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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 interstitials produced by displacement can aggregate 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 and for various oxides. In MgO, E_d is less along <100> than <110>; also, E_d decreases with increasing temperature, possibly due to thermally activated escape of interstitials from recombination volumes or softening of saddle points. 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 explicable in terms of theories of radiation-enhanced diffusion, with $D_{rad} \sim 10^{-15}$ cm^2 sec^{-1}. In oxides, damage gives rise to interstitial dislocation loop nucleation and growth in all cases, perfect {110} loops in MgO faulted basal and prismatic loops in Al_2O_3. Quantitative analysis of loop growth rates in MgO gives a migration energy of 3.3 eV for anion vacancies. Other radiation effects include sublimation of MgO and decomposition of $MgAl_2O_4$ and Mg_2SiO_4 into MgO plus other phases.

1. 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, descreased 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 and various radiation effects in nuclear waste storage media. 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, voids, or other aggregates 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 example, 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[15,8,19]. Our own investigations of Al alloys [20,21] 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[22], and the available information is not very definitive. HVEM studies of MgO at room temperature have been reported by Sharp and Rubmsy[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, $MgAl_2O_4$ and Mg_2SiO_4 are presented in the report.

Since many of the results obtained over the past years have been published[12,20,21,24-29], 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[30].

(b) Monitoring of the specimen temperature rise due to beam heating[31].

(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. In addition we have recently been able to use the high resolution Siemens 102 to obtain lattice fringe images of dislocation loops produced by electron irradiation in Al_2O_3 (Figure 1). This is a very exciting discovery since it points to the possibility of imaging and identifying small defect clusters in a variety of materials.

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 basic modification, goniometer stage and tilt control have already been installed and have been found to be a remarkable improvement in our capabilities. The rest of the system is due to be installed in August 1977.

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[33]).

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 a wide variety of fcc, bcc and hcp metals as a function of orientation[8,29]. The easy displacement direction is generally <110> for fcc metals and <100> for most bcc metals, as expected for replacement collision sequences. A good correlation is found to exist between the threshold energy and cohesive energy.

E_d has also been determined as a function of orientation for MgO and Al_2O_3. In MgO E_d is found to be less along <100> than <110>. This is not surprising since <100> is the closest-packed direction for anions and cations together and has the largest "windows"; however, <110> is the closest repeat direction, showing that replacement collision sequences along rows of like ions may not be so important as in other systems.

2.3. 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 and nickel alloys.

Results on Al-Cu alloys have already been described[20,21]. Growth of G. P. Zones and θ" precipitates is inhibited but precipitation of θ" is enhanced by irradiation. Quantitative analysis shows that growth follows radiation-enhanced diffusion kinetics due to annihilation of point defects at precipitates.

Nucleation and growth of Si precipitates in the Al-Si alloys is enhanced but the great variety of precipitate size and shapes (circular, triangular, hexongonal, needle, plate) make quantitiative analysis very difficult.

In Ni-Al alloys, irradiation-enhanced growth of γ' precipitates occurs in both the aged and solution-treated conditions at temperatures up to 750°C (thermal aging is dominant at higher temperatures). Again quantitative analysis shows that growth follows radiation-enhanced diffusion kinetics, $D^{rad} \sim 4 \times 10^{-15}$ cm^{2}/s at a displacement rate of 2×10^{-3} dpa/s In the solution-treated condition, the formation and growth of faulted interstitial Frank loops is observed to accompany γ' precipitation. In the overaged condition, interfacial dislocations are induced to climb away from the interface but loops are then nucleated at the resulting coherent interface.

2.4. Radiation Damage in Oxides

(a) MgO. Damage has been observed at temperatures from ambient to 800°C.[34]. In the higher temperature range, the damge is identifiable as interstitial dislocation loops on {110} planes with perfect 1/2 <110> Burgers vectors. At the highest temperature, the loops become elongated in the <100> direction, as in the alkali halides[35], due presumably to anisotropic nucleation and migration of jogs. Loop growth rates have been analysed by adapting theories developed for metals[36], and it is found that the migration energy for oxygen vacancies is ∿3.3eV. In addition, pits are observed on the undersurface of the foils, indicating that sublimitation is induced by irradiation; polycrystalline MgO diffraction rings are also induced on the single crystals.

