Orientation Relationship formed during irradiation induced precipitation of W in Cu

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Keywords: Cu, W, Misorientation, Transmission electron microscopy, Irradiation

1. Abstract

Irradiation of dilute Cu-W alloys with 1.8 MeV Kr⁺ between 300K and 573K is found to induce nucleation of a high density of W nano-precipitates. HRTEM and aberration-corrected STEM reveal that the ~3 nm precipitates have a preferred orientation relationship with the matrix. A variant of the Bain relationship exists with preferred alignment occurring along Cu<220>||W<010>, with small angular differences amongst the particles, which is compensated by interfacial dislocations or strain. The formation mechanism for such an orientation relationship is rationalized on the basis that small W clusters form within the local melt of an energetic displacements cascade, resulting in the partial alignment of the nanoprecipitates with the Cu lattice as the Cu solidifies.

Introduction

Advanced designs for nuclear power call for structural materials that can resist damage when exposed to prolonged, high levels of radiation. [1]. To this end, various attempts have focused on increasing the number of point defect sinks in the sample, either via solute atoms, precipitates or interfaces. The high concentration of point defect sinks provides both structural stability as well as strength retention under high flux conditions. This approach is successfully employed in modern oxide dispersions strengthened (ODS) alloys [2] as well as in other morphologies such as multilayered Cu-Nb[3]. Experimental and theoretical data have demonstrated, for example, that thin multilayer composites of strongly immiscible metals exhibit a high degree of phase and dimensional stability during prolonged irradiation at high temperatures [4, 5]. These properties have been attributed to a crucial role played by specific orientation relationships developed at the composite interfaces during sputtering deposition or roll bonding [6, 7], with certain interfaces providing efficient sites for the recombination of irradiation-induced defects.

The important role of unique interface structure on point defect sink strength was demonstrated in both ODS-alloys [8] as well as nano-composite metal-metal systems [4,5]. In one study, *in situ* measurements of irradiation-enhanced creep (IEC) response performed over a wide range of temperature and radiation fluences in nanostructured Cu_{93.5}W_{6.5} and Cu₉₉W₁ alloys [9] revealed that W nano-precipitates formed between 300K and 573K, served to prevent grain growth in Cu and stabilized Cu grain size at 30 nm. Moreover, no dislocations or other signs of radiation damage were observed in

either irradiated alloy. The size of the nano-precipitates in the two alloys were 2-3 nm with densities of $\sim 2.4 \times 10^{-5}$ and $\sim 5.9 \times 10^{-6}$, in atomic fraction, in the $\text{Cu}_{93.5}\text{W}_{6.5}$ and Cu_{99}W_1 alloys, respectively.

A surprising result of this creep investigation was that despite the significant difference in the density of nano-precipitates, the creep rate was relatively large and approximately equivalent in the two alloys [9]. If the nanoprecipitates were effective sinks for point defects, the creep rate should have been small, and smaller in the sample with the higher density of nanoprecipitates. Since this was not observed, it was suggested that W nano-precipitates might not be effective sinks for point defects in Cu, in comparison to grain boundaries, and that their role in suppressing radiation damage is primarily to suppress grain growth. The present work is thus designed to clarify the sink efficiency of W nanoprecipitates in Cu by elucidating the interface structure of the nano-precipitates that form in Cu during high-dose ion irradiation.

2. Experimental

The specimens studied in this investigation were taken from the same two Cu-W alloys used for the irradiation creep experiments. These specimens were initially free-standing 300 nm thin films of $\text{Cu}_{93.5}\text{W}_{6.5}$ and Cu_{99}W_1 alloys **suspended across a gap in a SiO_2 on Si substrate**, which were prepared using magnetron sputtering and standard photolithography [9]. **The alloy compositions were verified by Rutherford backscattering, and no major impurities were observed.** The films were irradiated with 1.8 MeV Kr ions to various doses at 573K. Applied stresses during the creep experiments were small, 5 to 10 MPa. **Samples for transmission electron**

microscopy (TEM) were prepared by 5 keV Ar⁺ ion milling (Gatan CryoPIPS), the free-standing thin films at a 12° incident angle.

