Microstructure and Nano-hardness of Pure Copper and ODS Copper Alloy under Au Ions Irradiation at Room Temperature

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Received: 9 April 2016/Revised: 8 June 2016/Published online: 14 September 2016
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Abstract The microstructure and nano-hardness of the pure copper and oxide dispersion-strengthened (ODS) copper alloy subjected to 1.4 MeV Au ions irradiation at room temperature were investigated. After irradiation, dislocation-loops form in both materials, while voids can only be generated in the pure copper. Compared with the irradiated pure copper, larger average diameter and lower number density of irradiation-induced dislocation-loops were detected in the ODS copper alloy, revealing that high-density dislocation and large volume of Al₂O₃ particles existing in the ODS copper alloy can act as effective sinks for the irradiation-induced defects. It was also detected that irradiation hardening in the ODS copper alloy is lower than that in the pure copper. The microstructure and nano-hardness results reveal that the ODS copper alloy has a better irradiation tolerance than the pure copper. In addition, the average diameter of the Al₂O₃ particles in the ODS copper alloy decreases after irradiation, because the Al–O chemical bonds are decomposed and the atoms are redistributed in the matrix during the irradiation process. This work reveals that the irradiation tolerance of the copper can be effectively enhanced by adding nano-sized Al₂O₃ particles into the matrix.

KEY WORDS: Oxide dispersion-strengthened copper alloy; Ions irradiation; Microstructure evolution; Nano-hardness

1 Introduction

Oxide dispersion-strengthened (ODS) copper alloys, which contain fine and high-density dispersed Al₂O₃ particles in the matrix, exhibit excellent high strength, high thermal conductivity and thermal stability at high temperature [1–4]. These materials are of potential use in electrodes resistance welding, frictional brake parts, integrated circuit sealing materials and heat sink materials for the first wall and divertor in international thermonuclear experiment

reactor (ITER) [5–8]. The heat sink materials in ITER are subjected to high-energy neutron irradiation. During the irradiation process, high-energy particles interact with target material atoms and induce a large number of point defects. These defects can aggregate together and form defect clusters, such as voids, dislocation-loops and stacking fault tetrahedrons [9–12], which severely degenerate the mechanical properties [13–15]. It is of great interest to develop irradiation-tolerant materials that can promote the annihilation of irradiation-induced defects.

It was reported that irradiation damages can be suppressed by adding nanoparticles into matrix, because the interfaces between nanoparticles and matrix may act as preferential trapping sites for irradiation-induced defects and their clusters [16–19]. For example, McClintock et al. [20] reported that the tensile strength in the irradiated ODS alloys was superior to an identical alloy, which contains typical oxide dispersions but lacks nano-clusters. Fave

Available online at <http://link.springer.com/journal/40195>

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et al. [21] investigated the irradiation resistance of the ferritic ODS steels and found that the Y–Ti nano-oxides (2–4 nm) having coherent interfaces with the matrix can act as the sites for point defects recombination. It was reported that the irradiated ODS copper alloys presented better tensile strength and electrical resistivity than the precipitation-hardened copper alloys [22, 23] under neutron irradiation. Hatakeyama et al. [24] investigated the ion irradiation effects of the ODS copper alloy in temperature range from 573 to 773 K and found that the voids did not form, where Al_2O_3 particles were present in high density. It reveals that the Al_2O_3 particles can act as sinks for irradiation-induced defects. Sumino et al. [25] illustrated that varying irradiation temperature can suppress the void swelling in the ODS copper alloy.

In this work, pure copper and ODS copper alloy were irradiated by 1.4 MeV Au ions at room temperature. The evolutions of the microstructure and the nano-hardness for both the un-irradiated and irradiated samples were investigated in detail.

2 Experimental

The ODS copper alloy is Cu–Al30 with 0.3 wt% Al content in a form of Al_2O_3 particles, and it was fabricated by an internal oxidation method. The ODS copper alloy was in cold-rolled condition, and the samples for irradiation were cut along the rolling direction. Pure copper samples were cut from a commercial T₂ copper (99.9%) plate with 1 mm thickness.

