Report No. COO-2119-17

A Progress Report for Research on

EXPERIMENTS IN HIGH VOLTAGE ELECTRON MICROSCOPY

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Abstract

High voltage electron microscopy (HVEM) is being used to study the effects of irradiation on a variety of materials. The vacancies and instertitials produced by displacement can agglomerate to form dislocation loops and voids, annihilate at sinks, or enhance various diffusion processes such as precipitation and recrystallization. Threshold displacement energies, E_d, have been determined for a number of fcc, bcc and hcp metals. Directions for minimum E_d have been correlated with the crystal structure and the magnitude of E_d has been related to the sublimation energy. The effects of electron irradiation on precipitation in Al-Cu, Al-Si and Ni-Al alloys have been investigated. Precipitation respectively of Θ', Si and γ' is enhanced and growth rates are being related quantitatively to theories of radiation-enhanced diffusion. Results on radiation damage in oxides (quartz, alumina and magnesia) have also been obtained. Displacement damage gives rise to dislocation loop nucleation and growth in all cases, including multi-layer loops in Al_2O_3. In SiO_2, ionization damage also occurs, which destroys the crystallinity. Threshold displacement and temperature effects have also been investigated.

Introduction

The advantages of HVEM over conventional 100kV microscopy are well-known. (See for example, reviews by Mitchell[1] and Cosslett[2] and the various International Conferences on HVEM[3]). The experiments described in this report concentrate on the application of HVEM to in situ electron irradiation studies. However, other aspects of HVEM - increased penetration, decreased aberrations, improved selected area diffraction - are being used routinely in the investigations, as described previously.[4]

The ability to perform radiation damage studies is important in its own right and to simulate damage produced by neutrons in nuclear reactors. Very high displacement rates in the 10^{-3} dpa/sec range are available in the HVEM. Displacements produce vacancy-interstitial pairs which can subsequently annihilate each other, annihilate at sinks, cluster to form dislocation loops and voids, or enhance various diffusion controlled processes such as precipitation and recrystallization. All of these effects occur under neutron irradiation and have significant effects on the properties of nuclear materials. Thus void formation causes swelling in structural materials of fast reactors[5]. The effect can be simulated by both heavy ion and electron irradiation[5-11]. Irradiation in the HVEM clearly has the advantage of continuous observation and monitoring of the processes involved, but has the disadvantage of the uncertain influence of the foil surfaces. Such effects have been characterized by our investigations[12] and others,[13,14] and the important influence of dislocations in void formation has been confirmed.

Strong effects of neutrons on precipitation have been observed. (For review, see Hudson[15] and Rosenbaum[16].) An example is the precipitate induced in 316 stainless steel[17] which only occurs under the influence of irradiation. Ion irradiation has also been found to influence precipitation in Ni-base alloys[17]. A few studies have been made using the HVEM[15,19,20]. Our own investigations of Al alloys [21,22], stainless steel[23] and Ni-base alloys are described in the report.

Radiation damage in non-metals has received much less attention than metals. Neutron damage in some ceramic oxides has been reviewed by Wilks[24], and the available information is not very definitive. HVEM studies of MgO at room temperature have been reported by Sharp and Rumbsy[25]. However, as with metals, we have found that it is much more instructive to irradiate at higher temperatures where point defects can cluster into identifiable loops. Results on MgO, Al_2O_3 and quartz are presented in the report.

Since many of the results obtained over the past year have been published[12,21-23,26-30], the rest of the progress report will mostly consist of summaries of the most important data and their interpretation.

2. Results and Discussion

2.1 Experimental Techniques

Various experimental techniques which have been developed for the HVEM over the past few years, have been reported previously[4]. Some of the important techniques are as follows:

(a) High flux irradiation, giving displacement rates in the range 10^{-3} dpa/s[31].

(b) Monitoring of the specimen temperature and temperature rise due to beam heating[32].

(c) Preparation of ceramic foils by ion bombardment thinning. Foils are also annealed to remove the damage and carbon coated on one side to avoid charging effects.

