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Microstructural stability of nanostructured Cu alloys during high-temperature irradiation

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The stability of model nanostructured $Cu_{90}Mo_{10}$ and $Cu_{90}W_{10}$ alloys during irradiation with 1.8 MeV Kr^+ at very high temperatures was investigated. Significant coarsening occurs only above $\sim 0.6T_m$ in $Cu_{90}Mo_{10}$ and $\sim 0.8T_m$ in $Cu_{90}W_{10}$ (T_m is the melting point of Cu). Below these temperatures, nanoprecipitates nucleate and grow to a saturation diameter of ~4 nm. These very small nanoprecipitates confer remarkable microstructural stability, with the Cu grain size remaining below 40 nm. Computer simulations help to explain why these nanostructures are so stable.

Keywords: Cu alloys; Thin films; Nanostructures; Implantation

A key to developing radiation-resistant materials for advanced nuclear systems is providing high densities of internal, unbiased sinks or traps for irradiation-induced defects. This is not a new strategy; additions of solutes that trap point defects have long been suggested for this purpose [1]. The difficulty has been maintaining the high densities of traps/sinks during prolonged irradiation, particularly at very high temperatures, owing to such processes as radiation-induced (or enhanced) segregation, precipitation and grain growth. Various methods are presently being tested to overcome these problems. For example, nanocrystalline alloys are prepared with solutes that segregate to grain boundaries and have dramatically reduced grain boundary energies [2]. Other works use self-organization to stabilize two-phase alloys [3,4]. Perhaps the simplest method for maintaining high densities of defect sinks is the addition of high densities of nanometer inclusions [5]. Indeed, extensive investigation is now underway for synthesizing and testing nanoscale oxide dispersion strengthened steels for nuclear applications [6]. In the present work we adopt an approach that combines ideas of self-organization and nanoparticle dispersions using model alloys systems. As we will show, dilute Cu–Mo and Cu–W can be exposed to irradiation doses exceeding 75 displacements per atom (dpa) while at temperatures over $0.65T_m$ for $Cu_{90}Mo_{10}$ and $0.85T_m$ for $Cu_{90}W_{10}$, without significant alteration of their microstructures. By investigating these rather simple alloys, we have been able to elucidate their remarkable stability under irradiation at high temperatures through modeling and computer simulations. The study thus provides fundamental guidelines for designing new, more complex alloys for extreme irradiation environments.

The dilute Cu alloy specimens were grown on oxidized Si wafers using a DC magnetron system with two separate sources. Typical film thicknesses were ≈200 nm. The base pressure in the growth system was $\sim 2 \times 10^{-8}$ torr, and the operating pressure during growth was $\sim 2 \times 10^{-3}$ torr Ar. The precise compositions and thicknesses of the alloy films were determined after growth using Rutherford backscattering. The samples were irradiated with 1.8 MeV Kr^+at different temperatures; the pressures were less than $\sim 5 \times 10^{-8}$ torr. The projected range of Kr at this energy is ~300 nm [7], which is more than the thickness of the film. The deposited damage energy, moreover, is nearly uniform throughout the entire film, increasing by ~20% from the front to the back side of the film. The beam current was maintained at ~100 nA, which limited beam heating to less than ~10 °C, as measured during irradiation. All of the samples for a given irradiation temperature, including non-irradiated samples, were part of the same wafer and were held at temperature for the same length of time. In this way, the thermal growth of precipitates

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could be distinguished from that enhanced by irradiation. The samples were characterized by X-ray diffraction, using the Scherrer equation to determine the sizes of the precipitates and Cu grains. Selected samples were examined by transmission electron microscopy (TEM) using either bright-field or high-angle annular dark-field imaging.

The effects of thermal annealing and irradiation at high temperatures on the sizes of Mo and W precipitates are shown in Figure 1(a), and the effects on grain size are shown in Figure 1(b). The irradiation dose was 3×10^{16} ion-cm^{-2}, or ~75 dpa, which is sufficiently high for the specimens to reach a near-steady-state microstructure. The total time at temperature was $\sim 1 \times 10^4$ s. TEM images of selected thermally annealed and irradiated samples of both alloys are shown in Figure 2. Reasonably good agreement between the particle sizes deduced from the TEM images and X-ray diffraction is obtained (see the caption to Figure 2).

As seen in Figure 1(a), Mo and W begin to precipitate thermally at ~400 and ~550 °C, respectively. After this precipitation stage, the particle size remains nearly constant, until the annealing temperature is raised an additional 200 °C, $\sim 0.65T_m$ for Cu–Mo and $0.85T_m$ for Cu–W, where T_m is the melting temperature of Cu, 1083 °C. Tracer impurity diffusion coefficients of Mo and W in Cu are not available in the literature; however, if we assume that precipitation results from solute diffusion to grain boundaries, and that the nucleation barrier for precipitation is negligible, then using $\tau^{-1} = \frac{3\pi^2 D}{L^2}$, with $\tau \sim 10^4$ s and $L \sim 30$ nm, we obtain $D \sim 3 \times 10^{-17}$ cm^2 s^{-1}. While the self-diffusion coefficient of Cu reaches this value at ~350 °C [8], diffusion coefficients of refractory solutes such as Ir and Ru do not until ~550 °C [9], a temperature that is consistent with the onset of precipitation of Mo and W in Cu.