Samples with 3 mm diameter and 0.1 mm thickness were prepared for irradiation. Au ions with energy of 1.4 MeV were implanted to the samples at room temperature with the fluences of 10^{14} , 5×10^{14} and 10^{15} ions/cm² by using highly charged ions comprehensive experimental platform at the Institute of Modern Physics, Chinese Academic of Science. The beam current was 0.2–0.5 μA . The values of displacement per atom (dpa) were calculated using the stopping and range of ions in matter (SRIM) code [26]. The densities of pure copper and ODS copper alloy for simulation are 8.92 and 8.85 g/cm³, respectively. The threshold displacement energies (E_d) for O, Cu and Al atoms are 40, 25 and 25 eV, respectively. The corresponding dpa values for the irradiation fluences of 10^{14} , 5×10^{14} and 10^{15} ions/cm² are 1.1, 5.4 and 10.8 dpa, respectively.

Ion milling method was used to prepare all samples for transmission electron microscopy (TEM) by using Gatan-691 precision system. The beam energy was gradually reduced from 5.5 to 2 kV, and the irradiated samples were thinned from the un-irradiated side. TEM observation was performed on a JEOL 2010 electron microscope operated

at 200 kV. Nano-hardness of the samples was measured at room temperature using MST nano-indenter XP instrument with continuous stiffness method. Approximately 10 indents were taken for each sample.

3 Results and Discussion

SRIM code [26] was used to calculate the defects and ion distribution for the pure copper and ODS copper alloy. As shown in Fig. 1, the defects and Au ion distribution in these two materials are almost same. The damage peak induced by Au collisions is 10.8 dpa with a depth of 75 nm, and the range of irradiation damage zone extends to a depth of 250 nm. Au ions concentration reaches a peak at a depth of 125 nm.

TEM micrographs of the un-irradiated pure copper and ODS copper alloy samples are shown in Fig. 2. Figure 2a presents an overview of the pure copper, the average grain size is about 555 nm, and some dislocation lines with low density were observed in its grain interiors. The microstructure of the ODS copper alloy is presented in Fig. 2b, and typical elongated grain structures, which are parallel to the rolling orientation, were observed. The average grain size is around 500 nm, which was calculated by the smallest dimension of the grains across its width. In addition, high-density dislocations due to the cold working during fabrication are observed in Fig. 2b. Although the dislocation density in both materials is important, unfortunately, the dislocation lines in ODS copper alloy tangled together forming dislocation networks, so it is very difficult to calculate its density. Figure 2a and b is obtained from the same zone axis [011], so these two photographs can be used to compare the dislocation density of the two materials. The dislocation density of the ODS copper alloy is

Fig. 1 Depth profile of the irradiation damage in unit of dpa and Au ion concentration for the pure copper and ODS copper alloy with a fluence of 10^{15} atom/cm² irradiation

Fig. 2 TEM micrographs of the un-irradiated samples: **a** pure copper, **b** ODS copper alloy, **c** enlarged part of (**b**)

much higher than that of the pure copper obviously. Figure 2c shows the un-irradiated microstructure at higher magnification. Here, the small Al_2O_3 particles were observed to disperse homogenously in the matrix, and the total Al_2O_3 particle density is about $(2.1 \pm 0.4) \times 10^{22} \text{ m}^{-3}$. The measured particle size distribution is shown in Fig. 3. It shows that the Al_2O_3 particles size is about 3.5 nm.

The bright-field TEM images of the pure copper and ODS copper alloy irradiated with the dose of 10.8 dpa at room temperature are shown in Fig. 4. Figure 4a reveals that many dislocation-loops formed in the irradiated pure copper, and many voids were also detected (Fig. 4b). Figure 4c shows the microstructure of the irradiated ODS copper alloy, where dislocation-loops were observed, but no voids were detected. It is well known that voids originate from the aggregation and growth of the vacancies, and it can lead the materials swelling [27]. No voids were detected in the ODS copper alloy, which may be attributed to the Al_2O_3 particles and the dislocations, since most of the mobile defects produced by the irradiation can be annihilated at these defect sinks. The average diameter and

