtained from the experiment did not agree with the

DETERMINATION OF THE BURGERS VECTOR OF A BOUNDARY DISLOCATION BY WEAK-BEAM IMAGING USING A HIGH VOLTAGE ELECTRON MICROSCOPE

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ABSTRACT

Burgers vector of a boundary dislocation is determined rigorously from weak-beam micrographs with diffracting vectors common to the adjoining crystals. Termination of thickness extinction contours at the end of the boundary dislocation on the surface of the thin foil specimen was counted for the three diffracting conditions. Fair quality weak-beam micrographs with many extinction contours were obtained by HVEM for relatively high order diffractions such as 311. It was found statistically that majority of the boundary dislocations in twin boundary of annealed Cu-40%Ni alloy was $a/6[211]$.

INTRODUCTION

The observation of a boundary dislocation by transmission electron microscopy traces back to 1960s(1)(2). The determination of the burgers vector, however, is still an unsolved problem; The identification in a well defined bicrystal was successful(3), where the type of dislocations in the dislocation network is anticipated. The determination in a general polycrystalline specimen has been the problem. The standard zero-image technique of Hirsch et al (4) was not applicable; The dislocation image gets too weak to observe when the diffracting vector g and the burgers vector b is nearly orthogonal to each other, because the burgers vector is generally small in magnitude. Besides, the technique fails to give the size and sign of the burgers vector. A computer simulation technique by Head et al(5,6) copes with the problem. A large amount of laborious calculations, however, is involved and still the identification was often incomplete. The procedure proposed by Marukawa(7) only determines the range of possible burgers vectors.

The present weak-beam method is superior to the above techniques, where the size and sign of the burgers vector are determined by the number and the side of terminating thickness extinction contours at the exit of dislocations on either surface of the thin foil specimen. A high voltage electron microscope is necessary since weak beam conditions with many fringe contours are required. A good transmission power of electrons is prerequisite. The procedure has been applied successfully in the determination of the burgers vector of the lattice dislocation by the authors(8). The present experiment applies the same procedure to the boundary dislocation. A fringe counting technique has been proposed by Bollmann(9). The method, however, relies majorly on the curvature of the thin foil specimen at its edge, which differs from the present method.

THICKNESS EXTINCTION CONTOURS NEAR A DISLOCATION AT WEAK BEAM CONDITION

At a weak beam imaging condition, the dark field image of a thin foil specimen is with very fine thickness fringes along its edge. A high voltage microscope allows observation of many fine thickness fringes. The extinction distance of the electron beam is given by the following equation (1),

$$\xi_g^s = (\xi_g^{-2} + s^2)^{-1/2} \quad \text{----- (1)}$$

which decreases with increase in the amount of the deviation S from the Bragg diffraction condition. A high voltage electron microscope give relatively fair dark field image by simply shifting the objective aperture to the diffracted beam. No correction of the optical axis of the microscope is required, since the diffraction angle itself is small. The image of the dislocation is so fine that splitting of the dislocation into partials are examined using the method(10). At the weak beam diffraction condition, where $\xi_g^s \gg 1$ the thickness extinction contour decreases inversely proportional to S and interacts monotonously with the strain field surrounding the dislocation. The strain field R near the dislocation can be approximated by the following equation parallel to the electron beam direction Z by a simple averaging procedure except very near the dislocation core (11).

$$\langle g \cdot dR/dZ \rangle = g \cdot [R(t) - R(0)]/t \quad \text{----- (2)}$$

where $\langle \quad \rangle$ means averaging and t means the thickness of the specimen foil. The thickness contour is expressed by an equation $t \cdot s_{\text{eff}} = \text{const.}$, which is defined by the following equation (3).

$$s_{\text{eff}} = S + \langle g \cdot dR/dZ \rangle \quad \text{----- (3)}$$

from (2) and (3)

$$t \cdot s_{\text{eff}} = t \cdot s + g \cdot [R(t) - R(0)] \quad \text{----- (4)}$$

The equation (4) is expressed followingly on the right hand side and left hand side of the dislocation.

$$\begin{aligned} (t \cdot s_{\text{eff}})_r &= t \cdot s + g \cdot [R(t) - R(0)]_r \\ (t \cdot s_{\text{eff}})_l &= t \cdot s + g \cdot [R(t) - R(0)]_l \end{aligned}$$

The difference of the two is equal to the shift of the thickness extinction contour n ,

$$n = (t S_{\text{eff}})_T - (t S_{\text{eff}})_I = g \cdot \{ [R(t) - R(0)]_T - [R(t) - R(0)]_I \}$$

-----(5)

The second term with a large bracket in equation (5) is equal to b which is the total displacement when one extrapolates the term near a dislocation.

$$n = g \cdot b \quad \text{-----}(6)$$

where b is defined right-handedly surrounding the dislocation. The $t \cdot S_{\text{eff}}$ is equal to the number of thickness extinction contours counted from the edge of the specimen. If the edge of the specimen is placed at the top of the figure, $g \cdot b = 1$ when one contour fringe terminated on the right hand side at the upper end of the dislocation. The value $g \cdot b = -2$ if two contours ended as shown by the figure 1. According to the definition above, it doesn't matter whether the particular dislocation ended on the upper or lower surface of the thin foil specimen. A gradual curvature of the specimen in that area does not affect very much, since only the ending of the fringe is counted.

