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**IN SITU ION BEAM RESEARCH IN ARGONNE'S INTERMEDIATE
VOLTAGE ELECTRON MICROSCOPE***

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IN SITU ION BEAM RESEARCH IN ARGONNE'S INTERMEDIATE VOLTAGE ELECTRON MICROSCOPE*

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ABSTRACT

Since Fall 1995, a state-of-the-art intermediate voltage electron microscope (IVEM) has been operational in the HVEM-Tandem Facility with in situ ion irradiation capabilities similar to those of the HVEM of the Facility. A 300 kV Hitachi H-9000NAR is interfaced to the two ion accelerators of the Facility, with a demonstrated point-to-point spatial resolution for imaging of 0.25 nm with the ion beamline attached to the microscope. The IVEM incorporates a Faraday cup system for ion dosimetry with measurement aperture 6.5 cm from the TEM specimen, which was described in Symposium A of the 1995 MRS Fall Meeting. The IVEM is now employed for a variety of in situ ion beam studies ranging from low dose ion damage experiments with GaAs, in which damage zones individual displacement cascades are observed, to implantation studies in metals, in which irradiation-induced noble gas precipitate mobility is studied in real time. In this presentation, the new instrumentation and its specifications will be described briefly, several basic concepts relating to in situ experiments in transmission electron microscopes will be summarized and examples of in situ experiments will be presented which exploit the experimental capabilities of this new user facility instrumentation.

INTRODUCTION

Any experiment which is performed in such a way that some relevant measurements or observations of change are made during the course of the experiment is said to be performed "in situ", a term so common that we no longer bother to italicize it. In a symposium devoted to the evolution of microstructure under irradiation it is especially appropriate to take a good look at the in situ technique involved in various irradiation effects studies performed with transmission electron microscopy. To promote this type of study in the United States the US Department of Energy in 1981 established the HVEM-Tandem Facility at Argonne National Laboratory near Chicago as a dedicated user facility, that is, one which is open to the materials research community, especially (but not exclusively) for in situ ion and electron irradiation studies of material behavior. To shrink the barrier to coming to the facility for potential non-Argonne users, the experimental time is offered free of charge for non-proprietary research.

The HVEM-Tandem Facility now consists of two transmission electron microscopes, (1) the modified AEI HVEM (EM 1200), installed in 1979, with accelerating voltages ranging continuously from 0.1-1.2 MV, and (2) the Hitachi H-9000NAR intermediate voltage electron microscope (IVEM), with accelerating voltages from 100-300 kV, installed in 1995. Both microscopes are interfaced to a 2 MV tandem ion accelerator and a 0.65 MV ion implanter. The characteristics and capabilities of the HVEM and the ion accelerators have been described previously [1,2], as have those of the IVEM

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[3]. In both the HVEM and the IVEM, ion dosimetry is performed either intermittantly with a Faraday cup rod which replaces the specimen holder or continuously with a Faraday cup system permanently installed within the microscope column. The latter system has been described previously for the Argonne HVEM [6] and IVEM [3]. Ishino [4] has presented a brief historical overview of this type of instrumentation as it has evolved over the past nearly quarter century and Allen *et al.* have reviewed recently the existing facilities of this type throughout the world [5].

In order to use either the HVEM or IVEM, prospective users prepare a brief research proposal which is reviewed by a Steering Committee, composed of scientists from universities, industrial laboratories and national laboratories [7]. Studies based on accepted proposals usually can be initiated within a few months of proposal submission.