(d) Adaptation of the weak-beam method of imaging to the HVEM[32] for high resolution pictures of small defect clusters.

(e) Use of the so-called "2-1/2 D" technique to obtain pseudo-stereo pictures of precipitates and differentiate them from other defects[34].

As described in the last proposal, a completely new side-entry stage system has been designed and ordered from Gatan for the HVEM. The basic modification and environmental cells are being paid for under a grant from NSF and the goniometer and heating tilting specimen holder from the present contract. (Similar modifications are being made to the Oak Ridge, U. S. Steel and HEDL microscopes.) The system is due to be installed this Fall and will improve our analytical and experimental capabilities by a quantum jump.

2.2 Threshold Displacement Energies

Threshold energy measurements are generally performed using electron accelerators with the specimen at a low temperature and by measuring some physical property such as resistivity (for review, see Lucasson [35]). HVEM measurements have the advantage that specimen orientation is easy to control, but have the disadvantage that measurements are usually made at room temperature, so that the threshold for the production of interstitials which can escape from their vacancies is determined (as in replacement collision sequences), rather than the threshold for close-pair formation. Nevertheless, the HVEM measurements are in many respects more relevant for practical radiation studies. Accordingly, the threshold displacement energy, E_d, has been determined by high voltage electron microscopy for Cu, Ag, V, Cr and Zn as a function of orientation[29,30]. The easy displacement direction is generally <110> for fcc metals and <100> for most bcc metals, as expected for replacement collision sequences. Also, <111> irradiation of Cu is consistent with the displacement occurring along the off-axis <110> directions. A good correlation is found to exist between the threshold energy and the sublimation energy (E_s) for a wide variety of metals, following the original suggestion of Seitz[36]. This is shown in Fig. 1 where the minimum E_d is approximately $4E_s$ and the average E_d is approximately $5E_s$. This gives a better correlation than with the elastic constants[37] or with the interatomic distances[38]; however, from the fact that Ag, Au, Zn and Pt deviate from the rule (Fig. 1), other factors must be important. E_d has also been determined in an alloy (304 Stainless Steel) since there is no well accepted value and because of the intrinsic interest in the effect of alloying. The minimum voltage for displacement is 400kV along the <110> direction, as in fcc metals.

2.3 Dislocation Loop and Void Formation in Pure Metals

Results on copper[12] and nickel[28] have been published, also some preliminary work on zinc[30].

2.4 Effects of Irradiation on Precipitation

Irradiation can influence precipitation through enhanced diffusion, enhanced nucleation, dissolution, disordering and re-ordering of precipitates, formation of new or unexpected phases, transmutation products and interaction with voids[9]. Some of these effects are illustrated by our experiments on aluminum alloys and stainless steels.

(a) Al-3.5% Cu. The effects of electron irradiation on precipitation in Al-3.5% Cu has been studied in the temperature range 20-200°C[19,20]. G.P. zones gradually disappear during irradiation and are replaced by θ' precipitates. The intermediate stage of θ'' precipitation is inhibited by irradiation. The growth of θ' precipitates is observed to be enhanced and has been explained in terms of a model of enhanced diffusion resulting from the annihilation at precipitates of the vacancies and interstitials created by irradiation; the irradiating conditions in the microscope are shown to give rise to a constant contribution to the diffusion coefficient, $D_{rad} \simeq 2 \times 10^{-16} cm^2/s$.

(b) Al-1% Si. This system is interesting because Si precipitates directly with no intermediate stages. Also, Si is a transmutation product of Al in a reactor environment[39]. We have observed that precipitation can be induced at room temperature by electron irradiation along with dislocation loops and that grain-boundary denuded zones are formed. At higher temperatures, enhanced growth of Si precipitates seems to occur; however, quantitative measurements are difficult due to the complicated morphology (circular, triangular, hexagonal, needle-like, plate-like. See Fig. 2).