DETERMINATION OF THE BURGERS VECTOR

Three weak beam micrographs with the diffracting vectors g_1 , g_2 and g_3 common to both the crystals but not in a single plane must selected in order to determine the burgers vector $b(x, y, z) = b_x \hat{x} + b_y \hat{y} + b_z \hat{z}$;

$$g_i(x, y, z) \cdot b(x, y, z) = n_i \quad (i=1, 2, 3)$$

The b_x , b_y and b_z values are determined by equating the above three equations. The number of the common diffracting planes are limited and constitute the major problem of the present technique. In case of a twin boundary, one(111), three(220)s, and six(311)s are the important common diffracting planes as is shown in figure 2. One must tilt the specimen foil so that the electron beam direction intersects with three of the common diffracting plane zone circles.

THE ANALYSIS OF TWIN BOUNDARY DISLOCATIONS

The material observed was Cu-40%Ni alloy, cold rolled to sheet specimen, annealed at 1073 K and furnace cooled. The sheet specimen was then electrolytically polished in chromic acid and phosphorous acid saturated solution. The 1 MV HVEM at the Experimental Laboratory, faculty of Engineering, Tokyo University was used.

Photograph 2 shows a pair of twin boundaries observed in a thin foil specimen with the diffracting vector 200. The twinned region is without an appreciable diffraction. A number of dislocations are seen in the two boundaries. Since lattice dislocations are also seen in the region right above, some of the dislocations could be lattice dislocations having moved into the twin boundaries. Following four photographs 3, 4, 5 and 6 are weak beam micrographs photographed with common diffracting vectors 111, $\bar{3}1\bar{1}$, 220 and $31\bar{1}$. Three

dislocations marked a, b and c are analysed. In photo 3 the coherent twin (111) is parallel to the incident electron beam, but the dislocation should be visible if $g \cdot b \neq 0$. In fact, some of the lattice dislocations are visible in the area right above. In photo 4, one extinction fringe terminated with one line surplus to the left of the dislocation at the upper end of the boundary dislocation so that $g \cdot b = -1$. Similarly in photo 5 and 6, the terminating fringe is on the right hand side of the dislocation so that $g \cdot b = +1$. From these four $g \cdot b = n$ equations three may be chosen to calculate the burgers vector. For an example using equations 3, 5 and 6,

$$g = 111 \quad n = 0 \quad x + y + z = 0 \quad (\text{photo 3})$$

$$g = 2\bar{2}0 \quad n = +1 \quad 2x - 2y = +1 \quad (\text{photo 5})$$

$$g = 31\bar{1} \quad n = +1 \quad 3x + y - z = +1 \quad (\text{photo 6})$$

Equating the above equations, $b(x, y, z) = 1/6[211]$ is determined. The above three dislocations were all $a/6[211]$ dislocations which is characteristic to the twin boundaries. A check of the analysis may be made if remaining micrographs were checked using the burgers vector.

DISCUSSION

Statistics of the burger vector is shown in Table 1, where twenty two dislocations were analysed. The $a/6[211]$ dislocation is one of the characteristic dislocations in twin boundaries and by far the largest in number perhaps because annealing twin was the major one in the present experiment. The remaining $a/2[110]$ dislocations are likely to be the lattice dislocations introduced into the boundary during processing of the specimen.

The analysis of other coincidence boundaries is the next problem. The present experiment is limited to twin boundaries. In common coincidence boundaries the number of common diffracting planes with low integers is rather small, which limits the present analysis. In figure 4, the case of $\Sigma 5$ and $\Sigma 7$ are shown.

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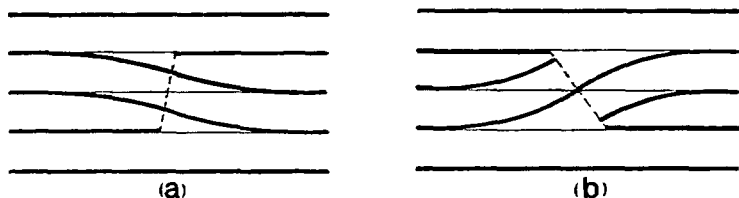


Fig. 1 Shape of thickness extinction contour for (a) $g \cdot b = 1$ and (b) $g \cdot b = -2$

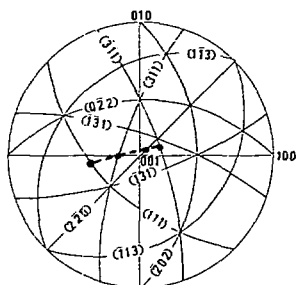


Fig. 2 Stereographic projection of common great circles for a twin

Table 1. Burgers vector dislocations observed in an annealed Cu-40%Ni alloy

Burgers vector	number of dislocations
$\frac{a}{6} \langle 2 \ 1 \ 1 \rangle$	17
$\frac{a}{3} \langle 1 \ 1 \ 1 \rangle$	1
$\frac{a}{2} \langle 1 \ 1 \ 0 \rangle$	4