In an in situ TEM experiment, the specimen holder becomes part of a microlaboratory in which the experiment is performed. The specimen, for instance, may be heated or cooled, or heated under stress, or irradiated or some physical parameter such as electrical resistance measured during the course of the experiment. Of course, the necessary TEM analytical techniques of imaging, diffraction and spectroscopies may be utilized as the in situ experiment proceeds. In the case of the TEMs in the HVEM-Tandem Facility, the specimen may be subjected to ion irradiation for damage and implantation studies (IVEM and HVEM) and/or to high energy electrons (HVEM). There are six specimen holders presently available to users of the IVEM. They are

Ambient Single Tilt Holder (Hitachi)

Ambient Double Tilt Holder (Hitachi)

Two Holders: Double Tilt Heating 300–1273 K (Gatan)

Single Tilt Heating/Tensile Holder 300–800 K (Gatan)

Double Tilt Helium Holder 15–300 K (Oxford)

In combination with the inherently good spatial resolution for imaging in the IVEM (0.25 nm point-to-point), the specimen holders present an array of exciting experimental possibilities for this microlaboratory.

APPLICATIONS OF THE ARGONNE IVEM

The IVEM has been operational for in situ ion beam studies since October 1995. A variety of irradiation effects studies is now ongoing, some of which began with the HVEM, at least parts of which did not require high energy electron irradiations, and others which have been initiated specifically for the more state-of-the-art capabilities of the IVEM. The examples cited are drawn from the recent work of several groups of users of the Facility. These studies fall into two main categories, fundamental defect studies and in situ ion and electron-stimulated reaction studies. The majority (12 of 15 total) are in the second category. With the kind permission of the users, brief excerpts from several of these studies are presented to illustrate the kinds of experimental studies which have been underway during the first year of IVEM operation.

Fundamental Defect Studies

Electrons, protons and ions impinging on a crystalline material with sufficient energy produce distributions of point defects, the subsequent evolution of which can profoundly alter microstructure and resulting material properties. Electrons and protons produce vacancy/interstitial pairs (Frenkel defects); heavier ions produce cascades of these defects and in some cases important ionization effects as well.

C. W. ALLEN

2/11

Fig. 1. $\langle 220 \rangle$ dark field stereo pair, following low dose in situ 300 K irradiation of Cu with 100 keV Kr^+ (10^{11} cm^{-2}). Defect clusters formed by collapse of irradiation-induced point defects, imaged under two beam conditions. Black line represents specimen normal. To be viewed with unaided eyes. (Courtesy of T. L. Daulton, Argonne National Laboratory.)

The resulting defects may reorganize subsequently in various ways depending on the type and severity of damage, the material, temperature, local stress and the like. Fundamental defect studies focus on the nature and structure of individual defects and of defect clusters and on their life cycles. The resulting knowledge base is at the core of understanding the materials science of the various, often complex, physical and chemical irradiation effects phenomena.

At present there are three approved IVEM projects in the fundamental defect studies category. The first is a collaboration involving M. Kirk (Argonne National Laboratory), H. Fukushima (Hiroshima University) and M. Jenkins (Oxford University) entitled "Search for Small Interstitial Loops". In this study, the character of small Frank loops in Cu, formed by low dose ion irradiation, is established by several contrast techniques which have been widely employed in the past, including the "two and a half D" and dark-light contrast techniques. The conclusion that results from the two and half D technique may not be reliable in this application has important consequences, because many published studies have employed only this technique, and their results have been input into models, for example, of irradiation-induced phenomena in reactor environments. Of several hundred loops, the vast majority which could be analyzed were determined to be vacancy-type and a few possibly to be interstitial-type; however, the loop character could not be established at all for a large fraction of the population.[8, 9]

The second study involves also individual defect clusters in Cu, produced by 100 keV Kr ion irradiation at room temperature. The high energy ions pass through the electron transparent region of specimen, producing defects which agglomerate and collapse to form small defect clusters such as dislocation loops or stacking fault tetrahedra. Figure 1 is a stereo pair of (220) two beam dark field images showing a distribution of such clusters, principally faulted Frank dislocation loops. This stereo pair is designed to be viewed with unaided eyes. In this case, stereo pairs are employed initially so that subsequent behavior of the defects can be correlated with their position in the thin foil in relation to the free surfaces, for example, during annealing. Free surfaces act as sinks for excess point defects; during rearrangement