(b) Al_2O_3. Interstitial dislocation loops are also produced. At ∿ 600°C, the loops lie on the (0001) basal plane with partial 1/3 [0001] Burgers vectors; at 800°C, the same loops are produced plus loops lying on {10$\bar{1}$0} prismatic planes with partial 1/3 <10$\bar{1}$0> Burgers vectors. Stacking fault contrast is observed, corresponding to a fault in the cations, but not in the anion sub-lattice. It was discovered that it was possible to image these loops by lattice fringes in the Siemems 102 high resolution microscope (4.3Å (0003) Bragg planes). This important observation is being pursued to see if very small (∿10Å) defect clusters can be imaged and identified.

(c) $MgAl_2O_4$. A variety of defect clusters are observed which have yet to be identified. Importantly, it is observed that polycrystalline MgO rings are produced in the diffraction patterns, showing that phase decompostion into MgO plus Al_2O_3 - rich spinel is induced by irradiation.

(d) Mg_2SiO_4. As with spinel, forsterite decomposes under irradiation into MgO plus one or more phases, possibly enstatite ($MgSiO_3$) for example. However, very strong steaking in the diffraction pattern shows that a plate-like precipitate is being produced which also gives rise to Moiré-fringe contrast in the image.

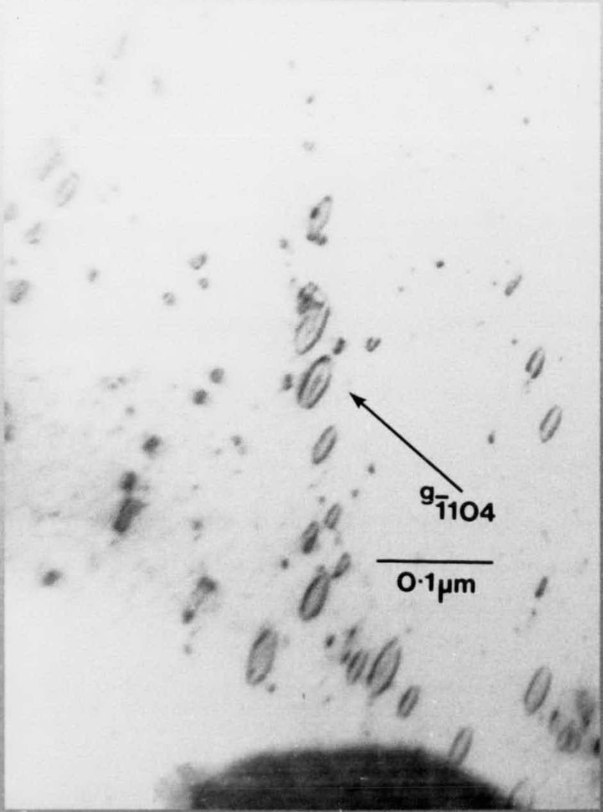
Figure 1

(1) Basal dislocation loops in Al_2O_3 irradiated in the HVEM at 700° C.

(2) Basal and prismatic dislocation loops in Al_2O_3 irradiated in the HVEM, showing stacking fault contrast.

(3) Elongated dislocation loops in MgO after extended irradiation in the HVEM at 800° C.

(4) Weak-beam dark-field images of perfect {110} dislocation loops in MgO at an early stage of HVEM irradiation at 800° C.