(c) Ni-8% Al. Thermal aging has been found to follow the Lifshitz-Wagner theory of coarsening for the γ' precipitates. Under electron irradiation at 300 to 500°C, coarsening rates are much higher (see Fig. 3) and appear to follow enhanced diffusion rate kinetics, as given below:

Temperature	Thermal Diffusion Rate	Enhanced Diffusion Rate
	cm^2/s	cm^2/s
500°C	10^{-18}	10^{-12}
300°C	$\sim 10^{-23}$	10^{-13}

Experiments are being performed at other temperatures, including >500°C where it has been reported that irradiation causes a sudden change to 100% γ' at a dose of $\sim$5 dpa[40]. This is a phenomenon quite different from enhanced diffusion and must represent a fundamental change in phase stabilities under irradiation.

2.5 Radiation Damage in Oxides.

(a) Quartz. Previous work[26] has shown that there are two types of damage caused by electron irradiation - displacement damage which increases with increasing voltage and ionization damage which decreases with increasing voltage. Displacement damage causes loop formation. Recently we have extended experiments to higher temperatures: at 300°C large loops grow so that their Burgers vectors could be analysed to be parallel to [0001]; at higher temperatures damage anneals out rapidly. Ionization damage causes a crystalline-to-amorphous transformation. This persists at higher temperatures, including the β phase region (750°C). The amorphous region is resistant to re-crystallization during annealing at 750°C.

(b) Alumina. The threshold voltage for displacement damage has been measured to be 350 kV for [0001] irradiation and 300 kV for [11$\bar{2}$0] irradiation. Irradiation at higher temperatures (450 to 800°C) produces interstitial loops on the basal plane. The loops are faulted and in many cases multi-layered. Dislocation dipoles introduced by prior deformation are found to break up into strings of loops and then to re-form into dipoles. The break-up is probably due to radiation-enhanced self-climb while the joining-up is due to the growth of the loops by absorbing radiation produced defects.

(c) Magnesia. The threshold voltage for displacement damage has been measured to be 480 kV for (001) foils. The higher threshold for MgO than for Al_2O_3 can be explained in terms of the higher cohesive energy of MgO. Irradiation at higher temperatures (700°C) produces perfect interstitial loops on {110} planes with 1/2<110> Burgers vectors. The growth rate of the loops is linear with time but the density saturates after increasing due to the impingement of the loops. Effects of purity are also being investigated. Some high purity MgO, obtained from ORNL, was found to precipitate out $Mg(OH)_2$ after heating to ∿800°C (Fig. 4), indicating the initial presence of hydrogen. Some "hydrogen free" MgO was also obtained from ORNL, but even this showed a V_{OH}^- peak on a FT-IR spectrometer. Techniques are being developed to remove the hydrogen by annealing.

3. References

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4. Publications

The following publications have resulted from the research supported by ERDA

G. Das and T. E. Mitchell, "Radiation Damage of Type 304 Stainless Steel by High Voltage Electron Microscopy", Proc. El. Mic. Soc. Am., p. 678 (1972) - Report No. COO-2119-3.

T. E. Mitchell, "High Voltage Electron Microscopy for Microstructural Analysis", in "Microstructural Analysis: Tools and Techniques", (Plenum Press), p. 125 (1973) - Report No. COO-2119-4.

E. A. Kenik and T. E. Mitchell, "Loop and Void Formation in Copper during High Voltage Electron Microscope Irradiation", Proc. El. Mic. Soc. Am., p. 22 (1973) - Report No. COO-2119-6.

G. Das and T. E. Mitchell, "Electron Irradiation Damage in Quartz", Radiation Effects, 23, 49 (1974) - Report No. COO-2119-7.

E. A. Kenik and T. E. Mitchell, "Co-operative Growth of Dislocation Loops and Voids under Electron Irradiation", Radiation Effects, 24, 155 (1974) - Report No. COO-2119-8.

P. S. Sklad and T. E. Mitchell, "Radiation-enhanced Precipitation in Al-4% Cu by High Voltage Electron Microscopy", Scripta Met., 8, 1113 (1974) - Report No. COO-2119-9.