Fig. 2 10–20 nm Au film under 200 keV Xe^+ irradiation at 300 K; bright field images, underfocussed approximately 1,000 nm, grabbed from unprocessed video tape (30 fps). Changes accompanying single ion impacts between Frames 1 and 3 and 79 and 80. (Courtesy of R. C. Birtcher, Argonne National Laboratory, and S. E. Donnelly, University of Salford, UK.)

one expects to find a systematic change in the relative shrinkage rates of interstitial and vacancy type defect clusters and between faulted loops and stacking fault tetrahedra during annealing as a function of their distance from a free surface. [10]

The third study in the fundamental defect study category is by H. Hahn and M. Rose (University of Darmstadt) on ion irradiation-induced damage in nanostructured Pd and ZrO_2 . If the grain size of a nanostructured material is comparable to the diffusion length of defects to interfaces, all such defects can readily annihilate instead of forming defect clusters during irradiation. A substantial reduction in residual radiation damage can be expected, therefore, in nanocrystalline materials, which this study has clearly demonstrated. [11].

In Situ Ion-Stimulated Reaction Studies

The fundamental defect studies above involve low dose irradiations in order to produce well separated defect clusters for analysis and subsequent in situ observation, for example, during recovery. With significantly larger doses, the elementary defect processes can result in a number of physical phenomena of considerable practical importance, such as radiation-induced elemental segregation or the creation of voids and swelling or amorphization of part of or all of the structure. In situ irradiation effects studies are very efficiently employed for such phenomena, provided, of course, that the thin area of the TEM specimen under study does not introduce essential artifacts in the results.

Ion impact study

A single ion impact study by R. C. Birtcher (Argonne National Laboratory) and S. C. Donnelly (University of Salford, UK) represents a fundamental defect study of sorts

as well as a reaction study. Ion-induced cratering in Au was observed some 30 years ago, based on observations following irradiation [12]. This in situ study of the phenomenon has enhanced the earlier interpretation very significantly. Figure 2 is a sequence of unprocessed video frames during 200 keV Xe irradiation at room temperature. These are bright field images of a 10–20 nm thick Au film, at a large underfocus of approximately 1,000 nm. Between two of the frame pairs shown, a single Xe ion has just struck the area of view, causing a major reconfiguration of the landscape. What is produced by one ion impact can be completely changed by a subsequent nearby impact, as evidenced by the changes in the holes in the Figure 2 sequence. Between Frames 1 and 3, a hole is created at B, causing hole A to become smaller, and between Frames 79 and 80, hole B has been enlarged further and hole A again has been diminished.

Figure 3 is an extensively image-processed, underfocussed TEM bright field image of a crater produced in a thin Au foil by a single Xe-ion impact, dramatizing the cratering action. The crater-like feature in Fig. 3 is approximately 7 nm in diameter. The cratering effect, accompanying both reflection and transmission sputtering, has been predicted by molecular dynamic simulation by Averbach [13]. What is clearly demonstrated throughout the in situ IVEM study is the extent of net material flow when a cascade event occurs near a free surface [14, 15].

Amorphization studies

The dynamics of irradiation-induced amorphization processes involve irradiation-induced damage on the one hand and a variety of thermal and damage-related recovery events on the other, with the result that there is a characteristic temperature (sometimes called the amorphization temperature) above which, during irradiation, recovery dominates and amorphization does not result for a given set of irradiation conditions. This temperature depends on the material itself and on the mass and flux of the projectile. There are fundamental aspects imbedded in each of the amorphization studies utilizing the IVEM and ion beam interface, the studies frequently determining the kinetics of amorphization and the amorphization temperature under each of several irradiation conditions, particularly with more than one ion mass.

Four IVEM projects in the area of irradiation-stimulated amorphization and crystallization of ceramic materials are connected directly or indirectly with scenarios

Fig. 3. Extensively image-processed bright-field TEM image at $\sim 0.1 \mu\text{m}$ underfocus. Crater-like feature at surface of Au foil, due to single 200 keV Xe ion impact. Crater about 7 nm in diameter. (Courtesy of R. C. Birtcher, Argonne National Laboratory, and S. E. Donnelly, University of Salford, UK.)

