THE NATURE OF DEFECT CLUSTERS IN ELECTRON-IRRADIATED COPPER*

S. M. Ohr
Solid State Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

ABSTRACT

An electron microscope study has been made of the clustering of point defects in electron-irradiated copper in the range of temperatures between Stage III and Stage V. The samples used were single crystals of copper irradiated at 4°K with 3 Mev electrons to a dose of 1.4×10^{19} electrons/cm^2. In all of the samples examined the defect clusters were in the form of dislocation loops, mostly less than 100 A in diameter. In samples warmed to room temperature, i.e. slightly above Stage III, the analysis of black-white contrast showed that the loops present were entirely of the interstitial type. In samples annealed at 90°C and 150°C, the defects were predominantly loops of interstitial type, but approximately 10% of the loops were of vacancy type. At 250°C, the fraction of the loops of vacancy type increased to about 40% but the total loop density decreased markedly. The evidence seems to indicate that in Stage III vacancies do not cluster into sizes large enough to be visible in the electron microscope.

The interpretation of Stage III recovery of irradiated metals has been a subject of controversy for a number of years.[1-3] At present, there are two contending models for fcc metals which have been known as the 1-interstitial model and the 2-interstitial model. The most prominent disagreement between the two models is that the 1-interstitial model assigns the migration of single vacancies to Stage III while the 2-interstitial model assigns the motion of free interstitials to the stage. Since the migrating species is expected to form clusters of its own, in addition to being annihilated by recombination, an insight to the problem can be obtained if the vacancy-interstitial nature of defect clusters formed during Stage III can be determined. As a joint program between Jülich, Stuttgart, and Oak Ridge, an electron microscope study was made of the nature of defect

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clusters in copper which had been electron-irradiated and annealed in the range of temperatures between Stage III and Stage V. This paper is a brief summary of the results obtained from this investigation.

EXPERIMENTAL

The sample materials used were (110) single crystals of high purity copper supplied by F. W. Young, Jr. of Oak Ridge National Laboratory. The crystals were chemically thinned to about 0.2 mm in thickness and disks of about 3 mm in diameter were punched out. The disks were annealed at 630°C for 2 hours in a vacuum of 2×10^{-6} Torr. Electron irradiation was carried out at the 3 Mev Van de Graaff facility of Kernforschungsanlage, Jülich at an irradiation temperature of 4°K. The electron dose was 1.4×10^{19} electrons/cm^2 which resulted in an electrical resistivity increase of $1.3 \times 10^{-7}\Omega$-cm. Assuming a specific resistivity of $2 \times 10^{-6}\Omega$-cm/at% for Frenkel pairs, the increase corresponded to a Frenkel pair density of about 650 ppm. The samples were kept in a liquid nitrogen dewar prior to the high temperature annealing treatments. The resistivity data indicated that about 75% of the damage generated had annealed out during Stage I.

The samples were annealed for 30 minutes at a series of temperatures starting just above Stage III, i.e. 23°, 90°, 150° and 250°C. The latter two temperatures correspond approximately to Stages IV and V. The annealing was not accumulative in that separate samples were used for each annealing temperature. Thin foils suitable for electron microscope observation were then prepared in two steps. The first polish was carried out in a mixture of orthophosphoric acid and ethanol at room temperature and the final polish in a solution of nitric acid and methanol at -60°C. Small gold islands were vacuum deposited on the bottom surface of the foil in order to facilitate the depth measurement of the defect clusters. The microscope observations was performed in a Siemens Elmiskop 102 operated at 125 KV.

RESULTS AND DISCUSSION

Figure 1 shows the electron micrographs taken from samples annealed at each of the temperatures indicated. The damage clusters appear as black spots under the kinematical diffraction condition. Some of the spots exhibit black-white contrast under the dynamical diffraction condition. From the directions of the black-white contrast, most of the defects were identified as dislocation loops with Burgers vectors $\frac{a}{3}<111>$. The size distribution curves plotted in Fig. 2 show peaks in the distribution at approximately 35 A for annealing up to 150°C. An increase in the density of the larger loop sizes occurs with increasing annealing temperature with the large diameter tail extending to large loop sizes at the highest temperature (250°C). These results suggest that up to 150°C the smaller loops may be coalescing to form larger loops. At 250°C, only about 10% of the loops remain and their average size has increased by a factor of two. These results are summarized in Table 1. In this table, $C(T_a)$ is the density of point defects estimated from the total area of the loops and hence it is proportional to the second moment of the size-distribution curve. It remains essentially constant up to 150°C and decreases by a factor of two at 250°C.