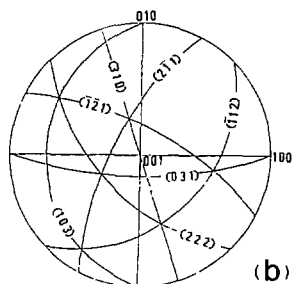
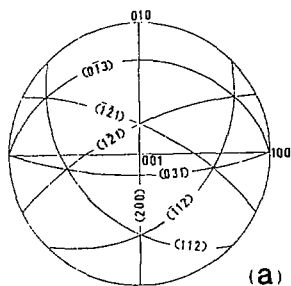


Fig. 3. Great circles of common diffracting planes for (a) $\Sigma 5$ and (b) $\Sigma 7$ systems

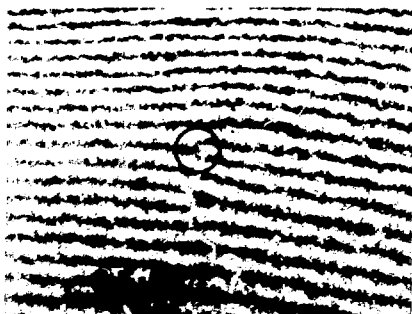


Photo 1. A weak-beam micrograph corresponding to Fig. 1 (a)

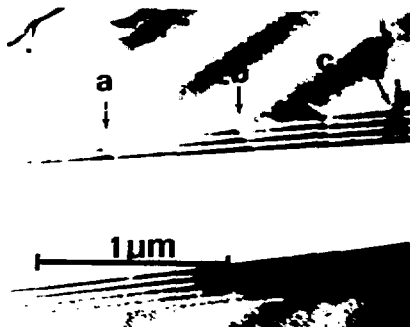


Photo 2. An example of a pair of twin with dislocations ($g = \bar{2}00$)

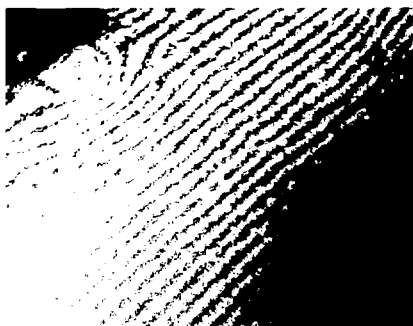


Photo 3. A (111) weak-beam image



Photo 4. A $(\bar{3}1\bar{1})$ weak-beam image

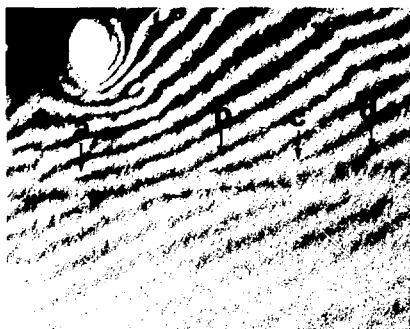


Photo 5. A $(2\bar{2}0)$ weak-beam image

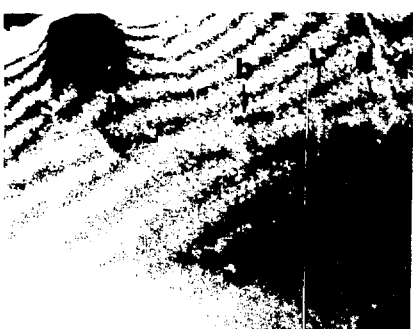


Photo 6. A $(31\bar{1})$ weak-beam image

HIGH VOLTAGE ELECTRON MICROSCOPY OF DISLOCATION CLUSTERS IN LEC InP

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ABSTRACT

Large dense tangles of dislocations, sometimes called 'grappes' but more usually referred to as dislocation clusters, are often observed in single crystals of InP grown by the liquid-encapsulated-Czochralski (LEC) technique. These defects have been studied extensively by HVEM and are shown to consist of a central core surrounded by a dislocation network. Two types of dislocation cluster have been identified, each with a different core morphology and surrounding dislocation distribution. These are described and possible mechanisms for their formation are discussed.

INTRODUCTION

The semiconductor InP is becoming increasingly important for a variety of electronic device applications. The fabrication of these devices generally requires the deposition of epitaxial layers on to single crystal InP substrates which are prepared from single crystals grown by the LEC technique [1]. When defects are present in substrate material, they can propagate into the epitaxial layers and produce deleterious effects in device performance. Dislocation clusters have been shown to be particularly damaging when present in substrates used for microwave [2] and optoelectronic devices [3]. Fortunately it is now possible to control dislocation cluster formation during Czochralski growth [4] but the mechanisms by which they form and generate dislocations are still not fully understood. This study characterises their microstructure, as revealed by electron microscopy, and establishes mechanisms whereby dislocations can be generated from the cluster cores.

Chemical defect etching has shown that the total cross-sectional diameter of dislocation clusters is typically up to 20-30 μm and that they occur at a density of 10^2 - 10^3 cm^{-2} [4,5,6]. Conventional 100 kV electron microscopy is therefore difficult because firstly, the size of the total defect is larger than a typical foil thickness, and secondly, the low density reduces the probability of encountering a defect in a thin area. These problems can be minimised, however, by using a high voltage electron microscope where thick foils (up to 5 μm) can be used and also by selecting material containing the highest density of clusters observed ($1.2 \times 10^3 \text{ cm}^{-2}$).