G. Das and T. E. Mitchell, "Recrystallization Induced by Electron Irradiation of Deformed Nickel", Scripta Met., 8, 1135 (1974) - Report No. COO-2119-10.

G. Das and T. E. Mitchell, "Irradiation Damage in Nickel in a High Voltage Electron Microscope", J. Nucl. Mater., 56, 297 (1975 - Report No. COO-2119-11.

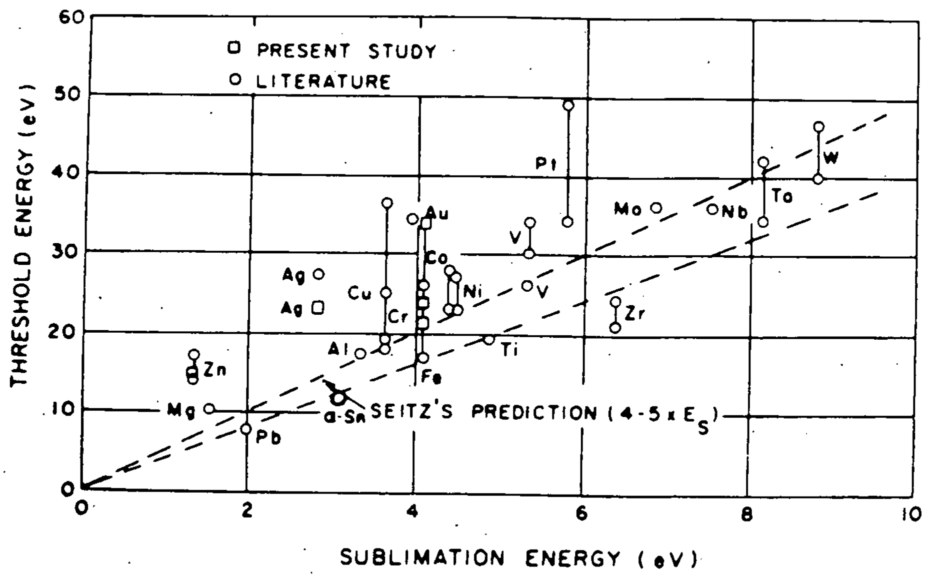
P. S. Sklad and T. E. Mitchell, "Efforts of Electron Irradiation on Precipitation in Al-3.5% Cu", Acta Met., 23, 1287 (1975) - Report No. COO-2119-14.

E. A. Kenik and T. E. Mitchell, "Orientation Dependence of the Threshold Displacement Energy in Copper and Vanadium", Phil. Mag., 32, 815 (1975) - Report No. COO-2119-13.

T. E. Mitchell, G. Das and E. A. Kenik, "Determination of Threshold Displacement Energies by High Voltage Electron Microscopy", in "Fundamental Aspects of Radiation Damage in Metals"(U.S. ERDA - Conf. 751006-P1), p. 73 (1975) - Report No. COO-2119-16.

Over the past year, Prof. Mitchell also presented a number of talks on radiation damage at: the International Conference on "Fundamental Aspects of Radiation Damage in Metals" in Gatlinburg (October 1975), Stanford University (February 1976), Argonne West in Idaho Falls (March 1976), University of California at Berkely (April 1976) and the American Ceramic Society Spring Meeting in Cincinnati (May 1976). Dr. Das also gave talks at various laboratories.

During the 1975-76 academic year, Prof. Mitchell was on Sabbatical leave in Palo Alto, California. He spent part of his time on a project supported jointly by EPRI and by NASA Ames Research Center. The project was on the oxidation of zircaloy in connection with stress corrosion cracking problems induced by iodine, which is a fission product in light water reactors. The extensive electron microscope facilities at NASA Ames were used to study the structure of the oxide and the underlying zircaloy. A number of meetings were attended on the EPRI SCC program which served to educate the author in the broad range of materials problems in nuclear reactors and to make important contacts in various institutions. Prof. Mitchell also spent time at Stanford University in order to write papers and to keep in touch with the ERDA research at C.W.R.U. Beneficial visits were paid to Berkeley (Prof. Washburn et al.); Oak Ridge, (Drs. Steigler, Carpenter et al.); Argonne West (EBR-II facility); G.E. Vallecitos (Dr. Bell et al); IBM Research Center at San José, (Dr. Geiss); G.E. Sunnyvale, (Dr. Appleby) and others; all of these visits were to discuss radiation damage in materials.



