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VOID SWELLING AND PHASE INSTABILITY IN HEAVY ION IRRADIATED Mo-Zr ALLOY

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This paper reports on an investigation into swelling and phase stability in the binary Mo-Zr system under 14 MeV Cu ion irradiation as compared with similar irradiation of pure Mo. The 9.1 at% Zr alloy used contains particles of $\gamma(Mo_2Zr)$ in a saturated Mo-rich matrix. The oversized Zr atoms slow down or eliminate void nucleation in the temperature range 700-900°C, where voids form rapidly in pure Mo. In the alloy at 700°C, voids are suppressed up to 7 dpa, at 800°C they form only after an incubation dose of 6 dpa and even at 900°C, nucleation continues at 6 dpa. However, the growth of voids once nucleated is more rapid than in Mo. Dislocation loops nucleate and grow continuously in the alloy and only at 900°C and 6 dpa does a dislocation network form and inhibit further information. Although the alloy was aged to equilibrium before irradiation, many small additional precipitates of Mo_2Zr formed at the grain boundaries, especially during irradiation, at 900°C. These effects are understandable in terms of vacancy-solute binding for the oversized Zr atoms and this explanation is detailed.

1. INTRODUCTION

Radiation damage in molybdenum and its commercial alloy, TZM, has been widely studied [1]-[3] because of the interest in these materials for use in fusion reactors. Void swelling in TZM produced by heavy-ion or neutron irradiation is lower than that in pure molybdenum. This study was aimed at elucidating the effect of zirconium, one of the major solutes in TZM. A Mo-9.1 at.% Zr alloy was chosen and the damage microstructure produced by 14 MeV copper ion irradiation was studied. The effect of the oversized Zr solute on the nucleation and growth of voids was studied around the threshold temperature for void formation (700 ~ 900°C). The pre-irradiation annealing and heavy-ion bombardment were carried out in the two-phase ($\gamma(Mo_2Zr)$ and molybdenum solid solution) region but close to the phase boundary so that any effects of irradiation on phase stability could be investigated in the same experiment.

2. EXPERIMENTAL PROCEDURE

A Mo-9.1 at.% alloy was prepared by arc melting MARZ grade materials and homogenized at 1650° for 30h under high (10^{-8} torr) vacuum. The samples were then outgassed thoroughly at 1050°C after cutting and electropolishing. Finally, the alloy was equilibrated at the chosen irradiation temperature for ~40 hours under vacuum. The latter two annealing stages lay in the two-phase (Mo-rich solid solution + $\gamma(Mo_2Zr)$) region of the phase diagram.

Typical pre-irradiation microstructures contained γ-precipitates (~1 μm diameter), uniformly distributed in a homogeneous matrix of Mo-rich solid solution. The number density of γ-precipitates is small enough that a large region of matrix (Mo-7.5 at.% Zr between 700°C and 900°C) was available to observe damage structure produced by irradiation. The γ-phase (Mo_2Zr) particles were not transparent to the electron beam, since they were not polished by the polishing solution. The phase diagram [4] indicates that the matrix contained 7.5 at.% Zr. This composition was verified using x-ray microanalysis with reasonable quantitative agreement.

The specimens were irradiated with 14 MeV copper ions with a dose rate at 1 μm from the irradiated surface, where the damage structure was analyzed in the range ~5-8 × 10^{-4} dpa/sec.

3. RESULTS

3.1 Void formation

Void swelling data in the alloy are shown in Figures 1 and 2. No voids were observed in samples irradiated at 700°C up to 7 dpa. At 800°C, voids were observed only at 7 dpa and above, while void swelling was reduced compared to Mo. Zr additions also reduced swelling at low doses (≲ 4 dpa) at 850°C and 900°C, but high void growth rates were observed, resulting in larger swelling than pure Mo at higher doses. In pure Mo [5], voids were observed at all temperatures from 700°C to 1000°C, and the incubation dose for void nucleation, if it existed, was very small. In the alloy, however, void nucleation became difficult, while the void growth rates became relatively high. The incubation doses necessary to observe voids were estimated to be 1.5 dpa at 900°C, 3 dpa at 850°C, and 6 dpa at 800°C. Void formation in the alloy was supressed altogether at 700°C.