number density of the dislocation-loops in the irradiated pure copper and ODS copper alloy were calculated and are listed in Table 1. TEM images of the dislocation-loops in the irradiated samples are taken at the same $\vec{g}$ and the $\vec{g} = (200)$. In the pure copper, the average diameter of the dislocation-loops is 4.4 nm and the number density is $(1.5 \pm 0.4) \times 10^{22} \text{ m}^{-3}$. In the ODS copper alloy, the average diameter and number density of the dislocation-loops are 5.3 nm and $(1.0 \pm 0.3) \times 10^{22} \text{ m}^{-3}$, respectively. The average diameter of the dislocation-loops in the ODS copper alloy is larger than that in the pure copper, while the number density is lower than that in the pure copper, which indicates that the irradiation resistance of the ODS copper alloy is higher than that of the pure copper.

Lattice atoms diffusion by the vacancy mechanism is given by [28]:

$$D_a^v = f_v D_v C_v \quad (1)$$

where D_a^v is lattice atoms diffusion coefficient, D_v is vacancy diffusion coefficient, C_v is vacancy concentration and f_v is correlation coefficient. Equation (1) reveals that higher vacancy concentration leads to larger diffusion coefficient. In the pure copper, the vacancy concentration is higher than that in the ODS copper alloy, which leads to the diffusion coefficient of the pure copper larger than that of the ODS copper alloy. It means that the aggregation of the vacancies in the pure copper is much easier than that in the ODS copper alloy, and it also was confirmed by the TEM result (Fig. 4b). The high-concentration vacancies aggregate together and form voids in the pure copper.

Compared with the pure copper, low-density irradiation-induced dislocation-loops in the ODS copper alloy may be attributed to the following reasons. The cold-rolled state ODS copper alloy contains high-density dislocations (Fig. 2b), which can act as effective sinks for irradiation-induced defects. Similar phenomenon in the irradiated austenitic stainless steels was also observed [28]. Austenitic stainless steels containing higher density of dislocations showed better swelling resistance, since the

Fig. 3 Diameter distribution histogram of the Al_2O_3 particles in the as-received ODS copper alloy

Fig. 4 TEM images of the irradiated samples with the dose of 10.8 dpa, **a** dislocation-loops, **b** voids in the pure copper, **c** dislocation-loops in the ODS copper alloy

Table 1 Average diameter and number density of dislocation-loops in the irradiated pure copper and ODS copper alloy

	Diameter (nm)	Number density (m^{-3})
Pure copper	4.4	$(1.5 \pm 0.4) \times 10^{22}$
ODS copper alloy	5.3	$(1.0 \pm 0.3) \times 10^{22}$

dislocations act as sink for irradiation-induced defects. In addition, high-density nano-sized Al_2O_3 particles dispersed in the matrix provide a large volume of interfaces, which also can act as sinks for irradiation-induced defects.

Diameter distribution histogram of the Al_2O_3 particles in the irradiated ODS copper alloy at different irradiation dose is presented in Fig. 5. The diameter of the Al_2O_3 particles decreases after irradiation, and the reduction of the diameter is irradiation dose dependence. It shows that the most probable Al_2O_3 particles diameter is 3.5, 3.0 and 2.5 nm at the 1.1, 5.4 and 10.8 dpa, respectively. As reviewed by Zinkle *et al.* [29] and Wanderka *et al.* [30], the recoil process should be produce a shift in the Al_2O_3 particle size distribution toward small size. This effect was observed in the present work. The reason may be the unstable atoms existing at the interfaces between the Al_2O_3 particles and the matrix. During the irradiation process,

ballistic recoil process results in the atom collisions, and subsequent the decomposition of the Al–O chemical bounds, the redistribution of Al and O atoms into the matrix, and the decrease in average size of the Al_2O_3 particles after irradiation. The fate of the solute atoms ejected from an Al_2O_3 particle depends on the solute diffusivity and solubility. Nucleation of the ejected solute may occur under some circumstances, which would produce a refinement in the mean particle size while maintaining a constant particles density [29]. In the present work, number density of the Al_2O_3 particles in the irradiated samples is within the scattering range measured for the un-irradiated alloy. The measurement by Zinkle *et al.* [29] and Wanderka *et al.* [30] indicates that the mean particle size and number density of the Al_2O_3 particles both reduce after irradiation, suggesting that at least some of the ejected solute remains either in solution or in submicroscopic for their irradiation conditions.