PRESENT STUDY
LITERATURE
THRESHOLD ENERGY (eV)
SUBLIMATION ENERGY (eV)
SEITZ'S PREDICTION (4-5 x E_S)
Zn
Mg
Pb
Ag
Cu
Cr
Al
α-Sn
Au
Co
Fe
Ni
Ti
V
Pt
Mo
Nb
Ta
W
Zr
0
2
4
6
8
10
10
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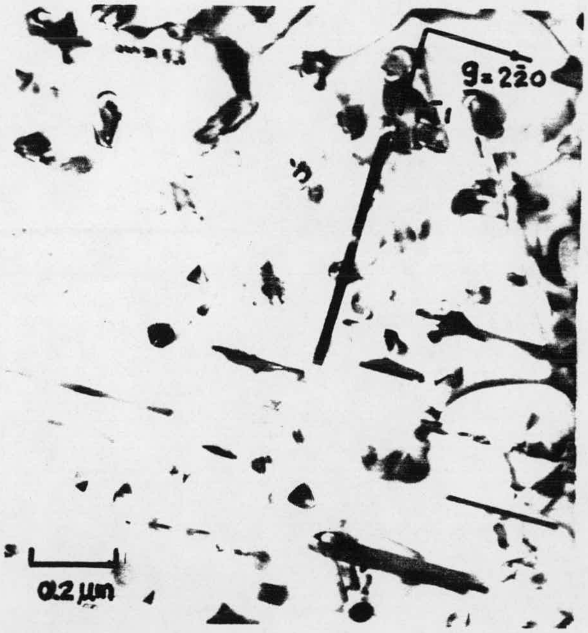
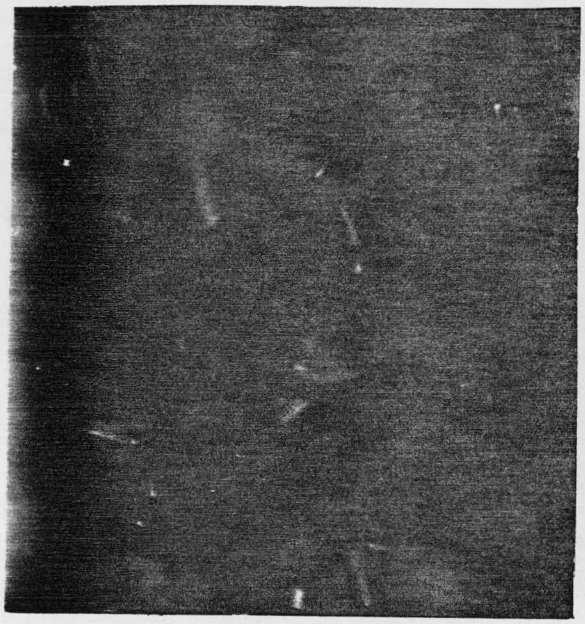
60

Fig. 1



(a)

(b)



(c)

(d)

Fig. 2- Effects of high flux irradiation at room temperature on a pre-aged specimen of Al-1wt.%Si for doses of: (a),(c) 0 dpa; (b),(d) 6.7 dpa. (a),(b) are bright field micrographs. (c),(d) are dark field micrographs imaged with first order (220) Si reflection.

