Conf-750982--1

By acceptance of this article, the publisher or recipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering the article.

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

EFFECTS OF PRECIPITATION ON ELECTRON DISPLACEMENT DAMAGE IN FCC ALLOYS: COPPER ALLOYS WITH RANDOM AND MODULATED MICROSTRUCTURES *

R. W. Carpenter

Metals and Ceramics Division, Oak Ridge National Laboratory
P. O. Box X, Oak Ridge, TN 37830, USA

HVEM experiments by many investigators have shown that when single phase fcc metals are irradiated between ~.3 to .5 T_m the point defects created generally lead to formation of interstitial loops, which ultimately coalesce into a dislocation network upon further irradiation. Voids may be nucleated at higher fluences if the dislocation network is sufficiently stable and dense in the foil.[1] The experiments described here were performed to qualitatively evaluate the effect of two morphologically different precipitation processes upon the electron displacement damage process. The alloys used were Cu-2 wt.% Co and Cu-4 wt.% Ti. The precipitation behavior of Cu-Co alloys is well-known;[2] upon isothermal aging at an appropriate temperature the Co atoms cluster to form essentially spherical coherent zones and then coarsen at longer aging times. Ultimately coherency is lost, when the zone size is sufficient. The zones in Cu-Co alloys are random in spatial arrangement and the strain field associated with them is of the vacancy type.[3] Several recent investigations have shown that Cu-Ti alloys undergo a phase separation when specimens quenched from the single phase region are isothermally aged in the range 375 to 500°C.[4,5] The modulated structure formed is continuous throughout the crystal volume and is thought to result from spinodal decomposition. If aging takes place at higher temperatures the equilibrium precipitate forms by a cellular precipitation reaction. The present work reports mainly observations on the electron displacement damage behavior of spatially random precipitate in Cu-Co alloys and the modulated structure in Cu-Ti alloys. A few observations of the damage structures in cellularly decomposed Cu-Ti were also made.

Experimental Methods.

The alloys were melted from Cu, Co, and Ti stock in nonconsumable electrode arc furnaces under a partial argon pressure on cold Cu hearths; after melting they were drop cast into cold copper molds. The castings were swaged to 3 mm rod and then homogenized for 1 hr at 900°C and drop quenched into ice water. For all heat treatments, cleaned sections of the swaged rod were wrapped in Ta foil and sealed in quartz or pyrex capsules backfilled with argon. All heat treatments were terminated by an ice water quench, with the glass tube broken under water. Transmission electron microscope specimens were made from 3 mm discs sliced from the heat treated swaged rod, and then thinned in a Fischone apparatus. The electrolyte used was essentially one-third HNO_3 and two-thirds methyl alcohol. Several polishing temperatures were used. In particular several Cu specimens (>99.9999 Cu) were thinned at −50°C, and voids were observed to form under the irradiation conditions used (noted below). The alloy specimens were thinned at temperatures between −20 and −50°C. Low temperatures were used to minimize the apparent effect of hydrogen pickup during thinning, noted earlier in certain nickel alloys.[6]

All specimens were irradiated at an indicated temperature of 250°C using a tilt-rotation hot stage in an HU-650 modified to operature at 1 MeV. Actual specimen temperature is estimated to be 300 ± 20°C due to beam heating.[7] Irradiation beam current was measured with a Faraday cup located below the specimen viewing chamber. Typical flux values used were 5×10^{19} to 1×10^{20} elec/cm^2·sec. These were converted to dpa values using cross-sections determined from other research on Cu: 54 barns for orientations near (011) and 38 barns for all other orientations.[8]

Experimental Observations and Discussion.