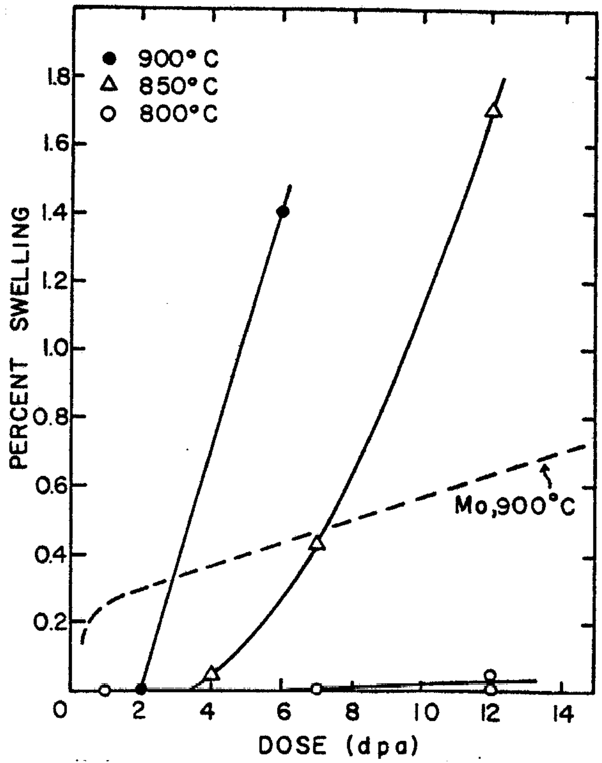

Fig. 1. Irradiation swelling of the Mo-7.5% Zr matrix at 800, 850 and 900°C. The swelling of pure molybdenum at 900°C [5] is included for comparison (dashed line).

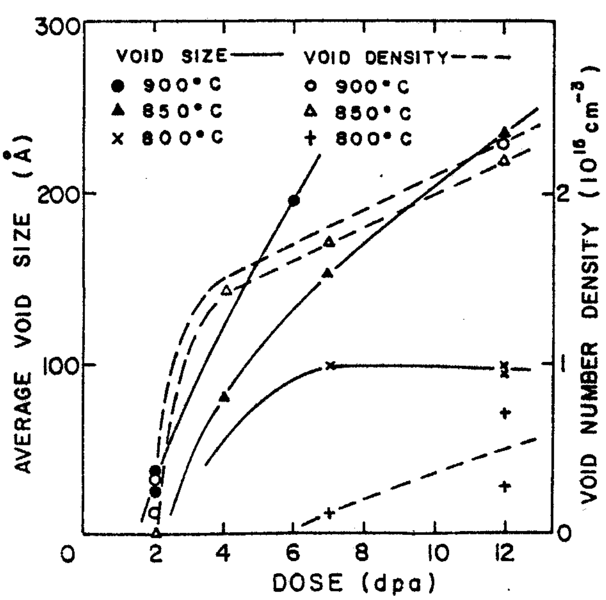

Fig. 2. Void density and average diameter versus dose for the 7.5% Zr matrix.

3.2 Dislocation structure

The addition of Zr to Mo was found to promote dislocation loop formation. A high density of dislocation loops of (~1×10^{16} cm^{-3}) was formed in the alloy in the early stages of irradiation. At 700°C and 800°C, small loop growth rates were observed, except for a few loops which intersected to form network dislocations at higher doses. Because new loops still nucleated as dose increased, the loop density remained approximately constant (1~2×10^{16} cm^{-3}) at 700°C and 800°C, and the variations in the average loop size were within experimental error ($\bar{d}_L \approx 55$ Å at 700°C; $\bar{d}_L \approx 90$ Å at 800°C). At 850°C and 900°C, however, large loop growth rates were observed. At 900°C and 2 dpa, the average loop diameter, $\bar{d}_L$, was 112 Å, and the number density, N_L, was 8×10^{15} cm^{-3}; almost all of these loops grew into a dislocation network ($\rho_d = 2 \times 10^{10}$ cm^{-2}) at 6 dpa. Electron micrographs of typical microstructures observed at 850°C are shown in Figure 3. Analysis of the loop nature was difficult because of the high loop densities and the small sizes. However, some larger loops (200 ~ 300 Å) were analyzed; they were of the interstitial type with $\vec{b}$ = 1/2 <110> which implies that the loops were faulted.

3.3 Radiation induced precipitation at the grain boundary

After irradiation, new precipitate particles were observed at grain boundaries (Figure 4). They were identified to be γ-phase (Mo_2Zr) by electron diffraction. The bright field and dark field micrographs in Figure 4 also show a shifted void denuded zone in the 900°C, 6 dpa sample due to the migration of the grain boundary during irradiation. The formation of γ-particles following migration of the grain boundary can be seen especially in the dark field micrograph. This irradiation induced γ-precipitation was not observed at low angle grain boundaries. At high angle boundaries, the amount of precipitate increased with temperature and dose.