The vacancy-interstitial nature of the loops was determined by the method of Rühle and Wilkens.[4] The method makes use of the fact that small loops close to the foil surfaces exhibit black-white contrast under the dynamical diffraction condition and the sense of the black-white streaking is determined by the vacancy-interstitial nature as well as their depth in the foil. The depth of the loops was measured by the stereoscopic technique with the gold islands serving as surface markers. The nature of the large loops was determined by the method of inside-outside contrast.[5] The results of the analysis are summarized in Table II. It shows that at 23°C, i.e. after Stage III annealing, there is no evidence for the clustering of vacancies. At the annealing temperatures of 90° and 150°C, approximately 10% of the loops analyzed are of the vacancy type. The fraction of the vacancy loops increases to nearly 40% at 250°C. However, the number of vacancies present in these loops (C_v) is only slightly higher than that observed at lower temperatures because the total loop density has decreased drastically.

It is somewhat surprising that in samples annealed through Stage III no loops of vacancy type are found. This may be taken as evidence that vacancies do not migrate in Stage III. It is also possible that the vacancies do migrate and cluster during Stage III but the clusters are too small to be visible in the electron microscope. Since the size of the smallest loops analyzed is about 15 A in diameter, it indicates that the vacancy clusters containing more than about 35 vacancies in collapsed loops are not present after the room temperature anneal. Another possibility is that in copper the vacancy clusters prefer to be in the form of either loose three-dimensional clusters or stacking-fault tetrahedra. These clusters have relatively weak strain fields and consequently are more difficult to observe in the electron microscope.

The number of Frenkel pairs estimated from the loop size-distribution curves agrees quite well with the resistivity data throughout the range of annealing temperatures studied in the present work. The appearance of vacancy loops at the annealing temperature of 90°C and above indicates that vanancy migration has occurred between room temperature and 90°C. It is not clear as to whether the vacancies are moving for the first time at these temperatures or these vacancies are emitted from clusters already formed at lower temperatures.

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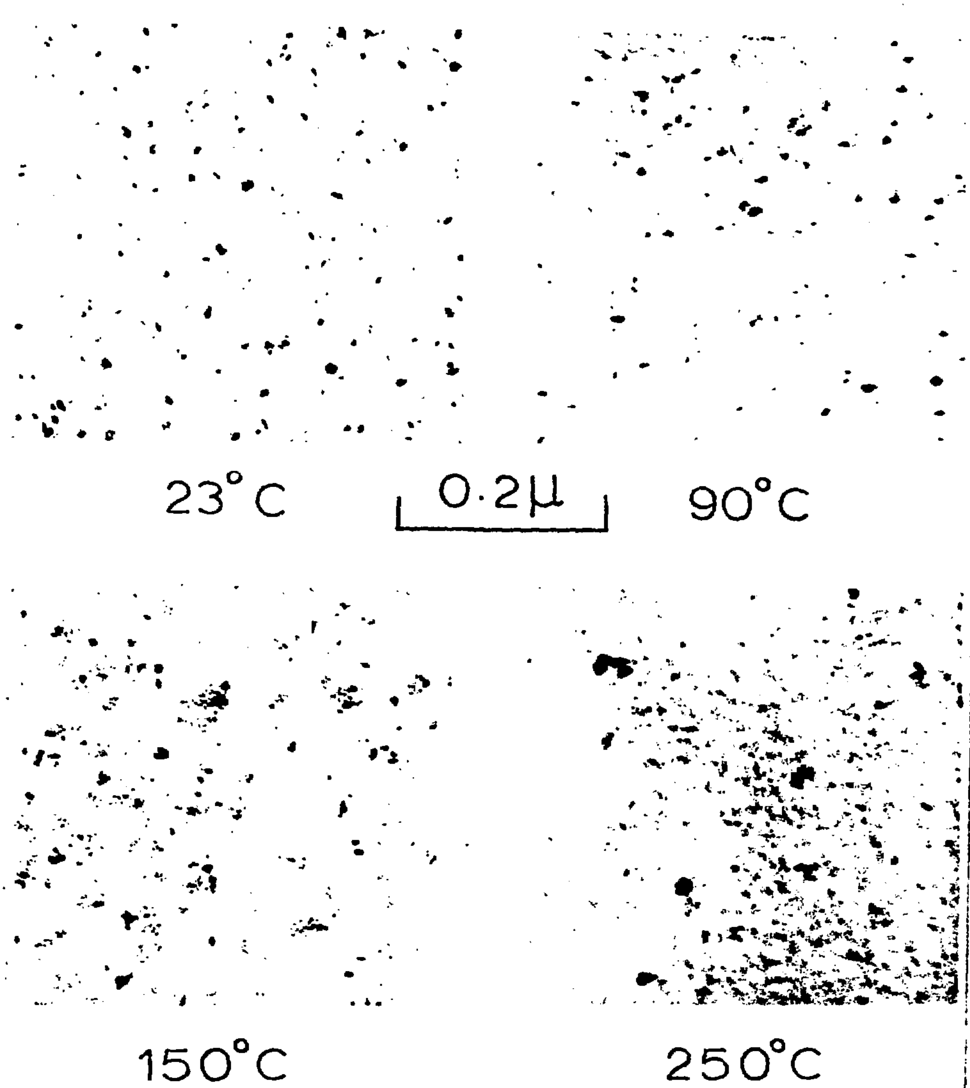

