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RADIATION-INDUCED DEFECTS IN COPPER
AT ELEVATED TEMPERATURES***

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TRANSMISSION ELECTRON MICROSCOPY STUDY IN-SITU OF RADIATION-INDUCED DEFECTS IN COPPER AT ELEVATED TEMPERATURES

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ABSTRACT

Neutrons and high-energy ions incident upon a solid can initiate a displacement collision cascade of lattice atoms resulting in localized regions within the solid containing a high concentration of interstitial and vacancy point defects. These point defects can collapse into various types of dislocation loops and stacking fault tetrahedra (SFT) large enough that their lattice strain fields are visible under diffraction-contrast imaging using a Transmission Electron Microscope (TEM). The basic mechanisms driving the collapse of point defects produced in collision cascades is investigated *in situ* with TEM for fcc-Cu irradiated with heavy (100 keV Kr) ions at elevated temperature. The isothermal stability of these clusters is also examined *in situ*.

Areal defect yields were observed to decrease abruptly for temperatures greater than 300°C. This decrease in defect yield is attributed to a proportional decrease in the probability of collapse of point defects into clusters. The evolution of the defect density under isothermal conditions appears to be influenced by three different rate processes active in the decline of the total defect density. These rate constants can be attributed to differences in the stability of various types of defect clusters and to different loss mechanisms. Based upon observed stabilities, estimations for the average binding enthalpies of vacancies to SFT are calculated for copper.

INTRODUCTION

Microstructures can greatly influence the physical properties of materials. Of particular interest is the effect of irradiation on the microstructures of materials subjected to environments containing high fluxes of energetic particles, such as nuclear reactors or space environments. It is important to understand the basic mechanisms of defect formation and the kinetics governing their behavior and interaction. Kinetics are strongly driven by temperature. In studying the formation of radiation-induced defects at elevated temperature and their isothermal stability, valuable insights into these mechanisms can be deduced. Many of the previous investigations at elevated temperature have been performed *ex situ*, leaving many ambiguous details. Here we discuss some of the preliminary results of our *in situ* TEM observations at elevated temperature, which may shed light into many of these processes.

EXPERIMENT

TEM samples were prepared from copper sheets of 99.99% nominal purity cut into 3 mm diameter disks. These disks were sealed in quartz tubes, evacuated to 2×10^{-6} torr, then backfilled with high purity argon, and annealed for 2 hours at 820°C. Annealed disks were single-jet electropolished 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 vacuum 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 in these experiments to produce 100 keV Kr ion beams with typical dose rates ranging between $(0.5 - 3.8) \times 10^{10}$ ions-cm⁻²-s⁻¹ with an error in the time integrated dosimetry measurements of $\pm 6 \times 10^9$ ions-cm⁻². The *in situ* ion-irradiations

Figure 1: Inverted contrast DF micrographs [using the $g = (200)$ reflection], recorded within several minutes after the ion-irradiation of Cu by 100 keV Kr ions at ambient and elevated temperatures, display the representative defect microstructure. These micrographs were recorded at 6.7 mins (300°C), 2.3 mins (350°C), 0.9 mins (400°C), and 2.0 mins (450°C) following the completion of the ion-irradiation. The ion-irradiation conditions are listed in the table found in Fig. 3.

were conducted in the TEM with the ion-beam incident normal to the foil's surface.

The microscope was equipped with a Gatan model 622SC image intensified video rate camera and a Gatan model 652 double-tilt, side-entry, elevated temperature goniometer stage. 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. A VCR was connected to the fiber-optic coupled camera enabling the recording of images during ion-irradiation and TEM micrographs were recorded at 100 kx magnifications using 2 second exposures. Further details describing the H-9000NAR TEM / accelerator arrangement are given by Allen [1].

RESULTS

Collision cascade collapsed defects were imaged under strong 2-beam dynamical ($s_g \approx 0$) dark-field (DF) conditions using the $g = (200)$ reflection at an orientation along the (200) Kikuchi band typically 15° from the [110] zone axis. Representative defect microstructures present shortly after elevated temperature ion-irradiations are shown in Fig. 1; a marked decrease in defect density is apparent as the ion-irradiation is performed at progressively higher temperatures. However, accurate measurements of the defect yield at elevated temperature are difficult to obtain. A significant number of defects can be lost during the isothermal anneal following the ion-irradiation, an effect that is generally neglected. Furthermore, during ion-irradiation increased defect loss rates have been observed over those rates measured under similar conditions without ion-irradiation [2, 3]; the increase in loss rates scales with ion-fluence. During the ion-irradiation, a number of defect clusters are annihilated by subsequent cascade events, e.g. Cu [4], Ni [5] and Ni-1% Si [6]. Further, ion-irradiation enhanced vacancy/interstitial evaporation rates are possible.

The only experimental technique which can investigate these effects is *in-situ* ion-irradiation. The rates at which defects vanish during isothermal anneal can be evaluated by performing isothermal defect density measurements as a function time following the ion-irradiation. The defect density present immediately after ion-irradiation can be extrapolated from this data, providing an effective defect yield. Defect loss during ion-irradiation can be evaluated by analyzing defect images recorded on video tape while the sample was irradiated.