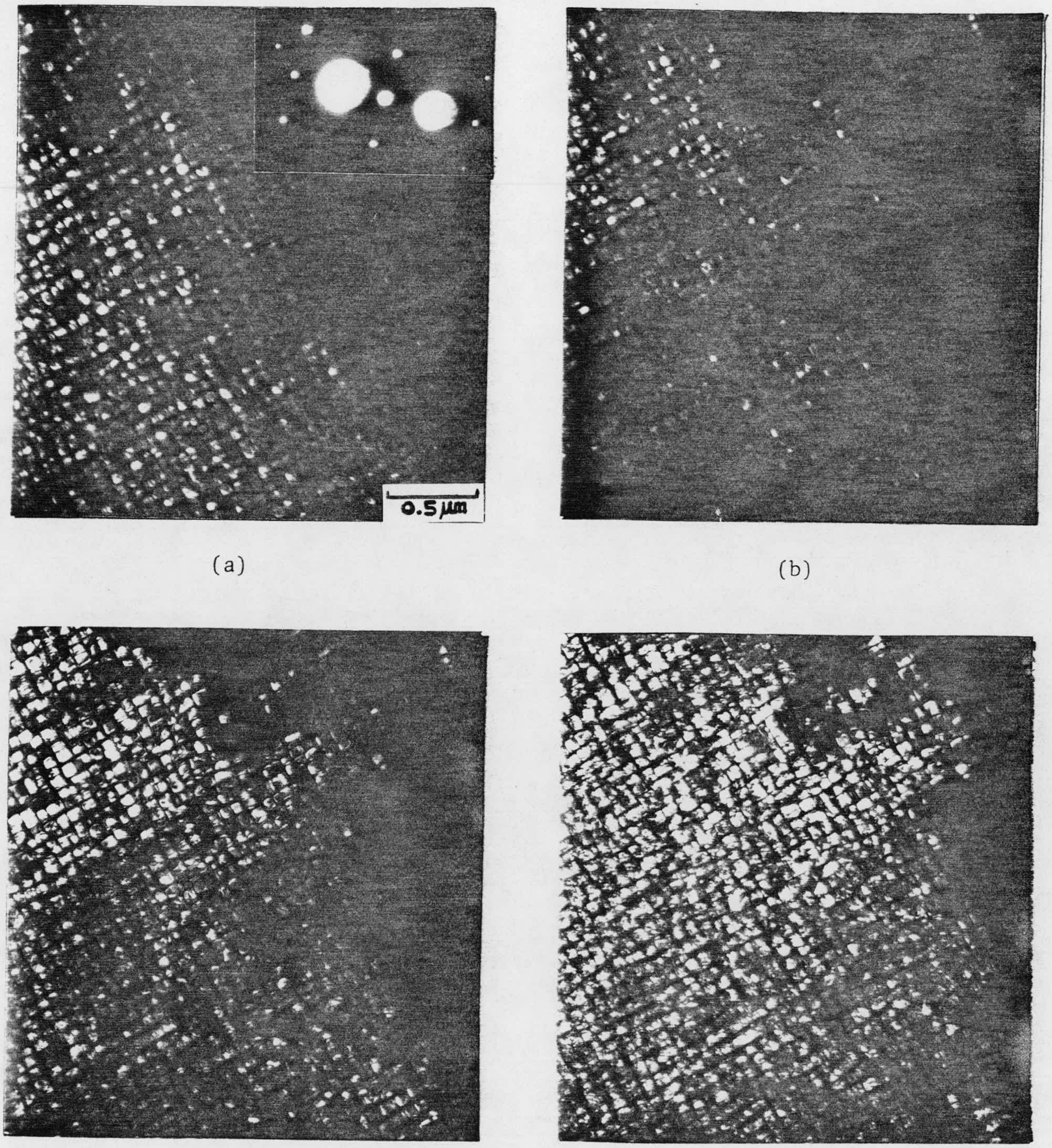


Fig. 3- Effects of high flux irradiation at 500°C on a preaged specimen of Ni-8wt.% Al for doses of: (a) 0 dpa; (b) 0.5 dpa; (c) 1.0 dpa; (d) 1.6 dpa. Dark field electron micrographs imaged with first order (110) γ' super lattice reflection.

