TRANSMISSION ELECTRON MICROSCOPY STUDY OF CASCADE COLLAPSE
IN COPPER DURING IN-SITU ION-IRRADIATION AT
ELEVATED TEMPERATURES*

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TRANSMISSION ELECTRON MICROSCOPY STUDY OF CASCADE COLLAPSE IN COPPER DURING IN-SITU ION-IRRADIATION AT ELEVATED TEMPERATURES

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ABSTRACT

The basic mechanisms driving the collapse of point defects produced in collision cascades are investigated by transmission electron microscope (TEM) characterization of defect microstructures produced in fcc-Cu irradiated with low-fluences of heavy (100 keV Kr) ions at elevated temperature (23 - 600°C). Areal defect yields are determined from direct TEM observation of the total defect production integrated over the duration of the *in-situ* ion-irradiation. They are unequivocally demonstrated to decrease with increasing lattice temperature. This decrease in defect yield indicates a proportional decrease in the probability of collapse of cascade regions into defects of size where visible contrast is produced in a TEM.

INTRODUCTION

Displacement collision cascades represent the primary mechanism of lattice displacement for high-energy ions and neutrons and consequently play an important role in the modification of physical properties. Collision cascades generate localized volumes within the solid containing high concentrations of interstitial and vacancy point-defects. At sufficiently large point-defect concentrations, these highly disordered regions are unstable; recombination of interstitial and vacancy point-defects can occur along with the aggregation of point-defects into clusters. These clusters can collapse into various types of dislocation loops and stacking fault tetrahedra (SFT) which are large enough to produce lattice strain fields which are visible under diffraction-contrast imaging in a TEM.

The basic mechanisms driving the formation of cascade regions and their structural evolution into collapsed point-defect clusters are not well understood. These mechanisms are strongly driven by temperature and governed by kinetics. As temperature is varied, changes in product microstructures should reflect the manner in which cascade processes depend upon temperature. These changes include the spatial distribution of point-defects within cascade cores and their probabilities of collapse into various types of dislocation loops and SFT. In addition, changes in the distribution of defect types produced as well as changes in their respective size distributions can occur. To develop a better understanding of the kinetics governing cascade formation and subsequent collapse into point-defect clusters, the defect yield produced during 100 keV Kr ion-irradiation of fcc-Cu is measured *in situ* as a function of lattice temperature using TEM.

In a previous paper [1], we reported preliminary measurements of post-irradiation defect yields at elevated temperatures. The post-irradiation yield is defined as areal defect density per incident ion present immediately after completion of the ion-irradiation. In that work, defect loss resulting from isothermal anneal following the ion-irradiation was measured and then fitted to a simple model describing defect loss rates. Post-irradiation yields were then determined by eliminating the effects of isothermal loss. The resultant post-irradiation yields exhibited a clear dependence on lattice temperature (Fig. 1), remaining relatively constant from 23°C to 300°C then abruptly decreasing above 300°C. This suggests a lattice temperature dependence for the probability of collapse of cascade regions into defects of size which produce visible contrast. However, before this can be established definitively the question of defect loss during ion-irradiation needs to be

Figure 1: Post-irradiation defect yields measured from extrapolations of isothermal anneal data for 100 keV Kr ion-irradiations of fcc-Cu. The bar represents the weighted average for measurements near 23°C. The curve through the data displays a trend and is not fitted to a model.

at elevated temperature. This can be accomplished through the analysis of video recorded TEM images. In this paper we discuss some of the preliminary results from our *in-situ* TEM observations of defect formation and loss during ion-irradiation at elevated temperatures.

EXPERIMENT

TEM samples were prepared from a rolled polycrystalline copper sheet of 99.99% nominal purity and a single crystal copper rod of 99.999% nominal purity cut into 3 mm diameter disks. The single crystal was sliced with the [100] zone axis near normal to the plane of the disk. The copper disks were sealed in quartz tubes, evacuated to 2×10^{-6} torr, then backfilled with high purity argon, and annealed for 2 hours (polycrystalline) or 4 hours (single crystal) at 1093°K ($0.8 T_{\text{melt}}$). Annealed disks were electro-polished to perforation using an electrolytic solution of 500 ml methanol, 30 ml nitric acid, and 5 ml 2-butylethanol at 238°K and stored under 10^{-8} torr prior to insertion into the TEM for examination.