Characterization of the samples employed high-resolution TEM (HRTEM, JEOL 2010Lab6 TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, JEOL 2010F (S)TEM or JEOL 2200FS (S)TEM).

3. Results

TEM images of Cu_{93.5}W_{6.5} films before and after irradiation are shown in Fig.1. The average grain size of the initial, as-deposited Cu_{93.5}W_{6.5} film was ~40 nm. A moderate density of twins is also observed in the as-prepared specimen, Fig. 1(a). The selected area diffraction (SAD) pattern inset in Fig.1(a) shows diffraction rings associated with Cu, but not W. Additionally, no W precipitates were observed in the HRTEM images or x-ray diffraction patterns (not shown). After irradiation-induced creep deformation, on the other hand, a high density of W nanoparticles is observed in this Cu_{93.5}W_{6.5} sample, with no measurable change in the grain size, Fig. 1(b). The corresponding SAD pattern reveals the presence of body centered cubic (BCC) W. Because of the weak diffraction intensity from the W nanoprecipitates, only the BCC (110) and (200) diffraction rings are observed. The measured planar spacing associated with each diffraction ring are listed in Table I and are reasonably consistent with expected values for FCC Cu and BCC W, also listed in Table I.

Images in Fig. 2 resolve the lattice fringes associated with both the Cu matrix and the W nanoparticles. The fast Fourier transform (FFT) images of the matrix and

nanoparticles are shown in the inset and indicate that the crystallographic orientation of the Cu matrix is close to the FCC $\langle 110 \rangle$ zone axis, and the W nano-precipitates are close to the BCC $\langle 111 \rangle$ zone axis. Some of the W particles are slightly misoriented with respect to one another. A significant fraction of the particles, $\sim 1/3$, have interface dislocations or disconnections at the Cu-W interface. Arrays of interface dislocations or ledges often accommodate misfit strain at incommensurate interfaces[10]. Strain in the Cu lattice fringes is also observed around some of the W particles.

Atomic-resolution high-angle annular dark field (HAADF) STEM images of the W particles (bright-phase) in Cu are shown in Figs. 3-5. Fast Fourier transforms (FFT) were used to determine the zone axis associated with each image. These three figures illustrate three different matrix orientations, Cu [100], [110], and [111], respectively, taken from three different grains. In each image, one can clearly distinguish atomic columns in both the Cu (darker) matrix and W (brighter) nano-precipitates. The zone axes of the W nanoparticles are approximately [100], [111], and [110], respectively. The planar spacings of individual W particles and particle-free Cu regions measured from the FFTs are listed in Table I. Energy dispersive spectroscopy confirmed that higher local W concentrations correlated with brighter image intensity.

4. Discussion

Based on Figs. 3-5, the orientation relationship between Cu and W measured here relates to the Bain relationship, FCC (010) $\parallel$ BCC (010) and FCC [001] $\parallel$ BCC [101],

but it deviates between individual particles as will be described in more detail below. Several specific “misorientation” relationships have been identified in FCC-BCC systems that are deviations from the Bain relationship, including; Kurdjumov-Sachs (KS), Nishiyama-Wassermann (NW), Greninger-Troiano (GT), or Pitsch relationships [11]. In order to characterize which misorientation relationship best describes the system, the misorientation angle, θ , between 65 W particles and the Cu matrix was measured in ImageJ Software from these sets of images. Misorientation distributions are shown in Figure 6.

