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Effect of initial oxygen content on the void swelling behavior of fast neutron irradiated copper

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Abstract

Density measurements were performed on high purity copper specimens containing ⩽ 10 and ~90 wt ppm oxygen following irradiation in FFTF MOTA 2B. Significant amounts of swelling were observed in both the low-oxygen and oxygen-doped specimens following irradiation to ~17 dpa at 375 °C and ~47 dpa at 430 °C. Oxygen doping up to 360 appm (~90 wt ppm) did not significantly affect the void swelling of copper for these irradiation conditions. This implies that surface energy reduction associated with oxygen segregation and chemisorption on void surfaces is not a significant factor controlling the void swelling behavior in copper irradiated with neutrons to high doses at ~400 °C.

1. Introduction

It has been recognized for many years that minor concentrations of impurity atoms (particularly gaseous species) can have a significant impact of the defect cluster morphology in quenched [1,2] and ion-irradiated [3–5] face-centered cubic metals. There is also some evidence that high oxygen levels such as that found in electrolytic tough pitch copper may cause significantly higher neutron-induced void swelling than in oxygen-free pure copper specimens [6]. Recent work by Shimomura and coworkers found that vacuum re-melted specimens had a factor of 10 lower void density compared to as-received 'high purity' copper at low neutron doses (~0.5 dpa), but in general no appreciable difference in the swelling behavior was observed at doses above ~5 dpa [7–9]. Mixed results were obtained on Cu–Al and Cu–Ni alloys, with lower void swelling observed in vacuum re-melted Cu–5%Al specimens, whereas no difference was observed for vacuum re-melted versus as-received Cu–5%Ni specimens following fast reactor irradiation to ~40 dpa at temperatures near 400 °C [8]. Unfortunately, the concentration of gaseous impurities was not quantified in these earlier neutron irradiation studies [7–9]. The purpose of the present study was to provide further data on the effect of a controlled amount of oxygen on the void swelling behavior of neutron-irradiated copper.

2. Experimental

High purity (99.999%) 'Puratronic' wrought copper sheet (1 mm thickness) produced by Johnson Matthey Chemicals Ltd. was cold-rolled to a thickness of 0.5 mm and then recrystallized by annealing in high-purity helium at 400 °C for 1 h. Transmission electron microscopy (TEM) disks of 3 mm diameter were punched from the recrystallized sheet, and several of the disks were annealed in helium containing ⩽ 3 vol. ppm oxygen at a pressure of ~1 atmosphere (0.1 MPa) for 0.5 h at 950 °C in order to introduce a controlled amount of oxygen into the matrix [5]. The specimens were mechanically ground to remove punching burrs prior to annealing, with resultant final thicknesses of 0.35 and 0.25 mm for the 'low-oxygen' (400 °C annealed) and 'oxygen-doped' (950 °C annealed) disks, respectively. The oxygen contents in the low-oxygen and oxygen-doped samples were mea-

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sured at ORNL to be ⩽ 50 and 360 appm, respectively, by vacuum fusion techniques. There was no evidence of oxide precipitates in any of the specimens; the oxygen appeared to be uniformly distributed. Other measured impurity concentrations were ⩽ 5 wt ppm N, 3 wt ppm Fe and 3 wt ppm Si. It should be noted that copper is classified as 'oxygen-free' if it contains <40 appm oxygen. Electrolytic grade copper that has not been deoxidized typically contains 200–400 appm oxygen [4].

Two TEM disks each of the low-oxygen and oxygen-doped coppers were irradiated in the MOTA-2B assembly irradiated in the Fast Flux Test Facility to 16.9 dpa at 375 °C and 47.3 dpa at 430 °C (MOTA-2B packets 7X03 and 7T03, respectively, in the below-core and core regions). The TEM disks were laser engraved with a four-digit ID code at PNNL prior to irradiation, and the irradiation was performed in sealed, helium filled capsules with the specimens separated by thin molybdenum foils to avoid self-welding. Following irradiation, the radiation-induced swelling was measured at PNNL using immersion density techniques accurate to ±0.2% change in density.

3. Results and discussion

The swelling values for the low-oxygen and oxygen-doped copper specimens are summarized in Table 1, where the swelling levels were calculated based on a pure copper density of 8.9192 g/cm^3. Only one of the oxygen-doped specimens was measured for each of the two irradiation conditions. Significant amounts of swelling were observed in both the oxygen-free and oxygen-doped specimens following irradiation to ~17 dpa at 375 °C (2.3–4.7%) and ~47 dpa at 430 °C (11.9–15.1%). The two swelling levels in the specimens irradiated at 375 °C exhibited considerable variability, which may be partly due to a flux gradient in the below-core basket of MOTA, but which may also reflect some natural variability as often observed at low values of swelling [10]. It is interesting to note that the oxygen-doped copper exhibited slightly lower swelling than the low-oxygen specimens at both irradiation conditions. The amount of swelling in both the low-oxygen and oxygen-doped Johnson–Matthey copper specimens was significantly lower than the 0.5%/dpa trend line observed for several other grades of high-purity copper in previous fast reactor irradiations conducted at 375 and 423–430 °C [10–13].