We first examine the phenomenon of defect loss during isothermal annealing. Defect densities

were measured from micrographs recorded at predetermined time intervals during the isothermal anneal following the elevated temperature ion-irradiation. The same area of the specimen was imaged during the anneal. In the determination of the area of the foil surface analyzed, the tilt of the specimen was taken into account; the areas examined were typically $8 \times 10^{-9} \text{ cm}^2$. When time

Figure 2: Isothermal defect densities produced by elevated temperature 100 keV ion-irradiations were measured *in-situ* as a function of the time elapsed from the completion of the ion-irradiation. The curves represent least squares fits of Eq. (1) to the data.

Figure 3: Effective defect yield (or production efficiency) for ion-irradiations at ambient and elevated temperatures. The triangular data point represents a correction for the higher fluence (see text). The error bars reflect only the error in the dosimetry and the exponential fits. The curve through the data display trends and is not fitted to a function. The inset table lists the irradiation conditions for each experiment.

decay components could be active. Evidence of at least two different decay components have been observed in previous annealing experiments [3, 8]. It is not surprising that several different rate constants are observed. This is a consequence of the presence of several different defect loss

constraints allowed three images at slightly different s_g values were recorded for each time interval. Slight variations in s_g are known to affect the number of defects that have visible contrast [7]; local bending of the foil amplifies this problem. One micrograph was selected from each time interval, then digitized by a high-resolution LeafScan-45 negative scanner.

Overlay maps were combined with these image files to catalog the defect positions. In instances where regions exhibited poor contrast, additional micrographs from that interval were then examined. Maps from micrographs recorded at time t_{i+1} were superimposed onto micrographs recorded at time t_i . Coincidence between all the marked defect positions from t_{i+1} and the defects in micrograph t_i were confirmed. The remainder represented defects which were lost between t_{i+1} and t_i . In this manner, the evolution of each defect within the region analyzed was tracked during the course of the anneal.

Results from these isothermal areal density measurements are shown in Fig. 2. The data was least squares fit to a sum of exponential decay terms given by

$$\delta(t) = \sum_{i=1}^n \alpha_i \exp(-\beta_i t) \quad (1).$$

Optimum fits were attained with $n = 3$ for all except the 300°C data (which fit best to $n = 2$). Significant deviations between the fitted curve and the trends in the data were evident when fewer exponential terms were used, suggesting that upwards of three different

mechanisms. For example, Frank loops can convert to perfect loops which are glissile and glide to the surface. Frank loops can also evaporate by emission of point defects, as can the relatively more stable SFT. Furthermore, there might be differences between the evaporation (or transformation) rates for similar type defects that are vacancy or interstitial in nature.

The effective defect yield (or production efficiency) at elevated temperature can be defined as the areal defect density present immediately after ion-irradiation, normalized by the incident ion-fluence. Effective defect yields were estimated by extrapolating the fitted defect densities $\delta(t)$ back to $t = 0$, eliminating the influence of isothermal anneal losses (Fig. 3). It is interesting to compare these results to the *ex situ* elevated temperature defect yields measured by English, Eyre, and Summers [9]. In that work, substantially larger differences between defect yields produced by 30 keV Cu ions within the same temperature range were observed. This can be attributed, to a large part, to isothermal anneal losses incurred as their samples cooled following the ion-irradiation; defect losses that this present work demonstrates are significant. Our results provide an accurate measurement of the true effective defect yield corrected for isothermal anneal losses. However, before this new data can be interpreted, defect losses during ion-irradiation need to be considered.

In two of the elevated temperature ion-irradiations performed, it was possible to determine orientations in which the 2-beam TEM DF $g = (200)$ imaging condition was coincident with the direction necessary for normal incidence of the ion-beam onto the surface of the specimen. This allowed *in situ* observation and video recording of the defect production and loss during these ion-irradiations. The specimen surface area imaged by the camera was typically $0.8 \times 10^{-9} \text{ cm}^2$. Analysis of this video indicated that the fraction of total defects formed which were lost during the duration of the ion-irradiation was ≈ 0.13 (at 375°C) and ≈ 0.28 (at 400°C). In both ion-irradiations the same ion-fluence Φ was achieved. However, the effective defect yields for 375°C (0.54Φ) and 400°C (0.50Φ) are similar despite the factor of 2 difference in estimated defect loss fractions during irradiation. This discrepancy is likely attributed to measurement error because of the inherent difficulties involved with this type of video experiment.

This further suggests that the contribution to defect loss during ion-irradiation from isothermal annealing is not a significant component, otherwise a noticeable difference in effective defect yield for 375°C and 400°C would result from the factor of over 3 difference in ion-irradiation times. The destruction of collapsed defect clusters by subsequent cascade events during ion-irradiation cannot account for the entire loss fraction; the probability of cascade overlap at this ion-fluence is $\approx 7\%$ (assuming a 10 nm radius damage region). Additional loss mechanisms must be active. The energy deposited by incident ions may create localized hot regions which thermally destabilize the defect clusters. Mobile point defects which impinge onto existing defect clusters can further destabilize their structure, either destroying them by recombination or transforming them to perfect dislocation loops which are glissile and lost to the surface.