Figure 6 shows the nano-hardness as a function of the irradiation dose for the irradiated pure copper and ODS copper alloy. Before irradiation, the nano-hardness value of the ODS copper alloy is higher than that of the pure copper because of the strengthening effects of the Al_2O_3 particles. After irradiation, the nano-hardness values of both the pure copper and ODS copper alloy increase. The nano-hardness increases quickly at the low dose range and then decreases

Fig. 5 Diameter distribution histogram of the Al_2O_3 particles in the irradiated ODS copper alloy: **a** 1.1 dpa, **b** 5.4 dpa, **c** 10.8 dpa

Fig. 6 Nano-hardness as a function of irradiation dose for the irradiated pure copper and ODS copper alloy

at the high dose. Irradiation hardening is defined as follows:

$$\Delta H = H_{\text{irr}} - H_{\text{un-irr}} \quad (2)$$

where H_{irr} is the hardness of the irradiated sample, and $H_{\text{un-irr}}$ is the hardness of the as-received sample. The values of ΔH for the pure copper and ODS copper alloy with different irradiation doses are listed in Table 2. The values of ΔH decrease from 0.6 GPa at the damage level of 1.1–0.2 GPa at 10.8 dpa for the pure copper, while those decrease from 0.2 GPa at 1.1–0.1 GPa at 10.8 dpa for the ODS copper alloy. It shows that the increment of the nano-hardness decreases with increasing irradiation dose. The nano-hardness change in the irradiated pure copper and ODS copper alloy is a competition result between the generation of the irradiation-induced dislocation-loops and the recovery of the preexisting dislocation lines. After irradiation, the nano-hardness increases, indicating that the irradiation-induced dislocation-loops play a dominant role in the change of the nano-hardness. As the irradiation does increase, the value of the ΔH decreases, which reveals that the irradiation enhanced the preexisting dislocations recovery at higher dpa values. For the ODS copper alloy, there is another factor affecting the irradiation hardness, i.e., the changes in the Al_2O_3 particles diameter. In general, the hardness of the ODS copper alloy becomes higher with the increase in the Al_2O_3 particles number density, and decreases with the decrease in the Al_2O_3 particles diameter. In the present work, the Al_2O_3 particle number density in the irradiated samples is within the scattering range

Table 2 Irradiation hardening (ΔH) of the pure copper and the ODS copper alloy with different irradiation dose

	1.1 dpa	5.4 dpa	10.8 dpa
Pure copper	0.6	0.4	0.2
ODS copper alloy	0.2	0.1	0.1

measured for the un-irradiated alloy, but the diameter decreases, which results in the decrease in irradiation hardening. High-density pre-existing dislocation lines provide many trapping sites for the irradiation-induced defects, which leads the value of the ΔH be much lower than that of the pure copper (Table 2). These results reveal that the ODS copper alloy has a better irradiation hardening tolerance than the pure copper.

4 Conclusion

The microstructure and nano-hardness evolutions of pure copper and ODS copper alloy under Au ion irradiation at room temperature were investigated. Dislocation lines were observed in both the pure copper and ODS copper alloy. After the samples were irradiated with the dose of 10.8 dpa, dislocation-loops form in both materials, while only voids were detected in the pure copper. The average diameter of the irradiation-induced dislocation-loops in the ODS copper alloy is larger than that in the pure copper, while the number density is lower than that in the pure copper, which is attributed to the high-density dislocation lines and Al_2O_3 particles existing in the ODS copper alloy act as sinks for irradiation-induced defects. After irradiation, the average diameter of the Al_2O_3 particles decreases. Irradiation hardening of the ODS copper alloy is much lower than that of the pure copper. The microstructure evolution and nano-hardness results reveal that the ODS copper alloy exhibits a better irradiation tolerance than the pure copper.

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (Nos. 11175014, 50971030), the National Basic Research Program of China (No. 11163110) and the National Magnetic Confinement Fusion Program (No. 2011GB108002).

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