Table 1
Summary of swelling measured by immersion density on copper TEM disks

Irradiation condition	Material	% Swelling
16.9 dpa, 375 °C	Low-oxygen Cu	2.6
	Low-oxygen Cu	4.8
	Oxygen-doped Cu	2.3
47.3 dpa, 430 °C	Low-oxygen Cu	15.1
	Low-oxygen Cu	14.0
	Oxygen-doped Cu	11.9

A previous 3.6 MeV Fe^+ ion irradiation study performed on the same materials as the present investigation found that void formation did not occur at 375 and 475 °C in the low-oxygen copper for doses up to 17 dpa at a damage rate of $\sim 10^{-3}$ dpa/s, whereas pronounced void swelling (e.g., 5% at 10 dpa, 475 °C) occurred in the oxygen-doped copper [5]. This result is in good agreement with thermodynamic-based calculations [5] which predict that oxygen concentrations of ⩾ 50 appm are needed to stabilize void formation in pure copper at 400 °C if other gases are not present. In contrast, the present results demonstrate that significant cavity swelling has occurred in both the low-oxygen and oxygen-doped copper specimens during neutron irradiation to doses of 17 and 47 dpa.

This difference in behavior between the ion and neutron irradiated specimens might be explained by considering the effects of helium (generated by (n, α) transmutation reactions) on cavity stability. According to a simple energy-minimization model [4] and atomistic calculations [14,15], small amounts of helium greatly enhance the stability of void nuclei compared to stability of planar vacancy clusters. The calculated minimum concentration of helium needed to stabilize the cavities nucleated in neutron-irradiated copper is a strong function of temperature, ranging from ~0.1 appm He at 200 °C to ~0.001 appm He at 400 °C [4]. Using the fast reactor helium generation rate in copper of ~0.1 appm/dpa [16,17], energetically stabilized cavity nuclei would be predicted to occur at doses above ~0.01 dpa for neutron irradiation near 400 °C. Since the cavity population in the low-oxygen copper specimen would be stabilized by helium during the early stages of the neutron irradiation, no difference in the cavity density or size of low-oxygen versus oxygen-doped copper would be expected on the basis of the energy-minimization model [4].

The neutron irradiation void swelling data on as-received and vacuum-remelted copper reported by Yamakawa et al. [7] can also be explained by the oxygen [5] and helium [4] cavity stabilization models. In their study, neutron irradiation at ~330 °C to a dose of ~0.5 dpa resulted in a factor of 10 higher void density in the as-received copper specimens [7]. According to the helium cavity stabilization model [4], a helium concentration of ~0.01 appm is needed to stabilize the void nuclei at this irradiation temperature. This is comparable to the amount of helium which would have been generated during the entire low-dose irradiation (~0.05 appm He), and a reduction in visible cavity density for the low-oxygen samples compared to oxygen-bearing specimens is therefore qualitatively consistent with the model predictions. At higher neutron doses and temperatures (2–8 dpa, 390–420 °C), comparable levels of void swelling were observed by Yamakawa et al. in both as-received and degassed specimens [7]. The predicted amount of helium needed to stabilize cavity formation in neutron-irradiated copper at 400 °C is approximately an order of magnitude smaller than at 330 °C [4]. Therefore, the steady-state cavity density would be predicted to be stabilized in both low-oxygen and oxygen-free copper specimens for doses above ~0.01 dpa at 400 °C, and only minor differences in the cavity swelling would be expected at high doses.

At high oxygen levels, a chemisorbed oxygen layer is predicted to be thermodynamically favored to form on the growing void surfaces [5]. As summarized elsewhere [5], chemisorption of as little as 0.25 monolayer of oxygen on the surface of copper has been found to reduce the bulk surface energy to approximately 1/2 of the clean metal value. The reduction in surface energy associated with the chemisorbed oxygen would stabilize void nucleation and accelerate void growth (particularly at small void sizes), and is a possible contributor to the high swelling commonly observed in irradiated copper.

Using published [18,19] void densities for copper neutron-irradiated near 400 °C ($\sim 4\times10^{17}$ m^{-3}) and the measured void swelling (Table 1), oxygen levels as low as 100 appm could produce ~0.5 monolayer coverage on all of the ~1 μm diameter voids present in the high fluence specimens in the present study. Oxygen chemisorption coverages above one-half monolayer do not cause substantial further decreases in surface energy [5]. It is also worth noting that the effect of surface energy on void growth rate by suppressing vacancy re-emission from cavities is most pronounced for small cavity sizes [20]. Since a significant void swelling enhancement was not observed in the 360 appm oxygen doped specimens compared to the pure copper containing <50 appm oxygen, this implies that oxygen chemisorption-induced reductions in void surface energy are not a significant factor in the void swelling behavior of neutron-irradiated copper near 400 °C. It is possible that the effect of transmutation-produced He on cavity stabilization is dominant compared to oxygen chemisorption surface energy reduction effects for these high-dose, high-temperature irradiation conditions in copper. The physical mechanism responsible for the very high swelling rate (34% after 13.5 dpa, ~2.5%/dpa) [6] observed at 400 °C in neutron-irradiated electrolytic tough pitch copper (800–2000 appm oxygen) still remains to be determined.

4. Conclusions

Significant amounts of cavity swelling were observed in both the low-oxygen and oxygen-doped copper specimens following irradiation to ~17 dpa at 375 °C and ~47 dpa at 430 °C. Oxygen doping up to 360 appm (90 wt ppm) did not significantly affect the void swelling of copper for these irradiation conditions. These results imply that the effect of oxygen chemisorption on void surfaces (with an accompanying reduction in void surface energy) is not a significant factor in the swelling behavior of copper, at least for high-dose neutron irradiation near 400 °C where significant quantities of transmutant helium are produced. The cause of the lower overall swelling in both the low-oxygen and oxygen-doped specimens compared to previous high fluence fast neutron irradiated copper results is uncertain.

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