EXPERIMENTAL DETAIL

Previous studies using infra-red microscopy [7] and chemical etching [8] have revealed the existence of two different types of dislocation cluster. One has a triangular core whilst the core of the other is spherical. For this study, two crystals were identified which contained a high density of each type of dislocation cluster. Electron microscopy samples were prepared by chemically thinning in a solution of bromine in methanol and samples were examined at 800 kV

in an AEI-EM7. The defect structures observed were correlated with etch features characteristic of dislocation clusters as described elsewhere [8].

RESULTS AND DISCUSSION

Dislocation Clusters with Triangular Cores

Of the two types of dislocation cluster, those with triangular cores have been observed more frequently. Their macroscopic distribution and density have been recorded previously [4,5,6] by both chemical etching and infra-red microscopy. The infra-red absorption micrograph of Fig.1a shows the strongly absorbing triangular core whilst the associated etch pit distribution is shown in Fig.1b for a {100} surface etched in solution H [9]. Fig.1c is a corresponding electron micrograph for a triangular-cored cluster but since the foil is only 0.4 μm thick at this point and triangular cores are usually 2-5 μm in diameter, only part of the core is within the foil. The habit plane of the core was determined to be {111} by tilting the foil to a $\langle 112 \rangle$ beam direction and establishing that the core was vertical in the foil; the edges were shown to lie along $\langle 110 \rangle$ directions by trace analysis. The core thickness was in the region of 500 $\text{\AA}$ and in some cases when viewed edge-on, the core had a cellular appearance (Fig.2). No diffraction data was obtained from the core and although the contrast on the habit plane of the core resembled that of a dislocation network, it was not possible to discern any marked diffraction contrast effects.

Chemical analysis of a triangular core was carried out by energy dispersive X-ray analysis in a Philips EM400 STEM at 100 kV. No foreign impurities were detected, but by counting for long times (10^3 secs) and taking account of matrix absorption effects by measuring the foil thickness at the point probed, a small but significant local increase in In concentration was detected. Using a 50 $\text{\AA}$ beamwidth, checked periodically for drift, the dark and light areas of the vertically aligned core (Fig.2) were probed and the absorption-corrected PK α and InLa counts were compared to the values obtained for the matrix. The figures are tabulated in Table 1 and are normalised for a matrix composition of 50:50. It was noted further that the lighter areas of the core gave a much lower count rate than the darker areas.

TABLE 1

Part of triangular core probed	Normalised In Concentration	Normalised P Concentration
Dark contrast area	51.8 ± 0.2	48.2 ± 0.2
Dark contrast area	51.4 ± 0.2	48.6 ± 0.2
Light contrast area	51.7 ± 0.2	48.3 ± 0.2

The dislocations around a triangular core were characterised by conventional diffraction contrast analysis, from which both the Burgers vectors and slip planes were determined. For a core lying on a plane indexed specifically as {111} three Burgers vectors were determined, namely, $a/2$ [110], $a/2$ [011]

and $a/2 [101]$. These are the three $\langle 110 \rangle$ directions symmetrically disposed around and nearest to the $[111]$ habit plane normal. Slip was found to have occurred on the $(\bar{1}11)$, (111) and $(\bar{1}\bar{1}1)$ planes but not on the habit plane, $(\bar{1}11)$. From this analysis, it is evident that the deformation processes around a triangular core occur by glide on the three slip planes other than the habit plane and via the three Burgers vectors not contained within the habit plane. A schematic description of this process is shown in Fig.3. Further evidence for this deformation process, obtained from chemical defect etching studies of $\{111\}$ surfaces [8], is shown in Fig.4. Triangles of etch pits with sides parallel to $\langle 110 \rangle$ directions (Fig.4a) correspond to the dislocations generated by slip around cores close to and lying on planes parallel to the surface whilst the arrays of pits aligned along $\langle 110 \rangle$ directions (Fig.4b) correspond to the traces of the $\{111\}$ planes cutting across the edges of the core and are therefore also consistent with this deformation mechanism.

Dislocation Clusters with Spherical Cores

Typical infra-red absorption micrographs and etch pit distributions are shown respectively for a spherically-cored dislocation cluster in Figs.5a and 5b. The corresponding electron micrograph of a spherically-cored cluster is shown in Fig.5c. Since the diameter of a spherical core is approximately $2 \mu\text{m}$ and since the chemical polish used in foil preparation attacks the core are exposed, the foil thickness clearly needs to be greater than $2 \mu\text{m}$ for the core to be within the foil. In Fig.5c the core is retained within a $5 \mu\text{m}$ thick foil and gives bright contrast. No electron diffraction information was obtained which is surprising considering the core size; hence the possibility that the core is gaseous matter or a void must be considered. However, chemical analysis by EDX has not yet proved possible because of the prohibitive thickness of the foil.