4. DISCUSSION

The effective atomic volume of Zr [4] is 26 percent larger than Mo in the Mo-rich solid solution. Binding between the vacancies and Zr atoms is expected from strain field considerations. It is therefore tempting to ascribe the incubation period for voids to increased interstitial-vacancy recombination. However, the increased total swelling at high dose for the alloy over pure Mo at 850°C and 900°C indicates that this is not the case.

It is more likely that the Zr is gettering a necessary impurity for easy void formation (probably oxygen), so delaying void nucleation. The enchanced void growth rate compared to pure Mo is probably due to the higher dislocation

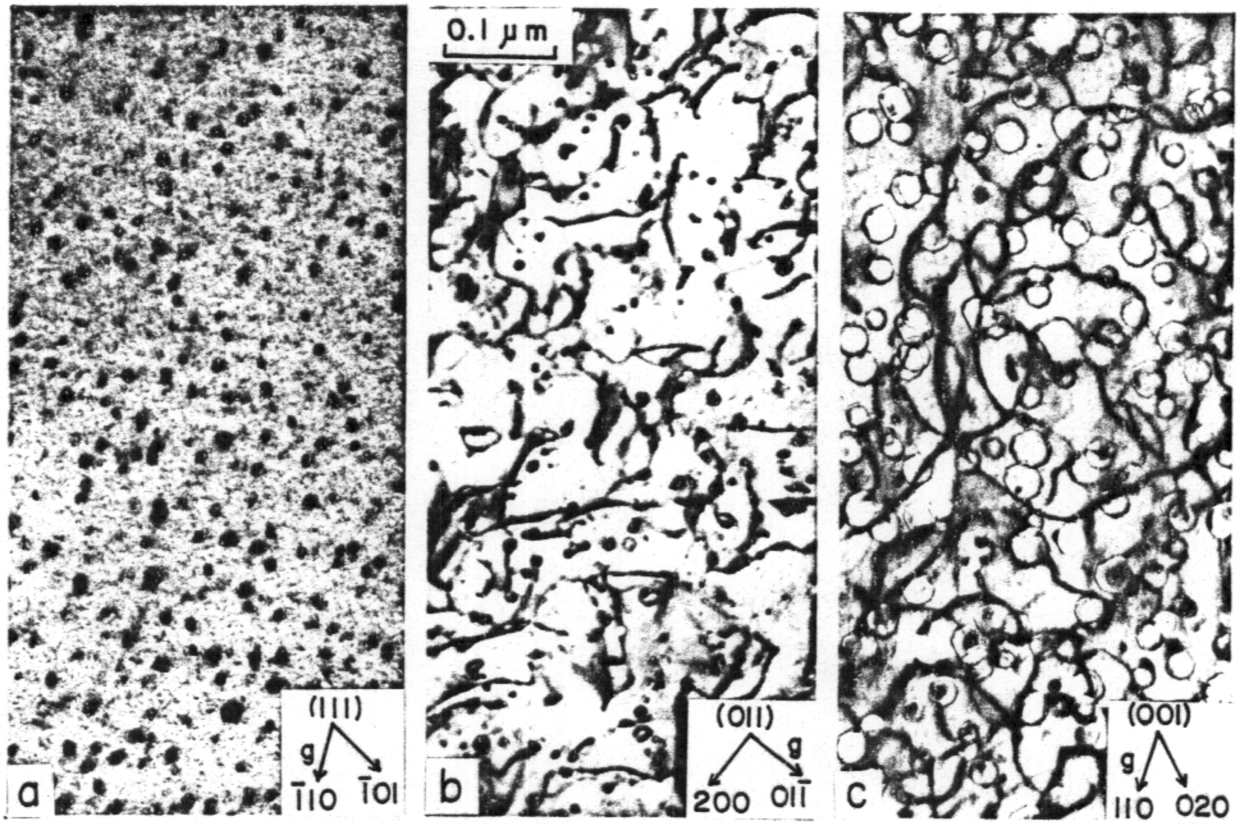

Fig. 3. Microstructural development of the matrix during irradiation at 850°C. a) 0.1 dpa. b) 4 dpa. c) 12 dpa.

density, which provides a larger biased sink strength for the point defects.

The enchanced loop nucleation when Zr is added to the BCC Mo solution is probably due to a reduction in the stacking fault energy, since faulted loops were observed. Loop nucleation becomes easier when the stacking fault energy is reduced but loop glide becomes difficult [6]. This explains the absence of loop "rafting" which is observed in pure Mo [6].