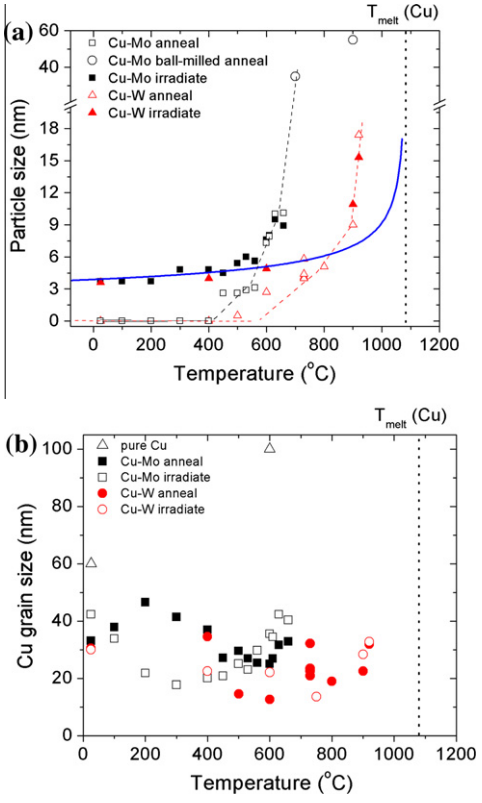

Figure 1. (a) Precipitate size vs. temperature during thermal annealing or irradiation at high temperature in Cu–Mo and Cu–W alloys. The blue solid line is a fit to Eq. (5). The data for annealed Cu–Mo at the highest temperatures are from Ref. [10]. (b) Grain size vs. temperature during thermal annealing or irradiation at high temperature in Cu–Mo and Cu–W alloys.

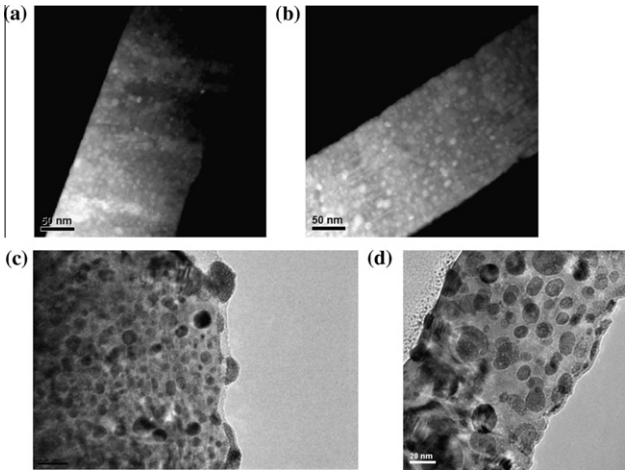

Figure 2. Scanning TEM Z-contrast image of (a) $Cu_{90}Mo_{10}$ annealed at 580 °C, where the average grain size is 6.8 nm, and (b) $Cu_{90}Mo_{10}$ 2×10^{16} irradiated at 630 °C, where average grain size is 7.2 nm. Bright-field image of (c) $Cu_{90}W_{10}$ annealed at 900 °C, where the average grain size is 8 nm, and (d) $Cu_{90}W_{10}$ 2×10^{16} irradiated at 900 °C, where the average grain size is 13 nm.

Precipitate growth in these same samples irradiated to a dose of $\sim 3 \times 10^{16}$ show different behavior. Surprisingly, both Mo and W precipitate during irradiation at room temperature (RT), but they show little additional coarsening until much higher temperatures. For both alloys, the precipitate size increases from ~3 to ~5 nm as the temperature is increased from RT to 550 °C. These sizes, moreover, had saturated, i.e. after ~10 dpa no additional growth was observed. Above 550 °C, Mo precipitates grew rapidly with increasing temperature, but this can be attributed to thermal and not irradiation-enhanced coarsening, as the unirradiated and irradiated sets of data overlap at these high temperatures. For the Cu–W alloy, the precipitates increase gradually in size to a significantly higher temperature, ~800 °C, but thereafter, similar to the Mo precipitates, they grow rapidly with temperature, closely following the thermal annealing curve. One difference observed for the Cu–W alloy is that at ~850 °C the precipitate size of the irradiated sample is noticeably larger than that of the thermally annealed sample (see Figs. 1 and 2(c) and (d)). This difference, which is explained below, is not likely due to an error in temperature measurement since the thermally annealed sample is part of the same film being irradiated, but just outside the irradiated area.

The high thermal stability of the microstructure of $Cu_{90}Mo_{10}$ and $Cu_{90}W_{10}$ alloys presumably derives from the combination of the low tracer diffusivity and small solubility of these two solutes in Cu, combined with Zener pinning of grain boundaries [5]. The effect of Mo additions on the microstructural evolution of Cu during thermal annealing had been reported previously on sam-