HVEM experiments by many investigators have shown that when single phase fcc metals are irradiated between ~.3 to .5 T_m the point defects created generally lead to formation of interstitial loops, which ultimately coalesce into a dislocation network upon further irradiation. Voids may be nucleated at higher fluences if the dislocation network is sufficiently stable and dense in the foil.[1] The experiments described here were performed to qualitatively evaluate the effect of two morphologically different precipitation processes upon the electron displacement damage process. The alloys used were Cu-2 wt.% Co and Cu-4 wt.% Ti. The precipitation behavior of Cu-Co alloys is well-known;[2] upon isothermal aging at an appropriate temperature the Co atoms cluster to form essentially spherical coherent zones and then coarsen at longer aging times. Ultimately coherency is lost, when the zone size is sufficient. The zones in Cu-Co alloys are random in spatial arrangement and the strain field associated with them is of the vacancy type.[3] Several recent investigations have shown that Cu-Ti alloys undergo a phase separation when specimens quenched from the single phase region are isothermally aged in the range 375 to 500°C.[4,5] The modulated structure formed is continuous throughout the crystal volume and is thought to result from spinodal decomposition. If aging takes place at higher temperatures the equilibrium precipitate forms by a cellular precipitation reaction. The present work reports mainly observations on the electron displacement damage behavior of spatially random precipitate in Cu-Co alloys and the modulated structure in Cu-Ti alloys. A few observations of the damage structures in cellularly decomposed Cu-Ti were also made.

Experimental Methods.

The alloys were melted from Cu, Co, and Ti stock in nonconsumable electrode arc furnaces under a partial argon pressure on cold Cu hearths; after melting they were drop cast into cold copper molds. The castings were swaged to 3 mm rod and then homogenized for 1 hr at 900°C and drop quenched into ice water. For all heat treatments, cleaned sections of the swaged rod were wrapped in Ta foil and sealed in quartz or pyrex capsules backfilled with argon. All heat treatments were terminated by an ice water quench, with the glass tube broken under water. Transmission electron microscope specimens were made from 3 mm discs sliced from the heat treated swaged rod, and then thinned in a Fischone apparatus. The electrolyte used was essentially one-third HNO_3 and two-thirds methyl alcohol. Several polishing temperatures were used. In particular several Cu specimens (>99.9999 Cu) were thinned at −50°C, and voids were observed to form under the irradiation conditions used (noted below). The alloy specimens were thinned at temperatures between −20 and −50°C. Low temperatures were used to minimize the apparent effect of hydrogen pickup during thinning, noted earlier in certain nickel alloys.[6]

All specimens were irradiated at an indicated temperature of 250°C using a tilt-rotation hot stage in an HU-650 modified to operature at 1 MeV. Actual specimen temperature is estimated to be 300 ± 20°C due to beam heating.[7] Irradiation beam current was measured with a Faraday cup located below the specimen viewing chamber. Typical flux values used were 5×10^{19} to 1×10^{20} elec/cm^2·sec. These were converted to dpa values using cross-sections determined from other research on Cu: 54 barns for orientations near (011) and 38 barns for all other orientations.[8]

Experimental Observations and Discussion.

The experimentally observed damage behavior falls naturally into three groups:

1. Cu-Co containing no visible zones or initially coherent zones differed little in its behavior under irradiation from elemental Cu. A typical example of sequential behavior is shown in Fig. 1. Initially faulted loops are nucleated, followed by

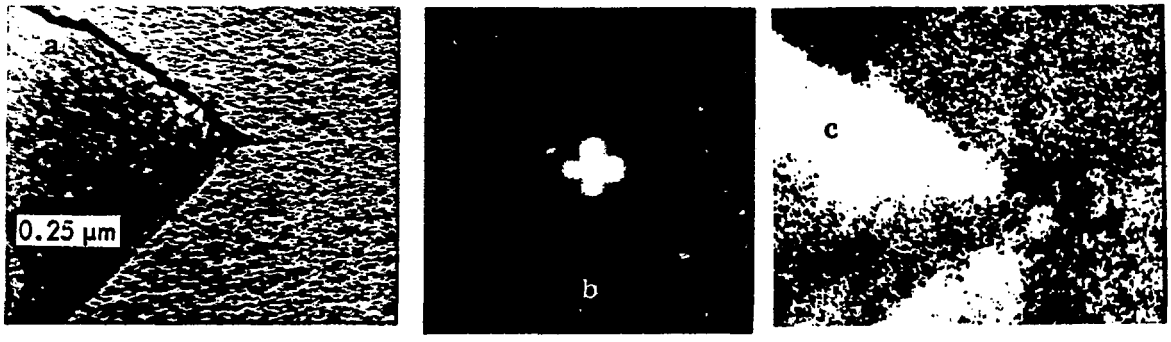
*Research sponsored by the U. S. Energy Research and Development Administration under contract with Union Carbide Corporation.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

to be lower than shown in Fig. 1, but the fluence is markedly higher. Apparently void nucleation is more difficult when incoherent precipitate and associated dislocations are present, for the same reason that numerous small loops were not observed at low fluence in this specimen.