Figure 1. Electron micrographs showing the black spot damage observed in copper samples electron-irradiated and annealed for 30 minutes at each of the temperatures indicated.

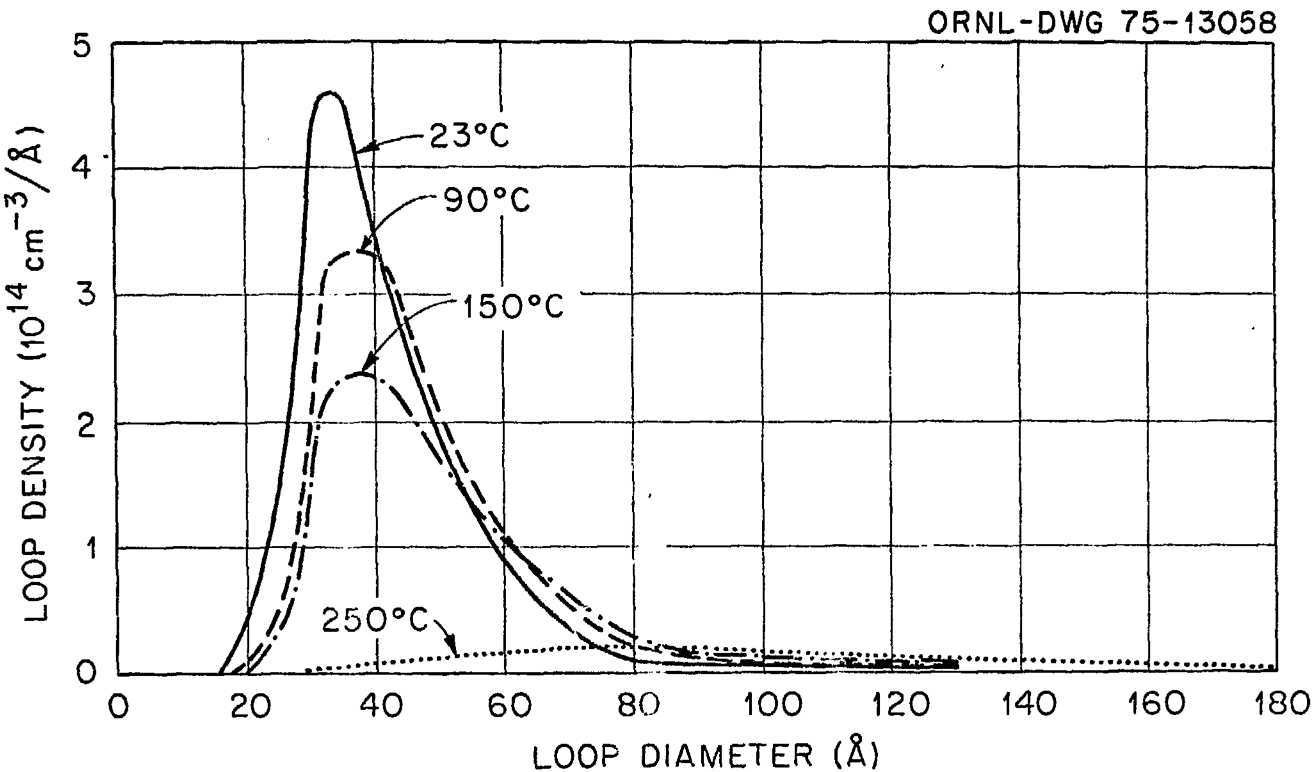

Figure 2. Size distribution curves for electron-irradiated and annealed copper.

Table I. LOOP DENSITY

T_a(°C)	n_{loop}(cm^{-3})	d(A)	$C(T_a)$ (cm^{-3})
23	11.5×10^{15}	41	3.3×10^{18}
90	9.4	46	3.3
150	7.6	48	2.9
250	1.2	95	1.9

Table II. LOOP ANALYSIS

T_a(°C)	n_v/n_{loop}	C_v(cm^{-3})
23	<5%	$<2 \times 10^{17}$
90	12	3.7
150	11	2.9
250	37	3.9