Fig. 4. Crystallization of amorphous fluorapatite $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$ at 300 K by 300 keV electrons. Material initially amorphized in situ by 800 keV Kr. (Courtesy of A. Meldrum L.M. Wang, Y.X. Guo, and R.C. Ewing, University of New Mexico—Albuquerque)

for long term nuclear waste storage. Lead by R. Ewing and L.-M. Wang (University of New Mexico—Albuquerque) and including a collaboration with W. Weber (Pacific Northwest National Laboratory), three of these studies range from ion beam amorphization studies of minerals such as titanite and zirconolite to irradiation-stimulated crystallization in orthophosphates [16, 17]. Fig. 4 is taken from a study of electron irradiation-induced phase segregation in crystalline and amorphous fluorapatite, in this instance showing electron irradiation-induced crystallization of fluorapatite nominally at room temperature; thermal crystallization occurs in this material above about 650 K [17, 18]. A fourth project in this category, entitled "In Situ Ion Irradiation Studies of Radiation Resistant Oxides", is being pursued by K. Sickafus and R. Davanathan (Los Alamos National Laboratory).

In addition to the studies of amorphization of ceramic materials, two other IVEM studies focus on amorphization in GaAs and in Zr-Fe multilayers. In the case of a chemically ordered material such as the compound semiconductors GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$, displacement processes of ion irradiation damage will produce chemical disorder, or occupancy of some Ga-type sites by As and vice versa (antisite defects),

Fig. 5. $\langle 110 \rangle$ lattice image of $\text{Al}_{0.6}\text{Ga}_{0.4}\text{As}/\text{GaAs}$ interface region following 293 K low dose implantation of 50 keV Xe^+ ($8 \times 10^{11} \text{ cm}^{-2}$). Small regions of darker contrast are highly damaged zones. (Courtesy of B. A. Turkot and I. M. Robertson, University of Illinois—Urbana-Champaign.)

a common result of high energy electron irradiation as well. The process of ion-induced amorphization is spatially heterogeneous, with an amorphous zone associated with each cascade of sufficient size. Fig. 5 is an IVEM high resolution image of an $\text{Al}_{0.6}\text{Ga}_{0.4}\text{As}/\text{GaAs}$ heterostructure after a relatively low dose of 50 keV Xe at room temperature. The small dark splotches in the background of the image are remnants of the cascade damage, in this case small amorphous zones along the atom columns of the crystal. Substitution of Al increases damage resistance. This is from a study by B. Turkot and I. Robertson (University of Illinois at Urbana-Champaign). One purpose of this study is to determine the quantitative characteristics of the amorphization process, including the effects of irradiation temperature and ion mass.

The final example in this category is an in situ study by A. Motta and co-workers (The Pennsylvania State University) of the effect of metallic multilayer modulation (wavelength) and average film composition on the nature of reaction products under ion beam mixing compared to solid state thermal reaction. The specimens in this study are Fe-Zr multilayers of average composition 45 and 50 atomic percent Zr, observed in plan view. Reactions are followed by selected area electron diffraction. The development of the product phases is followed as a function of annealing time or of irradiation dose. Thermal reaction of 50 %Zr specimens produces mostly an amorphous compound with some residual Fe and Zr for all wavelengths studied, as shown in Fig. 6c. For the 45% Zr specimens, there is a strong effect of wavelength; a 13 nm wavelength produces mostly amorphous material (similar to the 50 %Zr case), while a 25 nm wavelength produces the crystalline intermetallics Zr_2Fe and Zr_3Fe ,

as shown in Fig. 6b. In contrast, reaction produced by ion beam mixing with 300 keV Kr yields an amorphous phase in the 45% Zr film (Fig. 6d) and the 50% Zr film (not shown) for all wavelengths studied. The in situ capabilities of the IVEM permit direct determination of reaction kinetics under a wide range of irradiation and annealing conditions. This allows the study of the Zr-Fe system which, as this work shows, is an excellent candidate for comparison of existing models of both thermally-stimulated and ion irradiation-stimulated reaction. [19]