Analysis of the dislocation structure around the spherical cores proved difficult because of the complexity of the tangle as shown in Fig.5c. However, from etching studies, pairs of pits have been observed emanating along the six $\langle 110 \rangle$ directions which indicates that the dislocations are formed, at least initially, by the punching out of prismatic loops as described in an earlier study [10]. Attempts to identify dislocations in the prismatic orientations were not successful and it seems likely that for the clusters studied so far by HVEM there has been considerable dislocation interaction by climb and slip subsequent to the initial prismatic punching.

CONCLUSIONS

The microstructures of both triangular and spherically cored dislocation clusters have been studied by HVEM. Triangular cores have been shown to be indium-rich and the dislocations surrounding the core have been characterised. This has enabled a model to be proposed which explains the deformation processes around triangular cores. No chemical analysis has yet been possible for spherical cores although the dislocations around the core are consistent with the punching out of prismatic loops. However, it is clear that substantial dislocation interaction through glide and climb occurs subsequent to this punching process and a complex tangle of dislocations results.

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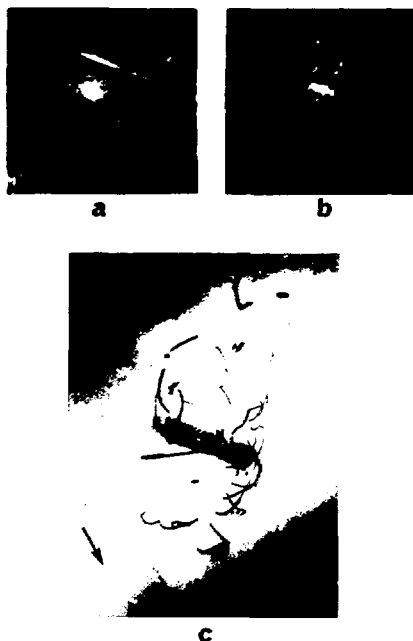


Fig. 1 Micrographs of a triangular cored dislocation cluster:
 (a) Absorption transmission infra-red micrograph of 400 μm thick $\langle 100 \rangle$ slice;
 (b) H-etched $\langle 100 \rangle$ surface imaged with Nomarski interference contrast (5 sec
 etch); (c) Electron micrograph with beam direction close to $[100]$ and a $[002]$
 diffraction vector.

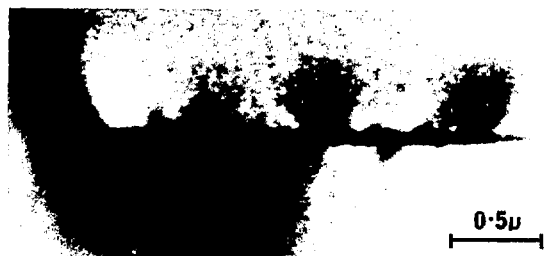


Fig. 2. A triangular core with the habit plane normal perpendicular to the
 $\langle 112 \rangle$ beam direction, $[220]$ diffraction vector.

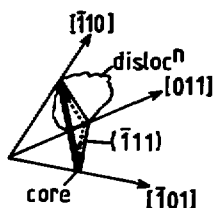


Fig. 3 Schematic of the dislocation distribution around a triangular core.



Fig. 4 (a) Triangle of etch pits produced by the H-etch on a $\langle 111 \rangle$ surface. (b) Etch pit distribution around a triangular shaped core for a H-etched $\langle 111 \rangle$ surface.

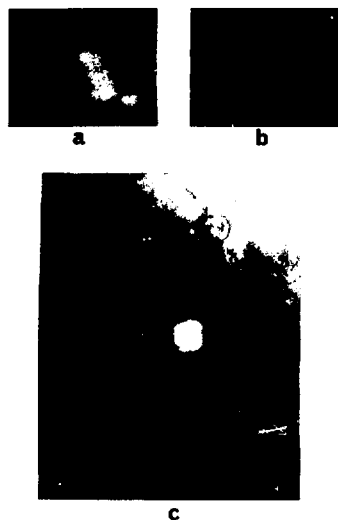


Fig. 5 Micrographs of a spherical-cored dislocation cluster, (a) Absorption transmission infra-red micrograph of 400 μm thick $\langle 100 \rangle$ slice. (b) H-etched $\langle 100 \rangle$ surface imaged with Nomarski interference contrast. (c) Electron micrograph with beam direction close to $[100]$ and a $[022]$ diffraction vector.

IN SITU OBSERVATION OF ELECTRON IRRADIATION IN SEMICONDUCTORS BY HIGH VOLTAGE ELECTRON MICROSCOPY

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ABSTRACT

Si, InP, AsGa and InSb single crystals have been irradiated in a high voltage electron microscope and the radiation damage has been recorded in situ. The specimens were irradiated at various temperatures between room temperature and 500°C with an electron flux of the order of 10^{19} e.cm⁻².s⁻¹. The agglomeration of point defects has been observed. The nature of these agglomerates has been assessed by conventional electron microscopy and computer simulations with the many-beam dynamical theory of diffraction contrast.