Imaging the Cu[100] zone axis indicates that the Cu<200> and W<110>, and Cu<220> and W<010> are misoriented by 2.0 ± 0.7 and 1.0 ± 1.0 degrees, respectively. The error is defined by the standard deviation associated with reproducing the misorientation measurement. The misorientation between Cu and W is observed to be much larger when viewed along the Cu[110] zone axis. Here, the average misorientation angles between Cu<200> and W<011>, and Cu<111> and W<011> are 4.4 ± 2.0 and 4.8 ± 1.2 degrees, respectively. Observations of the Cu[111] zone axis suggest that the Cu and W are almost perfectly aligned, where $\theta = 0.4 \pm 0.6$ degrees for Cu<220>||W<211>, Cu<220>||W<200>, and Cu<220>||W<220>. There are three variants for this orientation relationship. The variants appear to have similar misorientations in the image and they are thus noted as Cu<220>||W<hkl> in Fig. 6, where <hkl> represents either <211>, <200> or <220>. Ideal alignment of these crystallographic directions is not possible unless the W is tetragonally strained or slightly rotated out of plane. Overall, the analysis indicates the

strongest preference for alignment between Cu<220> and W<010>, as demonstrated by the cumulative misorientation distributions in Fig. 6. This particular alignment is unique to the NW relationship, however NW also predicts alignment of the Cu{111}||W{110}, which is not satisfied here. The difference may result from strain that may be accommodated by the small W crystals, the surrounding Cu matrix, and line defects at the interfaces. For example, some of the W{110} planes in Figs. 3 and 4 appear to be curved and interface dislocations are observed in a large fraction, ~1/3, of the particles in Fig. 2. Thermal precipitation of nanoparticles can result in Bain-related misorientations, but such particles often geometrically accommodate strain evolved during nucleation and growth through shape anisotropy and crystal defects [12]. Irradiation induced precipitation should follow a different reaction pathway in the temperature regime characterized here due to the absence of thermal diffusion of W in Cu. It is hypothesized that the precipitation mechanism can account for the broad range of misorientations and differences in lattice defects observed in the various W particles.

We now turn to how oriented nano-precipitates might form during irradiation below approximately 573 K. Past MD simulations of Cu-Mo alloys provide some insight into the formation mechanism of highly oriented nano-precipitates in a Cu matrix [13]. We will assume here that W precipitation in Cu under irradiation is similar to that of Mo. In the simulations, it was found that 50 keV cascades in Cu create liquid-like zones, ≈ 6 nm in diameter. Since Mo (or W) is highly immiscible with Cu even in the liquid state, the Mo (or W) can precipitate out of the liquid alloy.

Nano-precipitates can then grow by agglomeration, i.e., the small Mo clusters are mobile in the liquid Cu and find other clusters and coalesce. Once the nano-precipitates reach a size comparable to the melt volume, they are no longer mobile and the precipitate size is fixed. This explains why the size of the nano-precipitate in $\text{Cu}_{93.5}\text{W}_{6.5}$ and Cu_{99}W_1 is the same, and only the density of nano-precipitates is different. How the W nano-particles orient with the Cu matrix remains unclear. MD simulations show that 50 keV cascades initiated near a 2 nm Mo precipitate in Cu cause not only melting in the Cu matrix, but also melting of small Mo nano-precipitates. Subsequently as the local melt cools by heat transport to the surrounding region, the simulations show that the Cu re-solidifies by re-growth of the crystalline Cu from the surrounding crystalline Cu matrix. We suggest that the crystalline Mo (or W) then nucleates on the crystalline Cu matrix surrounding the particle and thereby becomes oriented. Unfortunately, this mechanism could not be directly observed, as the molten Mo nanoparticles did not crystallize during the MD simulation event, 10 ns, possibly because it supercooled below the glass temperature of Mo. In the case of W precipitation, we cannot discount the possibility that W nanoparticles remain solid in the thermal spike and can rotate rapidly enough in the melt zone to minimize the interfacial free energy.