The formation of γ-phase particles on the grain boundaries, which are sinks for point defects, may be explained by radiation-induced solute segregation if a large binding energy between the vacancy and the oversized Zr atom is assumed [7].

Since the alloy was previously equilibrated in the two-phase region, these new precipitate particles imply Zr enrichment of the grain boundary during irradiation. This could be produced by a coupling of either the vacancy or the interstitial flux with a solute flux. The size of Zr suggests that a vacancy coupling is more likely.

5. CONCLUSIONS

The addition of 7.5 at.% Zr to Mo (the saturated solid solution) causes the following changes in radiation damage microstructure.

(1) An incubation period was required for void nucleation (2 dpa at 900°C, 7 dpa at 800°C). This may be due to Zr gettering a gas impurity which stabilizes voids. Total swelling is increased at higher temperatures and doses in the alloy due to the higher dislocation loop density.

(2) Dislocation loop formation was promoted early in the irradiation. Analysis of the larger loops shows that they are faulted ($\underline{b}$ = 1/2 <110>), so that Zr clearly reduces the stacking fault energy and hence eases loop nucleation. Unlike pure Mo, the loops being faulted are not able to glide.

(3) Solute-defect flux coupling effects were observed in the form of incoherent precipitation of γ(Mo_2Zr) at the grain boundaries.

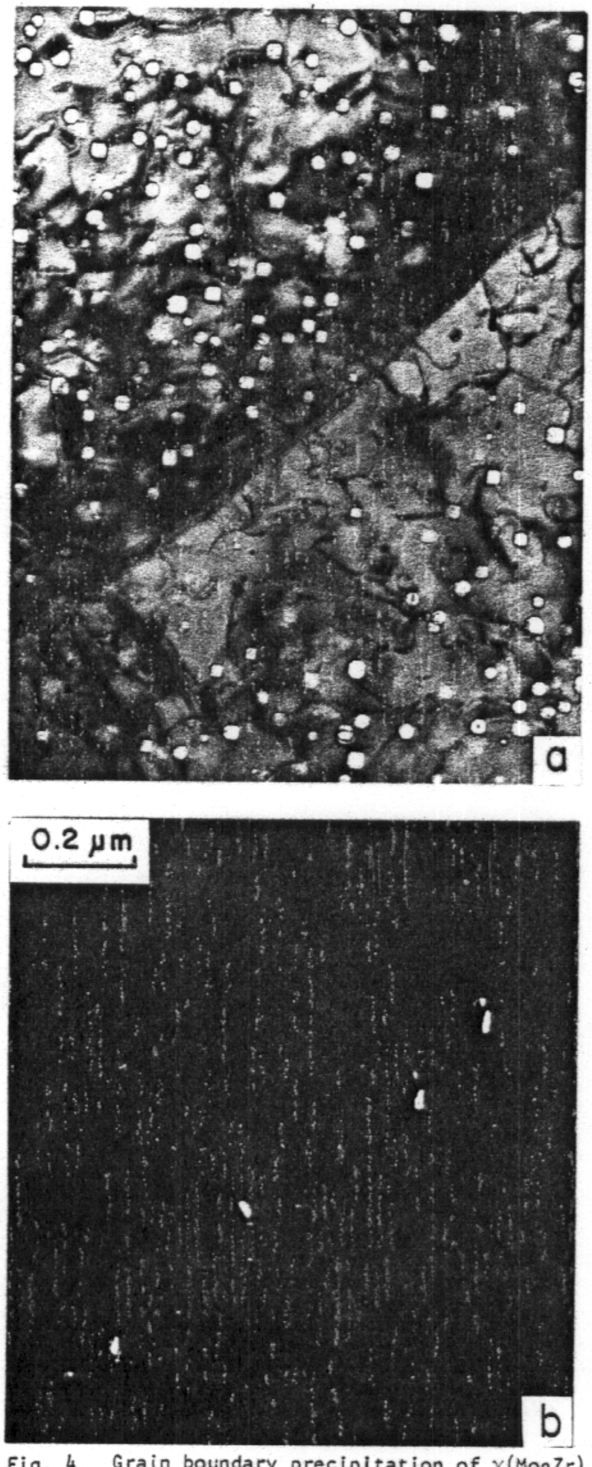

Fig. 4. Grain boundary precipitation of $\gamma(Mo_2Zr)$, a) Bright field and b) dark field, using a precipitate reflection. Note that the boundary has moved during irradiation, causing elongation of the precipitates.

6. ACKNOWLEDGEMENTS

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