SILICON

In accordance with similar observations by other authors in Si [1,2] and Ge [3], elongated ("rod-like"), faulted defects (fig. 1) and perfect dislocation loops have been found, both in Czochralski and zone refined single crystals. The Burgers vector of the perfect dislocation loops is $\frac{1}{2}a$ <110> and they have been shown to be of interstitial type, so that they are similar to the "A-swirls" [4] which have been observed in as made silicon single crystals. The elongated and the faulted defects are of the same nature, as postulated recently [2]. The displacement vector $\vec{R}$ of the stacking fault has been determined first as $a/11$ <311> ; however, a slightly different vector $a/20$ <611> or $a/25$ <611> has been proposed recently [3,5] in order to explain the residual contrast which is observed in the case of theoretical perfect extinction. In our opinion, the crystallographic vector $a/11$ <311> is much more reasonable and another origin for the residual contrast may be found, for instance the neglect of the $\vec{S}.\vec{R}$ term in the theories of contrast [6].

INDIUM PHOSPHIDE

After irradiation at room temperature, a large density of small agglomerates is seen. With increasing temperature, the agglomerate density decreases and their size increases, so that resolved dislocation loops are observed (fig. 2). These have been shown [7] by conventional electron microscopic techniques to be $\frac{1}{2}a$ <110> perfect interstitial loops. At higher temperatures, radiation induced thermal decomposition is observed. First, evaporation tracks parallel to the surface of the foil and elongated along the <110> directions are observed. Their contrast may be simulated [8] by considering the elastic deformation of the matrix caused by a line of dilation. Then, sublimation pits form ; they have a geometrical shape and are limited by (111) planes of the crystal. For instance, when the surface of the specimen is (100), they have a rectangular shape [9].

INDIUM ANTIMONIDE

The case of InSb is very similar to InP. After irradiation at room temperature, a large density of small agglomerates is observed. With increasing temperature, their density decreases and their size increases : $\frac{1}{2}$ a $\langle 110 \rangle$ perfect dislocation loops grow (fig. 3) and these are anticipated to be of interstitial type ; however, this latter point remains to be confirmed.

GALLIUM ARSENIDE

As in InP and InSb, perfect $\frac{1}{2}$ a $\langle 110 \rangle$ dislocation loops are created after irradiation at room temperature, followed by an irradiation at 400°C (fig. 4). Enlargements of some loops seen edge-on in fig. 4 are shown in fig. 5, together with the corresponding simulated images calculated with the two-beam dynamical theory of electron diffraction contrast.

In conclusion, the electron radiation damage is very similar in the various B3 compounds (InP, InSb, AsGa, ...), but it is very different from the corresponding damage in the A3 elements despite the similarity of both structures.

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Fig. 1. a/11 <311> stacking faults in Si irradiated 27 minutes at 400°C with $\phi = 10^{19} \text{ e.cm}^{-2}.\text{s}^{-1}$ at 2 MV.



Fig. 2. 1/2 a <110> interstitial dislocation loops in InP irradiated 10 minutes at 350°C with $\phi = 3 \times 10^{19} \text{ e.cm}^{-2}.\text{s}^{-1}$ at 2 MV.

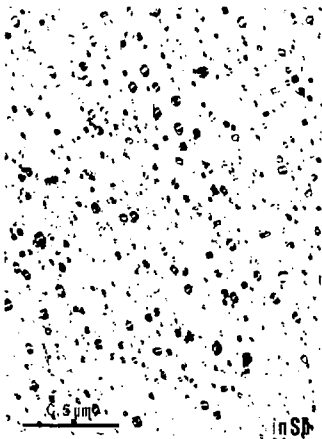


Fig. 3. 1/2 a <110> dislocation loops in InSb irradiated 23 minutes at 150°C with $\phi = 1.5 \times 10^{19} \text{ e.cm}^{-2}.\text{s}^{-1}$ at 2 MV.



Fig. 4. 1/2 a <110> dislocation loops in AsGa irradiated 15 minutes at room temperature, and then 15 minutes at 400°C with $\phi = 6 \times 10^{18} \text{ e.cm}^{-2}.\text{s}^{-1}$ at 1 MV. (220 dark field micrograph, 120 KV).