3. Cu-Ti alloys containing the modulated structure formed on quenching from the homogenization temperature, or the same structure coarsened by relatively low temperature aging did not form visible voids at any fluence up to the maximum reached during the experiments. An example of the initial structure and the observed changes after irradiation in a specimen aged 5 min at 410°C prior to HVEM irradiation is shown in Fig. 3. This particular specimen was irradiated in a thinner than usual area in an attempt to resolve individual irradiation caused defects. The attempt was not successful. It was possible to determine that the modulated structure still exists, as shown in Fig. 3c, but it may no longer be coherent. An interesting feature of these alloys (in the modulated condition) is the almost total absence of observable dislocation motion during HVEM irradiation. Thicker specimens (~0.5 μm thick) were also examined in the HVEM, and no evidence for voids was found using conventional imaging techniques.



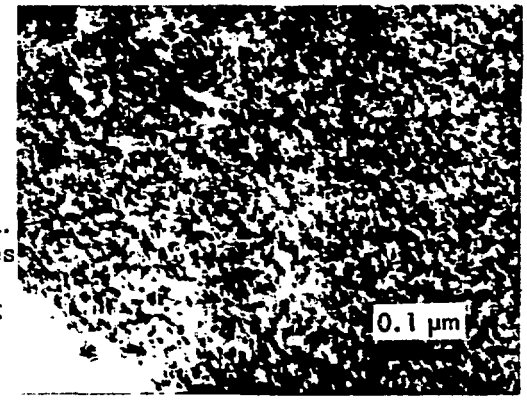


Fig. 3. Cu-4 Ti homogenized and aged 5 min at 410°C. Structure and effect of 1 MeV HVEM irradiation. Vertical edges of pictures along [020]; (001) foil plane. (a) initial modulated structure at 120 KeV. Thickness = 1050Å determined from {111} twin. g = (020); (b) Matrix (020) Bragg spot with satellites for unirradiated foil. Foil tilted to symetrical orientation. Satellites in [200] from multiple diffraction. Modulation wavelength ~55Å; (c) Same specimen as (a) during irradiation. After 122 min, 36 dpa; (d) High magnification of (c). No voids were observed.

The equilibrium precipitation product of the aging reaction in Cu-4 Ti is an ordered phase; the composition of the phase is the subject of some discussion. It is either Cu_3Ti or Cu_7Ti_2.[9] When aging occurs at a higher temperature, such as 600°C, the equilibrium phase forms by a cellular reaction often nucleated at the grain boundaries. An example of the microstructure is shown in Fig. 4a. The dark narrow plates are the ordered phase, and the lighter regions are the solid solution matrix. The effect of 1 MeV HVEM irradiation on this structure is shown in Fig. 4b. A very high density of defects, probably small loops, was formed. They are most easily seen in the matrix regions. Dislocation mobility in this microstructure is also lower than observed in Cu or Cu-2 Co alloys aged at low temperature before HVEM irradiation. The interfaces between the ordered and matrix phases are incoherent in this microstructure, and may be efficient sinks for point defects. The large interfacial surface area per unit volume would be expected to cause surpression of the point defect concentration and hinder void nucleation. The solubility of Ti in Cu at 600°C is 0.8 w/o; it decreases to ~0.2 w/o at 300°C.[9] It is possible that a modulated structure similar to that shown in Fig. 3 formed in the matrix of the microstructure shown in Fig. 4 during HVEM irradiation, as a result of the Ti solubility temperature dependence. If this occurred one would expect further surpression of void nucleation by the same mechanism operating in the microstructure shown in Fig. 3.

coalesence into a dislocation network and the nucleation and growth of voids. These stages are not mutually exclusive; some rather large faulted loops were observed well into the void nucleation stage. All specimens in this group exhibited high loop and dislocation mobility during irradiation, even those with initially coherent precipitate up to ~140Å in size (aged 10 hrs at 600°C prior to irradiation). Few precipitates appeared to be preferential nuclei for voids in this group. This may have been because the precipitates were rather small and difficult to see under void imaging conditions.