The rate of destruction of collapsed defect clusters by subsequent cascade events during ion-irradiation is to first approximation largely independent of the temperature, and dependent only upon the ion-fluence. The number of hot regions created by incident ions is dependent only upon ion-fluence, however their lifetimes depend on thermal conductivity and the surrounding lattice temperature. The diffusion rate of point defects is temperature dependent. However, since the irradiation time is far greater than the lifetime of these point defects, the rate of defect loss caused by the interaction of mobile point defects with existing defect clusters would be largely independent of the temperature as well. To first approximation, the fraction of defects lost during our short ($< 20 \text{ s}$) (100 keV Kr) ion-irradiations should be similar for similar ion-fluences.

The ion-irradiation performed at 450°C used a 1.6x higher ion-fluence than the other irradiations. The higher fluence was chosen to increase counting statistics in response to the low anticipated defect yield. Defect loss during irradiation by the discussed mechanisms should increase slowly with small integrated ion-fluences and then approach asymptotically a saturation limit at high ion-fluences. There should be a regime in which the loss rate's dependence on ion-fluence is linear. Assuming that the low fluences used in these experiments fall within this linear

Figure 4: The decomposition of the evolution of SFT and non-SFT populations during isothermal anneal. The curves through the non-SFT and SFT data display trends and are not fitted functions. The other temperatures exhibit similar trends.

Figure 5: Arrhenius plot for the rate constants β_1 estimated from least squares fit of the isothermal anneal data.

regime, a reduction in effective yield by a factor of 0.76 should result from the 1.6 factor increase in fluence. The triangular data point in Fig. 3 represents the correction for the higher ion-fluence.

The estimated loss rate during irradiation is insufficient to account for the differences in effective yields between the ambient temperature and the elevated temperature ion-irradiations (Fig. 3); the mechanism English et al. [9] attribute to the yield decline. Therefore, the differences in effective yields can be plausibly attributed to a temperature dependence for the probability of point defect collapse into defect clusters.

Let us return to the observation that three defect loss components were suggested by the exponential fit to the isothermal data. These rate constants presumably are related to the average loss rates for either different populations of defect types or different loss mechanisms. In attempts to identify the processes related to these rate constants, the isothermal evolution of SFT and non-SFT populations were examined (Fig 4).

The total defect population is initially dominated by non-SFT. Their numbers decline by transformation into SFT, evaporation by point defect emission, and possibly conversion to perfect loops which glide to the surface. After long anneal times, SFT eventually dominate the total defect population. The loss rate for the total

population which is dominant in this regime can be used to estimate the SFT loss rate. However, the dissociation of Frank loops into SFT will skew the measured SFT loss rates to artificially lower values. Numerical methods to separate these effects are currently being developed. However, extension of the isothermal anneal to sufficiently long times will substantially decrease the proportion of non-SFT in the total population, improving this approximation.

Activation enthalpies for rate processes usually satisfy an Arrhenius temperature expression,

$$\beta = A \exp(-Q/kT) \quad (2),$$

where A is known as the pre-exponential factor and Q represents an activation enthalpy or barrier to the process. In the case of vacancy evaporation from a defect cluster, Q can be interpreted as the vacancy binding enthalpy. An Arrhenius plot of the rate constants extracted from the fits to the isothermal anneal data (Fig. 2) is shown in Fig. 5; they differ by at least an order of magnitude. The smallest rate, β_3 , represents the most stable defect component, the SFT. The average vacancy binding enthalpy for SFT in Cu is estimated to be $Q = 0.7 \pm 0.2$ eV from a least squares fit to the estimated SFT rate loss data. Whether the other two rate processes are related to vacancy and interstitial loop evaporation, to loop transformation into perfect loops which are lost to the surface, or to recombination, remain open questions and are being investigated further.

CONCLUSIONS

The influence of isothermal annealing on the defect density produced at elevated temperatures was evaluated. For the first time, accurate estimations of the defect yield present immediately after elevated temperature ion-irradiation were obtained by the method of extrapolation which eliminated the affect of isothermal anneal. The influence of possible defect loss mechanisms occurring during ion-irradiation on defect yield were also evaluated. Observations suggest that isothermal annealing during the short (average 9.7 s ion-irradiations) did not contribute significantly to defect loss. Defect loss from cascade overlap, destabilization of defect clusters by energy deposition and impinging point defects are the most probable loss mechanisms. Since these loss mechanisms, to first approximation, are temperature independent, the observed difference in defect yield can be plausibly attributed to a temperature dependence for the probability of point defect collapse into defect clusters. The binding enthalpy of vacancies to SFT in Cu is estimated to be 0.7 ± 0.2 eV based on measurements of their isothermal stability.

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