The microscopy was performed in the HVEM-Tandem facility at Argonne National Laboratory using a Hitachi H-9000NAR TEM interfaced with a 2 MV tandem ion accelerator and a 0.65 MV ion implanter. The ion implanter was used to produce 100 keV Kr ion beams with typical fluences between $(9.4 \leq \Phi \leq 14.1) \times 10^{10}$ ions-cm⁻². *In-situ* ion-irradiations were conducted in the TEM with the ion-beam at near normal incidence to the foil surface. Further details describing the H-9000NAR TEM / accelerator arrangement are given by Allen [4].

The microscope was equipped with a Gatan model 622SC image intensified video rate camera which was connected to a VCR, enabling the *in situ* recording of images during ion-irradiations. A Gatan model 652 double-tilt, side-entry, elevated temperature goniometer stage was used. The microscope was operated at low-voltage (100 keV) to reduce the influence of electron irradiation on the production and subsequent evolution of defects produced by ion-irradiation. All TEM imaging was performed under strong dynamical 2-beam dark-field (DF) conditions utilizing the (200) operating reflection. The $g = (200)$ reflection can produce strong visible contrast for the maximum number of possible defect clusters in fcc-Cu: all Frank partial (sessile) dislocation loops ($\mathbf{b} = a/3\langle 111 \rangle$), all partially dissociated Frank partial (sessile) dislocation loops, four of the six

fully addressed.

During ion-irradiation an increase in defect loss rate over those rates measured under similar conditions without ion-irradiation has been observed [2, 3]; this increase was reported to scale with ion-fluence. The immediate question arises as to whether a temperature dependence for the isothermal loss rate during ion-irradiation can account for the change in post-irradiation yield. In our previous work [1], only limited data addressing this concern was available to support a temperature dependence for the yield.

To adequately resolve this point, it is necessary to directly observe the production and loss of defects during ion-irradiation at

perfect (glissile) dislocation loop Burger's vector variants ($\mathbf{b} = a/2\langle 110 \rangle$), and all (sessile) SFT.

RESULTS

The formation of defect microstructure during ion-irradiation is a dynamic process. Once a defect is formed, its position in the foil as well as its structure (Burger's vector, habit plane, or size) can be altered [5] or even destroyed upon further ion-irradiation. The integrated defect yield is defined as the total number of TEM visible defects per unit-area per incident ion formed over the duration of the ion-irradiation. The post-irradiation yield is obtained from the integrated yield by subtracting the number of defects per unit-area per incident ion lost during the ion irradiation.

Integrated yields can only be obtained from measurements of concurrent observations of defect formation during ion-irradiation; this was accomplished through the use of video recordings of 2-beam DF images in the TEM. The temporal resolution of VCR recordings is $\approx 1/30$ frames/second, and consequently, any defects which are formed and lost within a shorter time interval will not be imaged. Although VCR format tape offers substantially increased time resolution over a time sequence of micrographs, its spatial resolution is far inferior to that of conventional film. Small defects and closely spaced defects arising from subcascades are more difficult to resolve.

One major difficulty encountered in these experiments was the inability to consistently establish optimum imaging conditions prior to ion-irradiation. Furthermore, it was not possible to adjust the instrumental imaging parameters during the short durations (≤ 26 seconds) of the ion-irradiations limiting the clarity of the images. This was of particular concern if the ion-irradiation caused local buckling of the foil, which dramatically altered the 2-beam DF imaging condition.

Although the optimum TEM imaging condition is achieved when defects are ≤ 10 nm from the ion-entry surface, the influence of the near surface on the formation and stability of defects should be considered when the results of thin foil TEM studies are applied to bulk materials. To minimize the influence of the near-surface on the formation and loss of defects, near normal ion-incidence was used to distribute the defects the greatest distance from the near-surface. To allow *in-situ* observation, it is necessary to have a crystal oriented with the 2-beam DF $\mathbf{g} = (200)$ imaging condition coincident with the specimen orientation for near normal ion-incidence. Specimens satisfying this criterion were prepared from single-crystal Cu rods. However, specimens prepared from polycrystalline disks were also used when a grain possessing thin area had the required crystallographic orientation.

