EFFECT OF INITIAL OXYGEN CONTENT ON THE VOID SWELLING BEHAVIOR OF FAST NEUTRON IRRADIATED COPPER

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OBJECTIVE

The objective of this report is to summarize density measurements on oxygen-free and oxygen-doped copper following high dose fast reactor irradiation.

SUMMARY

Density measurements were performed on high purity copper specimens containing ≤10 wt.ppm and ~120 wt.ppm oxygen following irradiation in FFTF MOTA 2B. Significant amounts of swelling were observed in both the oxygen-free 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.

PROGRESS AND STATUS

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 remelted 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; lower void swelling was observed in vacuum remelted Cu-5%Al specimens whereas no difference was observed for vacuum remelted vs. 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 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.

Experimental Procedure

High purity "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 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, 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 measured to be ≤50 and 360 appm, respectively by vacuum fusion techniques. Other measured impurity concentrations were ≤5 wt.ppm N, 3 wt. ppm Fe and 3 wt. ppm Si.

Two TEM disks each of the low-oxygen and oxygen-doped coppers were irradiated in MOTA-2B of 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). The TEM disks were laser engraved with a 4-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.

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. The 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 [10]. It is interesting to note that the oxygen-doped copper exhibited slightly lower swelling than the low-oxygen Cu 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 at 375 and 423-430°C [10-13].

A previous 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, 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 $\geq$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 can be explained by considering the effects of helium on cavity stability. According to a simple energy-minimization model [4] and atomistic calculations [14,15], small amounts of helium (which would be generated by (n,α) transmutation reactions in neutron-irradiated copper) greatly enhance the stability of void nuclei compared to 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], stabilization of the 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 vs. oxygen-doped copper would be expected on the basis of the energy-minimization model [4].

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

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 under these irradiation conditions. This is comparable to the amount of helium which would have been generated during the low-dose irradiation (~0.05 appm He), and a reduction in visible cavity density 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 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 cavity density would be predicted to be stabilized in both low-oxygen and oxygen-free copper specimens for doses above ~0.1 dpa at 400°C, and only minor differences in the cavity swelling would be expected at high doses.

At very high oxygen levels, it may be possible to produce a chemisorbed oxygen monolayer on the growing void surfaces. The reduction in surface energy associated with the chemisorbed oxygen [5] would accelerate void growth, and is a possible explanation for the very high swelling (34%) observed in electrolytic tough pitch copper following fast reactor irradiation to 13.5 dpa at 400°C [6]. Since the maximum oxygen content investigated in the present study was 350 appm, further work on oxygen-doped copper specimens with oxygen levels comparable to that found in electrolytic tough pitch copper (800-2000 appm) would be necessary to further investigate the effect of very high oxygen contents on void swelling in neutron-irradiated copper.

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