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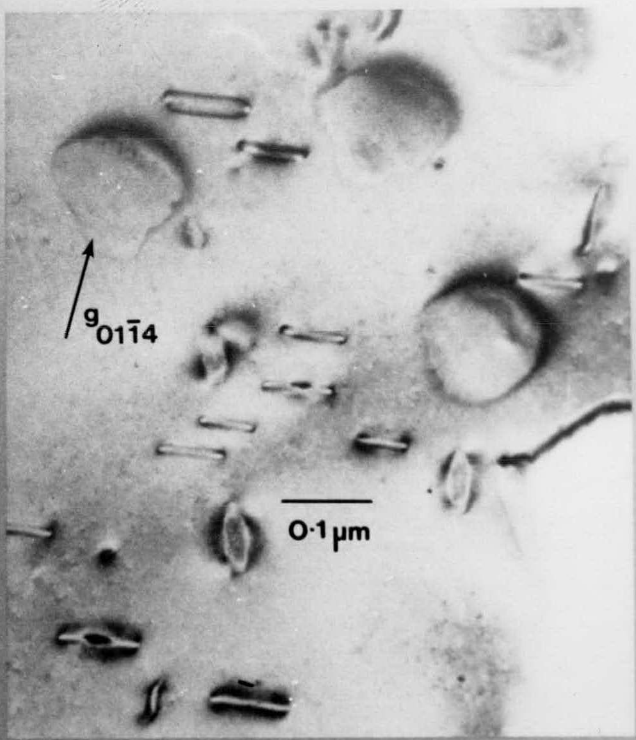

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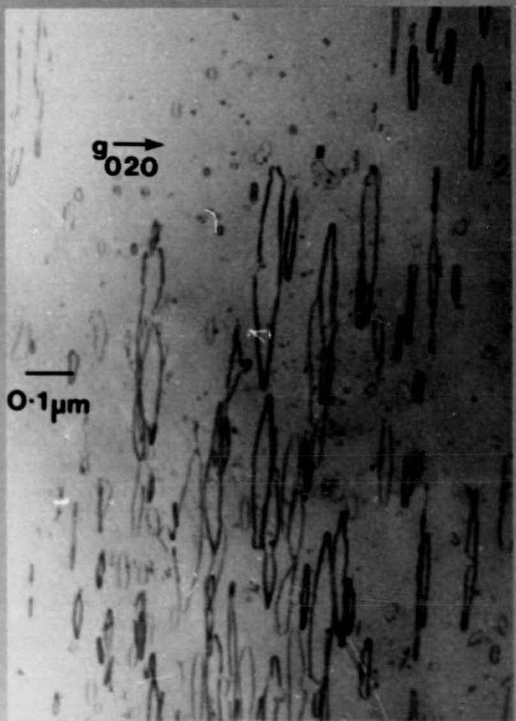

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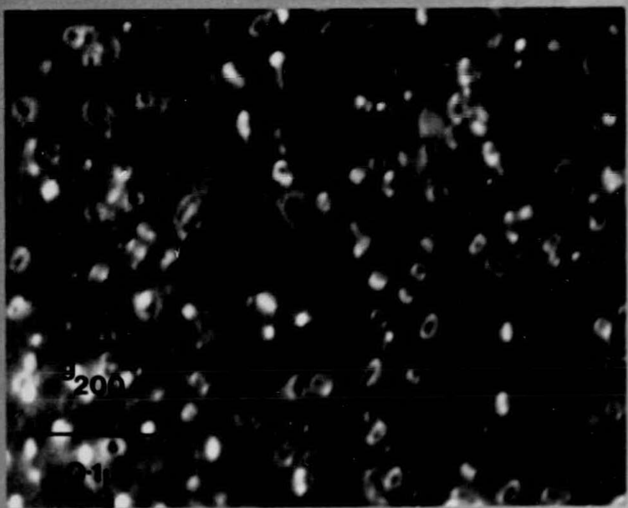