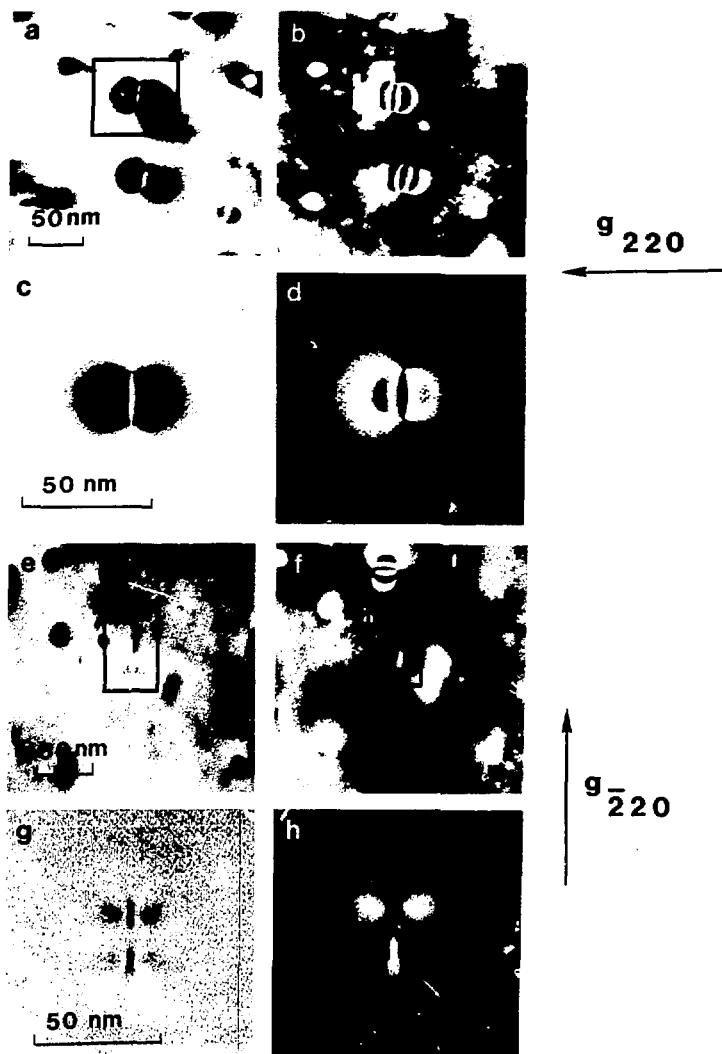


Fig. 5. $1/2 \langle 110 \rangle$ dislocation loops seen edge-on in AsGa and the corresponding simulated images: 220 bright (a) and dark (b) field micrographs and the corresponding simulations (c and d) with $g \cdot b = 2$; 220 bright (e) and dark (f) field micrographs and the corresponding simulations (g and h) with $g \cdot b = 0$.

HVEM INVESTIGATION OF DISLOCATION GENERATION DURING LOCAL OXIDATION

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INTRODUCTION

The local oxidation technique (LOCOS) allows to increase the packing density of integrated circuits by reducing the component size resulting in a lower power consumption and access time. A nitride mask is used to protect the active regions during oxidation. The isolation oxide penetrates under the nitride mask thus forming a 'bird's beak' which poses a limit to the component density. The high stresses exerted by the nitride film and the field oxide can activate several dislocation sources. The generation of dislocations at the nitride edge is investigated by oxidizing wafers with the nitride mask directly on the silicon substrate. It is shown by heating samples in the HVEM that surface damage is a very effective dislocation source.

EXPERIMENTAL PROCEDURE

In this study n-type, 8-12 Ωcm , 50 mm ϕ , 250 μm thick, (001) oriented Czochralski silicon wafers are used. The 120 nm LP (Low Pressure) CVD nitride pattern consists of 12 μm wide bands parallel to a $\langle 110 \rangle$ direction and with a spacing of 10 μm .

A specimen preparation technique for cross-sectional TEM investigation of integrated circuits is optimized [1]. This technique is used to study the geometry at the nitride edge after local oxidation [2]. Plan-view specimens are prepared by backside chemical thinning. The specimens are investigated in a JEOL 1250 electron microscope at 500 kV (for preventing radiation damage during the heating experiments) and at 1000 kV.

RESULTS AND DISCUSSION

Figure 1 shows the bird's beak formed after respectively 1 h and 10 h local oxidation at 975°C in wet oxygen. A polysilicon layer is used to protect the surface during specimen preparation and to improve the observability of the oxide surface. The origin of the sharp bend in the SiO_2/Si interface under the mask edge is clearly visible.

After 1 h oxidation no defects are found, indicating that the stresses in the nitride layer are initially not large enough to generate dislocations. After a 10h oxidation the well-known 60° dislocations parallel to the nitride edges are observed together with half loops perpendicular to the edge. The use of a

high voltage electron microscope allows to investigate regions with a thickness up to 8 μm so that a better understanding of the defect generation mechanisms can be obtained. Often cross-glide is observed close to the LOCOS edge where the combined stresses of the nitride mask and the oxide layer reach a maximum (fig.2). Dense networks resulting from interactions between the different dislocations are formed.

It is well known that surface damage is a very effective dislocation source during processing of integrated circuits. After covering the wafer with the nitride mask, specimens are prepared by backside chemical thinning. During the drilling of the 3 mm discs small scratches are introduced locally on the silicon surface. The specimens are heated in the microscope (at 500 kV to prevent radiation damage) thus simulating the first minutes of local oxidation. At a temperature of about 600°C small half loops are formed at the scratches near the nitride edge. These half loops lie in the $\{1\bar{1}1\}$ planes parallel to the $\langle 110 \rangle$ direction of the mask. They have a Burgers vector of the $\frac{a}{2}[011]$ type inclined to the surface. The loops grow with increasing temperature. When one dislocation end reaches the undamaged surface it starts to glide very quickly, depending on the heating gradient, parallel to the $\langle 110 \rangle$ direction thus forming a 60° dislocation (fig. 3). By further increasing the temperature to about 900°C dislocation lengths up to 800 μm can be generated even at very small scratches. When the temperature is kept constant e.g. at 800°C and equilibrium is reached the dislocation end comes at rest. Under these conditions the local heating produced by the electron beam while observing the dislocation end in the HVEM forces it to start gliding again in a controlled manner. Often more than one dislocation is generated. Sometimes the two possible Burgers vectors for 60° dislocations in a $\{1\bar{1}1\}$ plane parallel to the $\langle 110 \rangle$ direction are found $\frac{a}{2}[011]$ and $\frac{a}{2}[\bar{1}0\bar{1}]\}$. Interactions between the different dislocations are observed (fig.4). These experiments explain how surface damage could act as a source of rows of 60° dislocations with alternating Burgers vectors as were reported by Magdo and Bohg [5].