Ion implantation studies

Four quite different projects involve in situ ion implantation with the IVEM. Ion implantation is a source both of damage and of local changes in chemical composition, and, especially for large dose levels, can grossly alter microstructure

Fig. 7. Melting sequence of Pb particle in Al matrix during 60 keV Cd implantation, 22°C above the Pb-Cd eutectic. (a) Melting begins on {100} and (b-d) propagates in abrupt jumps over narrow range of Cd fluence. (Courtesy of E. Johnson and U. Dahmen, Lawrence Berkeley National Laboratory.)

of a material. One aspect of such a study by E. Johnson (Niels Bohr Institute) and U. Dahmen (Lawrence Berkeley National Laboratory) involved implantation of Cd into Al containing a fine dispersion of Pb [20]. Both Cd and Pb are insoluble in Al, and form a binary eutectic with each other with limited terminal solid solubility. Fig. 7 shows the eutectic melting sequence of a Pb particle on implantation of Cd at 545 K, 22 °K above the Pb-Cd eutectic temperature. What was expected was gradual melting of the Pb-rich particle, beginning when the solubility limit of Cd in Pb was reached (solidus at ~5 at. pct. Cd) and extending to the liquidus composition (18 at. pct.). In fact, what was observed was initial melting on {100} facets at an estimated fluence of $5 \times 10^{18} \text{ m}^{-2}$, followed by melting in abrupt increments within a fairly narrow range of composition. The sequence shown in Fig. 7 is representative of the abrupt changes during the melting process. Two studies involve implantation of noble gases into metal matrices. In the first, R. Birtcher (Argonne), S. Donnelly (Salford University) and C. Templier (University of Poitiers) are studying the response of gas bubbles to irradiation. In the second, C. W. Allen, R. C. Birtcher (Argonne) and K. Furuya (NRIM—Tsukuba) are probing the earliest stages of bubble precipitation. The fourth study deals with irradiation-induced microstructural changes in V alloys during implantation of He at various temperatures, a fusion reactor materials study by D. Narayanaswamy and D. Alexander (Argonne National Laboratory). Fig. 8 illustrates the effect of imaging conditions on the information content of a region of V-3.9Ti-3.8Cr (percent by weight) following 200 keV He irradiation at 300 K to a fluence of

Fig. 8. Bright field images of V-3.9Ti-3.8Cr (percent by weight) under various diffraction conditions. Specimen, preimplanted with less than 10 appm He, irradiated at 300 K by 200 keV He to 0.1 dpa. (a) (200), 2 beam; (b) (211), 2 beam; (c) near 111 zone axis; (d) near 110 zone axis; (e) (110), 2 beam; (f) (310), 2 beam. (Courtesy of D. Narayanaswamy and D. Alexander, Argonne National Laboratory).

$3.5 \times 10^{16} \text{ cm}^{-2}$ (0.1 dpa from TRIM). The specimen had been preimplanted with 40 keV He to less than 10 appm (2.2×10^{-3} dpa from TRIM). Areas shown are not identical but very near one another. [21]

CONCLUDING REMARKS

Several points are illustrated by the foregoing examples, both regarding performance of the Argonne IVEM/ion beam interface system and regarding in situ experiments in general. Good resolution under demanding conditions is a hallmark of the system. The facility for watching what happens to a specimen in real time is the essence of the in situ method; a simple before and after analysis may shed little light on the actual dynamics of a process. Also in almost every case, the in situ method is a very efficient technique because of its simultaneous analysis aspect.

Additional details regarding the capabilities of the HVEM-Tandem Facility and procedures for accessing its instrumentation may be obtained by writing one of the authors or by the following means: telephone: (630) 252-5222; FAX: (630) 252-4798; e-mail: edward_ryan@qmgate.anl.gov. An "HVEM-Tandem Facility User Guide" is available on request. Both the HVEM and IVEM are part of the DOE funded User Facility and are available to the scientific community for materials research, free of charge for non-proprietary studies.

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C. W. ALLEN

11/1

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