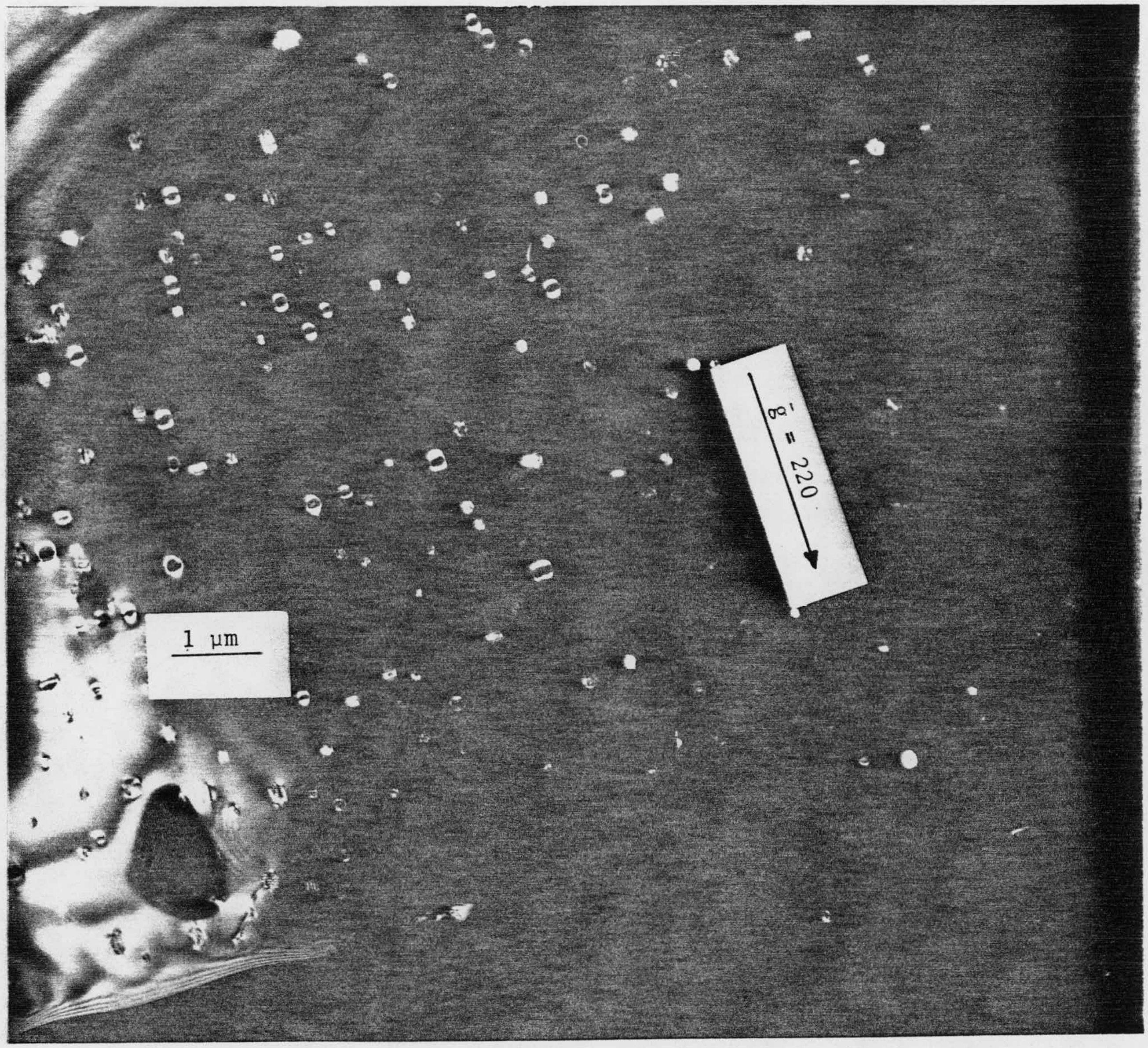


Fig. 4. $Mg(OH)_2$ precipitates in MgO produced by in situ ageing at 800 °C.