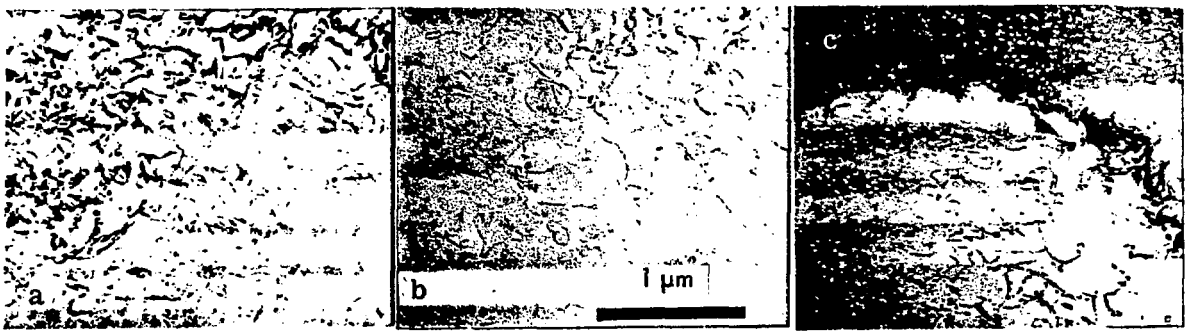


Fig. 1. The effect of 1 MeV HVEM irradiation on low temperature aged Cu-2 Co. The specimen was aged 100 min at 450°C following homogenization, prior to HVEM observations. Foil plane near (211); thickness = 0.46 μm; stripes are slip traces. (a) 6 min irradiation, 0.7 dpa. Faulted and unfaulted loops, dislocations present. (b) 20 min irradiation, 2.5 dpa. Faulted and unfaulted loops, dislocations and small voids. (c) 50 min irradiation, 6.2 dpa. Unfaulted loops, dislocations, and voids present.

2. A Cu-Co alloy containing initially incoherent cobalt precipitate did not exhibit faulted loop formation during the first part of an HVEM irradiation observed in alloys described in (1) above. The incoherent precipitate initially present in this alloy was responsible for the presence of a considerable dislocation density as well, developed when coherency was lost. The presence of the initial incoherent interfaces and dislocations evidently furnished a sink density for radiation induced point defects sufficiently large to prevent easy nucleation of faulted loops. During HVEM irradiation it was apparent that dislocation mobility was much lower than in pure copper or the alloys in (1) above. This was observed to be a result of dislocation pinning at the precipitate interfaces. Figure 2 shows examples of the microstructure observed during HVEM irradiation. There are several good examples of voids nucleated and growing at incoherent precipitate particles. Note that the void density appears

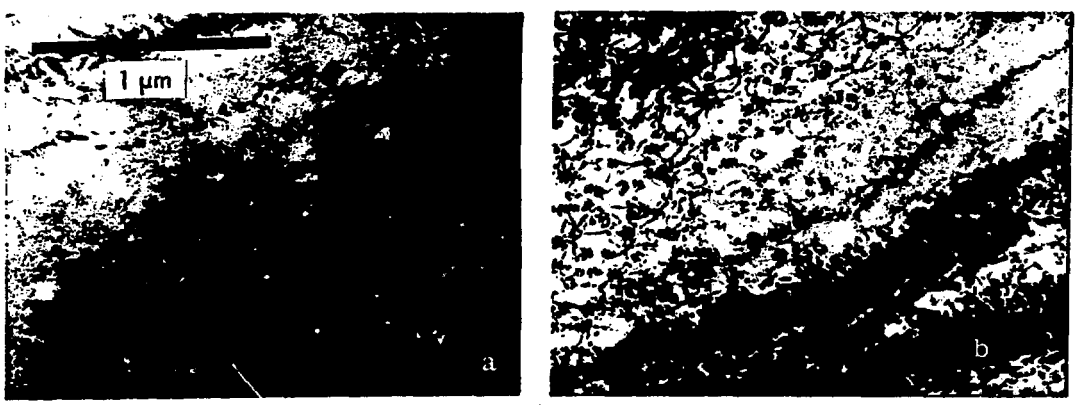


Fig. 2. Cu-2 Co alloy aged 100 hrs at 600°C after homogenization, prior to HVEM irradiation. 1 MeV HVEM irradiation at 300 ± 20°C. Foil plane near (013), thickness ~0.5 μm. (a) After 63 min, 13 dpa. Dark spots at center are surface dirt on foil. Note voids attached to precipitate particles. (b) The same specimen after 83 min irradiation, 18 dpa. Void growth and further nucleation have occurred; dislocation structure appears qualitatively unchanged.