CONCLUSION

Cross-sectional TEM is used to study the geometry of the $\text{Si}_3\text{N}_4/\text{SiO}_2$ structures after local oxidation. Plan-view HVEM allowed to characterize the dislocations generated at the nitride edge and to gain more insight in the generation mechanisms. Special attention is given to the generation of dislocations at surface damage by heating samples in the microscope.

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Fig. 1. Bird's beak formed after respectively 1 h (a) and 10 h (b) local oxidation at 975°C in wet oxygen.

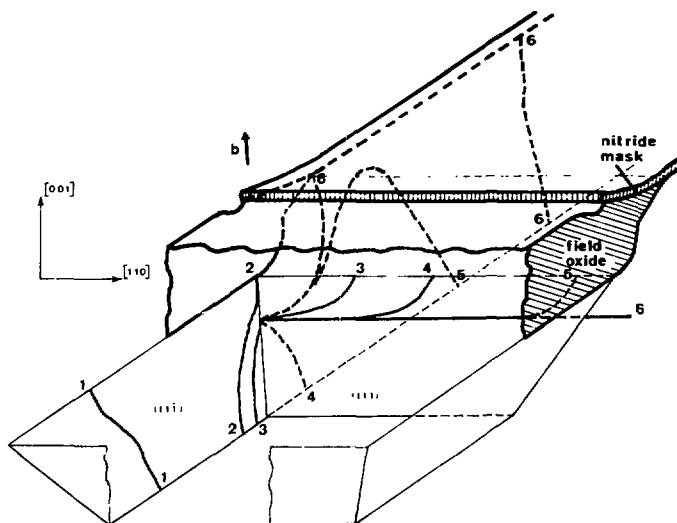


Fig. 2. Cross-glide mechanism at the nitride edge. Dislocation (1) glides inwards from the rim of the wafer in a $(11\bar{1})$ plane. The stresses exerted by the nitride mask and the field oxide reach a maximum near the bird's beak and force the upper part of the dislocation to cross-glide in the $(1\bar{1}1)$ plane parallel to the $\langle 110 \rangle$ edge [3], while the deeper part continues to glide in the original $(11\bar{1})$ plane and forms a half loop (1-6) [4].

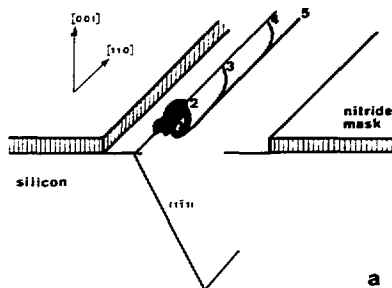


Fig. 3. a) Dislocation generation at surface damage :

- 1 a half dislocation loop with $b = \frac{a}{2}[011]$ is formed
- 2 one dislocation end reaches the undamaged surface
- 3-5 this end starts to glide parallel to the $\langle 110 \rangle$ direction and a 60° dislocation is formed.

b) HVEM micrograph showing 60° dislocations and half loops formed at surface damage near the nitride edge after heating to 850°C .

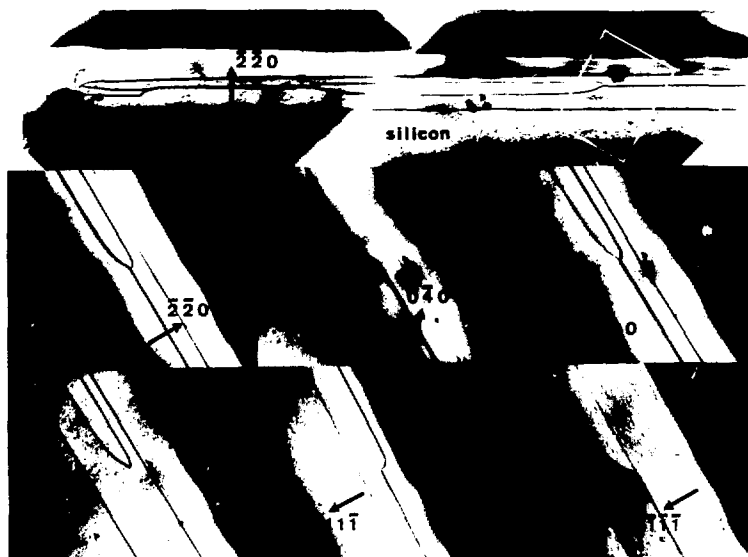


Fig.4. Interaction of 60° dislocations with different Burgers vector, generated at the same scratch. The observed reaction is $\frac{1}{2}[10\bar{1}] + \frac{1}{2}[011] \rightarrow \frac{1}{2}[110]$.

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