5. Conclusion

In conclusion, we have shown that irradiation of dilute Cu-W alloys with energetic particles leads to the formation of nano-precipitates that are equiaxed and strongly aligned, crystallographically with the matrix. This finding appears to be

general, and should apply not only to simple binary immiscible alloys but also to more complex systems involving ternary or quaternary components and refractory inclusions. We note in particular that similar orientation relationships between BCC core-shell nanoprecipitates and the FCC matrix have been recently reported in Cu-Nb-W subjected to ion irradiation [14]. The main requirements for observing such phenomena are that the matrix and precipitate phase have limited mutual solubility in the liquid phase and that they undergo local melting within cascades. The orientation relationships between W nanoprecipitates and the Cu matrix result in the formation of semi-coherent interfaces. Compared with incoherent interfaces, these Cu-W interfaces clearly possess fewer sites for trapping or eliminating point defects, thus reducing their sink efficiency. This is consistent with the irradiation-induced creep rates reported in the introduction. These findings should provide important insights into understanding the sink strength in new classes of radiation-resistant materials based nanoscale composites, such as nano-ODS ferritic alloys [8].

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award #DEFG02-05ER46217. It was carried out, in part, in the Materials Research Laboratory Central Facilities at the University of Illinois at Urbana-Champaign.

Fig. 1. (a) TEM bright-field image of $\text{Cu}_{93.5}\text{W}_{6.5}$ as-deposited state and the corresponding SAD, before and (b) after IIC deformation at 573K with the corresponding SAD

Fig. 2. HREM bright-field images of $\text{Cu}_{93.5}\text{W}_{6.5}$ after IIC deformation at 573K at two different magnifications. The corresponding FFT of the entire region, a single W nanoparticle, and a small region of the Cu matrix are inset. The arrows in the image show (1) a dislocation, (2) a region where the W fringes appear slightly misoriented despite no dislocations being present, and (3) a W particle whose lattice fringes appear to align well with the Cu matrix.

Fig. 3. High resolution STEM image of $\text{Cu}_{93.5}\text{W}_{6.5}$ after IIC deformation at 573K imaged along the Cu $\langle 100 \rangle$ zone axis.

Fig. 4. High resolution STEM image of $\text{Cu}_{93.5}\text{W}_{6.5}$ after IIC deformation at 573K imaged along the Cu $\langle 110 \rangle$ zone axis. Note the grain boundary running vertically in the image and the twin boundaries running diagonally in the right grain.

Fig. 5. High resolution STEM image of $\text{Cu}_{93.5}\text{W}_{6.5}$ after IIC deformation at 573K imaged along the Cu $\langle 111 \rangle$ zone axis.

Fig. 6. Distribution of misorientation between sets of planes in Cu and W determined from HAADF-STEM images at different zone axes. Note that data labeled $\text{Cu}\langle 220 \rangle\text{W}\langle hkl \rangle$ were obtained from the Cu[111] zone axis where the specific directions W directions ($\langle hkl \rangle = \langle 211 \rangle, \langle 200 \rangle, \text{ or } \langle 220 \rangle$) were difficult to distinguish possibly due to strain effects (see Fig. 5).

Table I: Lattice plane spacings of Cu and W including standard powder diffraction pattern (PDF) values, those measured from selected area electron diffraction, and those measured from fast Fourier transforms (FFT). The error listed is the standard deviation of the experimental measurement. No measurement errors are listed for values measured from SAD patterns, because the accuracy of the measurement is likely less than the precision.

	Cu (111)	Cu (200)	Cu (220)	Cu (311)	W (110)	W (200)	W (220)	W (211)
Cu (PDF Value)	2.0871	1.8075	1.2781	1.09				
W (PDF Value)					2.2274	1.575	1.1137	1.286
Unirradiated D.P.	2.11	1.82	1.29	1.1				
Irradiated D.P.	2.11	1.82	1.3	1.1	2.34	1.52		
Cu 100 FFT		1.9+/-0.05	1.2+/-0.1		2.1+/-0.05	1.5+/-0.15		
Cu 110 FFT	2.0+/-0.1	1.9+/-0.1			2.1+/-0.1			
Cu 111 FFT			1.2+/-0.15		2.1+/-0.1			

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