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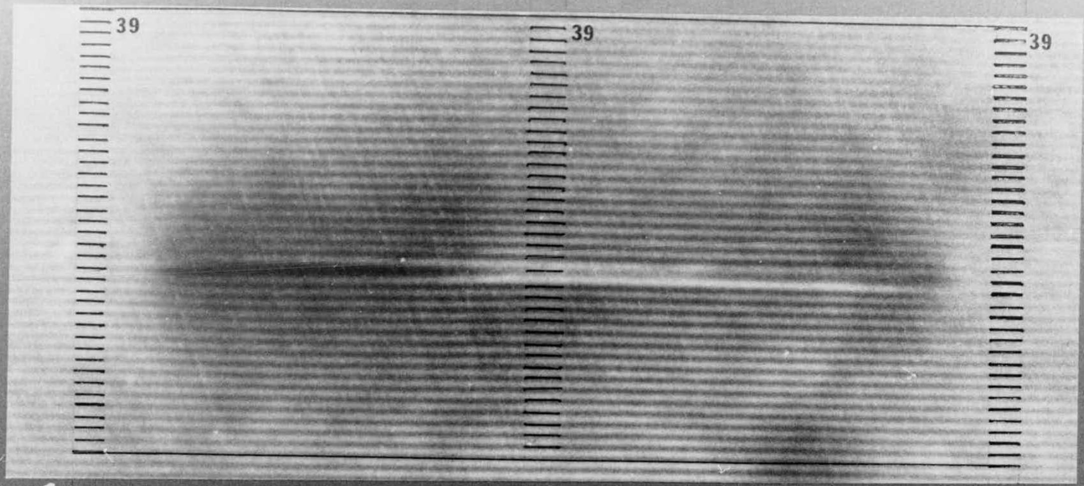
Figure 2

(1), (2) and (3) High-resolution dark-field lattice images from three pure edge dislocation loops in HVEM-irradiated Al_2O_3. The lattice images are formed by combining the $(11\bar{2}6)$ and $(11\bar{2}3)$ reflections. Burgers circuits through the centers of these loops do not confirm their character at this specimen thickness (about 500 Å).



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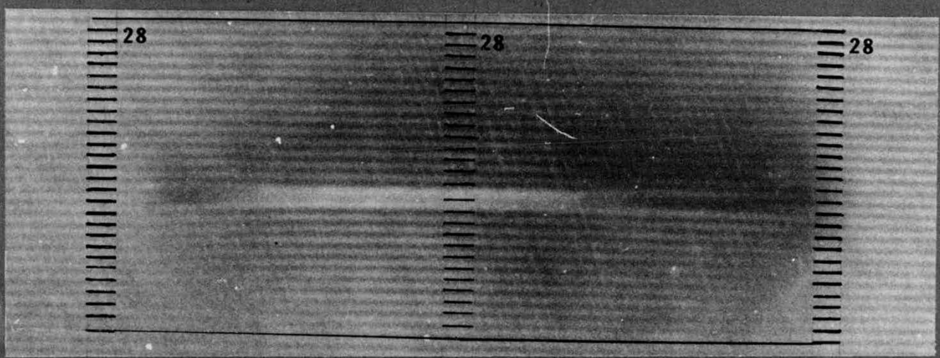

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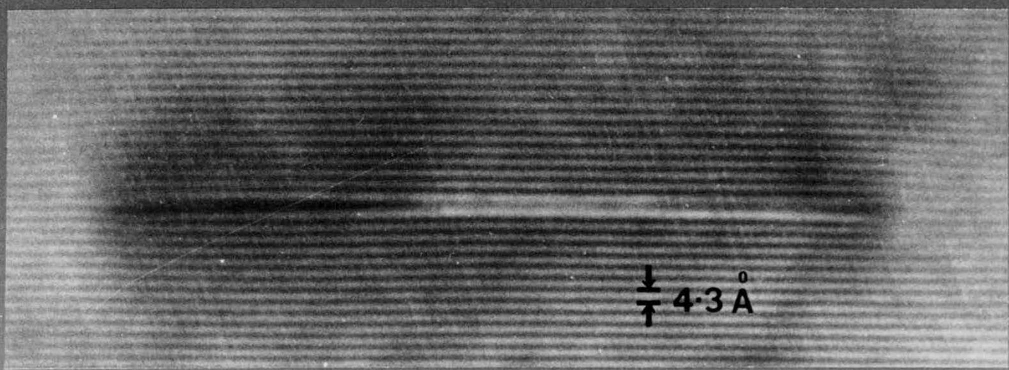

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4. Publications

The following publications have resulted from the research supported by ERDA

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