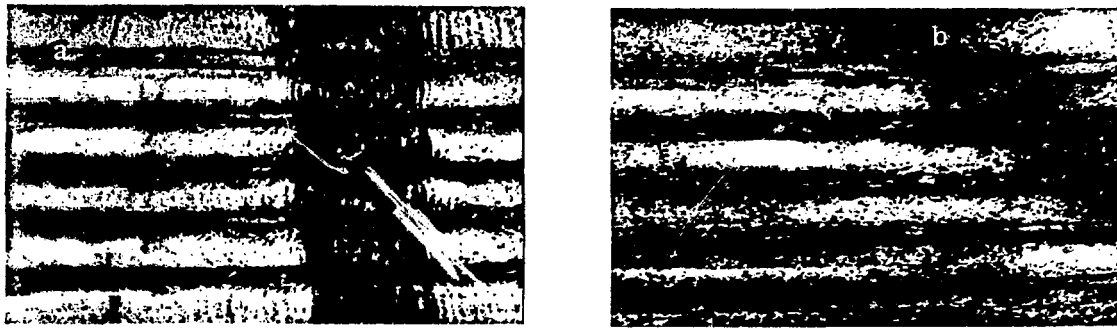


Fig. 4. Defect microstructure formed in Cu–4 Ti during 1 MeV HVEM irradiation. 36,000 X. (a) Initial microstructure before irradiation. The alloy was aged 10 hrs at 600°C after homogenization. Foil plane (110). Ordered phase (dark bands) plates seen edge-on, on {111} matrix plane traces. (b) The same area after 110 min irradiation, 43 dpa.

The experimental results allow one to conclude that (a) metastable quenched solid solution Cu–2 Co alloys, or the same alloys aged to produce coherent Co-rich zones, do not differ greatly from elemental Cu in their behavior under 1 MeV electron irradiation. When the same alloys are aged to form larger incoherent precipitate prior to HVEM irradiation surpression of the early small loop stage of damage occurs but voids are nucleated in both cases; (b) metastable modulated microstructures in quenched or low temperature aged Cu–4 Ti alloys completely surpressed void nucleation up to fluences on the order of 50 dpa. The very fine scale microstructural changes that occurred during irradiation in the modulated Cu–4 Ti alloys were not resolved in detail, but it appears that the basic difference between Cu–4 Ti and Cu–2 Co was a much larger point defect sink density in the former, resulting in surpression of void nucleation. Since only one irradiation temperature was investigated, namely ~300°C, these conclusions cannot be taken as a general statement concerning the merits of modulated structures with respect to radiation damage, but the results are encouraging. Certainly microstructural coarsening is to be expected during irradiation if the temperature is much above 350°C, and the results may be quite different.

References.

1. Wilkens, M. and Urban, K., (1974) "High Voltage Electron Microscopy," ed. by P. R. Swann et al., Academic Press (London), 332.
2. Kelly, A. and Nicholson, R. B., (1963) Prog. Mat. Sci., 10, 149.
3. Ashby, M. F. and Brown, L. M., (1963) Phil. Mag., 8, 1083.
4. Laughlin, D. E. and Cahn, J. W., (1975) Acta. Met. 23, 329.
5. Cornie, J. A., Datta, A., and Soffa, W. A., (1973) Met. Trans., 4, 727.
6. Buswell, J. T., Fisher, S. B., Harbottle, J. E., and Norris, D. I. R., (1973) Proc. International Conf. on Phys. Metallurgy of Reactor Fuel Elements, CEGB Berkeley Nuclear Lab. (England), paper No. 30.
7. Fisher, S. B., (1970) Rad. Effects, 5, 239.
8. Kenik, E. A., (1974) Ph.D. Thesis, Case-Western Reserve University.
9. Shunk, F. A., "Constitution of Binary Alloys, Second Supplement," (1969) McGraw-Hill, 296.