Once the specimen was brought to temperature, a 2-beam DF imaging condition within 12° of normal ion-incidence was determined. Residual deformation dislocations, when present, were used to adjust the 2-beam DF imaging condition, objective lens focus, and objective astigmatism prior to ion-irradiation. Images were then recorded on video tape during the ion-irradiation and later analyzed by overlaying a coordinate grid on the video monitor and examining each grid square in turn, marking the position of any defect which formed during the course of the ion-irradiation and those remaining upon completion of the ion-irradiation. The calibration of the horizontal and vertical length scales of the video images were estimated by comparing images of distinct thin-edge features recorded on both VCR tape at the magnification used during the ion-irradiation and TEM micrographs at 100 kx magnification.

The degree to which the lower resolution of VCR tape affected the identification of defects was evaluated at 23°C where the kinetics are slow enough to allow the comparison of the same post-irradiation microstructure recorded on both VCR tape and TEM micrographs. A comparison of

Figure 2: A comparison of the spatial resolution of the same post-irradiation defect microstructure (produced by 100 keV Kr ion-irradiations of Cu at 23°C) recorded on: a) VCR frame immediately following ion-irradiation and b) TEM micrograph. Images were formed under 2-beam DF using the (200) reflection.

these images (Fig. 2) shows that all the defects visible on the TEM micrograph are also visible on the VCR frame. However, it is evident that the closely spaced defects resulting from subcascades are not well resolved on the VCR frame. This is not an important concern for ion-irradiations performed at higher lattice temperatures where fewer subcascades are observed.

From the analysis of the VCR frames, both the post-irradiation and integrated defect yields were determined (Fig. 3 and Table I). The error estimations for the yields are based only on the combined effects of the uncertainty in the ion-fluence and area; they represent $\pm\sigma$ for the distribution of yields which are generated from all possible combinations of fluences and areas falling within their respective inclusive error ranges. The loss fraction incurred by the defect population during ion-irradiation is shown by the inset in Figure 3. Fewer defects survive during ion-irradiation as the temperature is increased. There are several mechanisms which could account for the loss of defects during ion-irradiation: isothermal anneal losses through thermally activated

Figure 3: Post-irradiation (squares) and integrated defect yields (circles) measured by analysis of VCR data for 100 keV Kr ion-irradiations of fcc-Cu between 23°C to 600°C. The curves through the data display trends and are not fitted to a model.

point-defect emission, ion-irradiation induced recombination of point-defects or thermal destabilization of clusters, destruction by cascade overlap, or an increased production of glissile perfect loops through either direct formation or ion-irradiation induced conversion of nascent sessile Frank loops into perfect loops which are then lost to the surface.

The maximum possible loss fraction (Table I) predicted by the isothermal anneal loss rates measured in [1] are deficient by upwards of an order of magnitude with respect to the loss fraction observed upon completion of the ion-irradiation. Furthermore, Table I demonstrates that the fraction of defects lost during ion-irradiation

Table I								
100 keV Kr Ion-Irradiations of fcc-Cu								
Ion-Irradiation Conditions				VCR Analysis				
Temp. (°C)	Fluence Φ ($\times 10^{10}$ Kr/cm ²)	Irradiation Time (s)	Ion- Incidence Angle ($\pm 15^\circ$)	Area Analyzed ($\times 10^{-10}$ cm ²)	Post-Irradiation Yield (Normalized to Fluence)	Integrated Yield (Normalized to Fluence)	Loss Fraction	Predicted Isothermal Anneal Loss
23	9.4 ± 1.1	11.8	78°	7.8 ± 2.1	1.11 ± 0.08	1.12 ± 0.09	0.089	0.000
300	9.6 ± 0.9	14.4	85°	17.1 ± 4.3	0.89 ± 0.07	0.94 ± 0.07	0.059	0.004
350	9.5 ± 1.0	7.6	82°	19.3 ± 6.4	0.69 ± 0.07	0.79 ± 0.08	0.125	0.003
450	9.5 ± 1.0	15.0	80°	52.1 ± 16.6	0.22 ± 0.02	0.39 ± 0.04	0.437	0.117
500	10.8 ± 0.8	26.0	87°	138.2 ± 36.6	0.030 ± 0.003	0.070 ± 0.006	0.574	0.048
600	14.1 ± 1.4	17.9	78°	202.7 ± 59.2	0.0056 ± 0.0004	0.018 ± 0.001	0.692	0.049

does not correlate with the ion-irradiation times, contrary to that anticipated for losses by isothermal anneal. Inspection of the VCR frames reveal that the majority of the defects which are lost during the ion-irradiation have very short life-times and are lost within only several VCR frames ($t < 0.25$ seconds) following formation.

In comparison, English *et al.* [6] calculated dislocation loop life-times as a function of isothermal anneal temperature and defect size to explain the temperature dependence of the yield in terms of losses from point-defect emission during ion-irradiation. Defect life-times on the order of seconds for all but possibly the smallest defects (diameter < 25 Å) were predicted. This is in excess of the observed life-times of the majority of defects lost during ion-irradiation, suggesting that the mechanism of their loss was not by simple evaporation through point-defect emission.

The short life-times of these defects further excludes their destruction by cascade overlap. The probability that a defect will be formed, directly engulfed and annihilated by a second subsequent cascade all within < 0.25 seconds is negligible for the low ion dose-rates used in these ion-irradiations. However, it is possible that the flux of energy deposited by nearby incident ions could thermally destabilize a defect quickly after its formation. The flux of point-defects generated

could also recombine with these defect clusters. Alternatively, these short life-time defects could be explained as near-surface glissile perfect loops which were lost to the surface through glide. In support of this interpretation, a small fraction of defects observed on the VCR recordings were identified as glissile loops, exhibiting motion that oscillated between two fixed points before eventually disappearing from the foil. Perhaps these defects were not immediately lost after formation because they were pinned between obstructions in their glide cylinders.

Figure 4: A comparison of the post-irradiation yields measured from extrapolations of isothermal anneal (circles) and analysis of VCR data (squares). The curve through the data displays a trend and is not fitted to a model.

Figure 3 and Table I demonstrate that defect losses through the course of the ion-irradiation are insufficient to account for the observed variation in post-irradiation yield,

the mechanism English *et al.* [6] attribute to an apparent yield decline. Defect loss during ion-irradiation is likely attributed to surface effects. Long-range strain fields are dissipated at the free surface and this establishes a decreasing gradient in the total energy of lattice displacements around dislocation cores with decreasing core distance from the surface. The forces derived from these gradients can attract glissile dislocation loops whose glide cylinders intercept the surface. The free surface is an efficient sink for mobile interstitials and glissile dislocation loops which are annihilated upon reaching the surface. The variation in the observed loss fraction with temperature may indicate a redistribution of defect types toward greater numbers of perfect loops. However, other mechanisms of defect loss such as irradiation-induced destabilization of defect clusters resulting from energy deposition or impinging point defect fluxes cannot be ruled out.

From Figure 3 it is clear that the integrated and post-irradiation yields depend upon the lattice temperature during ion-irradiation. Furthermore, as evident in Figure 4, the agreement between the post-irradiation yields estimated using two very different methods of extrapolation of isothermal anneal data [1] and direct measurement of VCR recorded images instills confidence in their determination.

CONCLUSIONS

Both the post-irradiation and integrated defect yields were determined by direct observation through analysis of video recordings of TEM 2-beam DF images. Post-irradiation yields measured using this technique are in close agreement with values previously determined from extrapolations of isothermal anneal loss data. The defect loss fraction incurred during ion-irradiation increases with increasing temperature, suggesting a redistribution of the defect types produced. However, defect losses through the course of the ion-irradiation are insufficient to account for the observed variation in yields. Areal defect yields are unequivocally demonstrated to decrease with increasing lattice temperature in fcc-Cu. This variation with temperature can be plausibly correlated to a lattice temperature dependence for the probability of point defect collapse into defect clusters.

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REFERENCES

1. T. L. Daulton, M. A. Kirk, and L. E. Rehn, *Mat. Res. Soc. Symp. Proc.*, **439**, 313-318 (1996).
2. N. Sekimura, Y. Yamanaka, S. Ishino, 14th International Symposium on Effects of Radiation on Materials, ASTM STP 1046, **1**, 596-608 (1990).
3. S. Ishino, N. Sekimura, K. Hirooka, and T. Muroga, *J. Nucl. Mater.*, **141-143**, 776-780 (1986).
4. C. W. Allen, L. L. Funk, and E. A. Ryan, *Mat. Res. Soc. Symp. Proc.*, **396**, 641-646 (1996).
5. J. S. Vetrano, I. M. Robertson, and M. A. Kirk, *Scripta Met.*, **24**, 157-162 (1990).
6. C. A. English, B. L. Eyre, and J. Summers, *Phil. Mag.*, **34**, 603-614 (1976).