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RADIATION-ENHANCED RECRYSTALLIZATION IN COPPER ALLOYS*

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Abstract

Two high-strength copper alloys, cold-worked-and-aged AMZIRC (Cu-Zr) and AMAX-MZC (Cu-Cr-Zr-Mg), were irradiated with 14-MeV Cu ions to a damage level of 10 dpa at temperatures of 100 to 500°C. Cross-section examination of the irradiated foils using electron microscopy revealed signs of irradiation-enhanced recrystallization for irradiation temperatures above 300°C. The recrystallization temperature for both alloys is about 450°C during thermal annealing for a time similar to the ion-irradiation time — 1.5 h. A simplified analysis of the results suggests that the accelerated recrystallization kinetics is due to radiation-enhanced diffusion (RED). This process may restrict the maximum operating temperature of fusion reactor components that incorporate these types of alloys to temperatures as low as 200°C.

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Introduction

Recent studies have shown that ion irradiation causes an acceleration of recovery and recrystallization processes in two high-strength, high-conductivity copper alloys (Cu-Zr and Cu-Cr-Zr-Mg) [1–3]. Such alloys are under consideration for various applications in fusion reactors. There have been several previous observations of radiation-enhanced recrystallization effects in metals following neutron, ion, or electron irradiation [4–10]). The acceleration of the recrystallization process during irradiation has been attributed either to an increase in the grain boundary mobility due to a supersaturation of vacancies and interstitials (radiation-enhanced diffusion) or to an increase in the grain nucleation rate [5,7,8,10]. However, there has been relatively little effort devoted to making quantitative predictions of the magnitude of these effects. It is important to quantitatively determine the effect of irradiation on the lowering of the recrystallization temperature of high-strength copper alloys such as AMZIRC (Cu-Zr) and AMAX-MZC (Cu-Cr-Zr-Mg), since a large portion of their strength is lost when recrystallization occurs [11].

Foils of AMZIRC (Cu-0.15 wt.% Zr) and AMAX-MZC (Cu-0.65% Cr-0.15% Zr-0.04% Mg) were cold-rolled to produce a 90% reduction in thickness and were then aged for 30 min at 375°C and 400°C, respectively. Specimens of both alloys were then irradiated with copper ions to a damage level of 10 dpa (1 μm depth) over the temperature range of 100 to 500°C (0.28 to 0.57 T_m), as described elsewhere [1,2]. The calculated damage rate was 2×10^{-3} dpa/s and the corresponding irradiation time was about 1.5 h. Following the irradiation, the foils were prepared using a cross-section technique [12] and examined in a JEOL 200CX electron microscope.

The degree of radiation-enhanced recrystallization as a function of irradiation temperature may be quantified by making appropriate measurements of the subgrain size in irradiated and nonirradiated regions of the foils. The most common procedure is to measure the grain size using the intercept method. In the present analysis, no distinction was made between the nucleation of subgrains versus grains. Instead, the approach of Vaidya and Ehrlich [9] was adopted where recrystallization is taken to start with the formation of subgrains and to proceed until grain growth processes become important. This approach, therefore, includes the latter portion of the recovery stage as part of the recrystallization process.

Results

Figure 1 shows the change in grain size in the rolling (longitudinal) direction as a function of irradiation temperature for AMZIRC and AMAX-MZC, as determined from TEM measurements. Figure 2 shows the dependence of subgrain area (i.e., the product of the mean normal and longitudinal subgrain dimensions) on irradiation temperature. Both large-angle and small-angle boundaries have been included in the measurements presented in Figs. 1 and 2. It has been proposed that the subgrain area is a better parameter for determining the degree of recrystallization [9]. Measurements on specimens irradiated at the same temperature but at different damage levels ranging from 1 to 40 dpa indicated that there was no dose dependence of subgrain size for this range of damage levels. This is in agreement with another study [6] which found that recrystallization effects in cold-worked copper were independent of neutron fluence for damage levels >0.01 dpa. Figures 1 and 2 show that the subgrain size and area are independent of the ion irradiation temperature over the interval

100 to 300°C for both AMZIRC and AMAX-MZC. The subgrain size in this temperature range is equal to the as-received value (0.4 and 0.34 µm for AMZIRC and AMAX-MZC, respectively).

The subgrain size and area increased following ion irradiation at temperatures greater than 300°C, indicating that recrystallization and grain growth had occurred. Subgrain nucleation was visible in irradiated regions of the foils. The subgrains were generally found along preexisting high-angle grain boundaries. In the absence of irradiation, the subgrain size of both alloys was determined to be constant up to 475°C for a 1 h anneal, with a rapid increase at higher temperatures. Figure 1 (subgrain size) suggests that during ion irradiation AMZIRC begins to recrystallize at ~350°C, while AMAX-MZC does not start to recrystallize until irradiation temperatures of ~450°C are reached. Figure 2 (subgrain area) indicates that recrystallization has started to occur following ion irradiation at 300°C in AMZIRC and 400°C in AMAX-MZC. The latter analysis represents an effective shift in the recrystallization temperature of these two alloys due to ion irradiation of ~75°C for AMAX-MZC and ~150°C for AMZIRC.

The grains formed during radiation-enhanced recrystallization of AMZIRC and AMAX-MZC were generally not equiaxed, but instead were elongated in the rolling direction. This is in contrast to the general observation of equiaxed grains following thermal-activated recrystallization [10]. Measurements of the grain size in cross section provided results on the longitudinal (ℓ) and normal (z) components of the grain size (the z direction is perpendicular to the rolling plane — i.e., at right angles to the longitudinal and transverse directions). The cross-section grain size ratio (ℓ/z) decreased slightly with increasing irradiation temperature. The AMAX-MZC subgrains were closer to being equiaxed ($\ell/z = 1$) than the AMZIRC subgrains. The values of ℓ/z for the as-received, 100°C irradiated, and 400°C irradiated cold-worked-and-aged alloys were (2.6, 2.6, 2.3) for AMZIRC and (2, 2, 1.5) for AMAX-MZC. Some of the anisotropy in grain size in the present case may also be due to the experimental conditions — the irradiated zone in which radiation-enhanced recrystallization occurred was essentially unlimited in the longitudinal and transverse directions, but it extended only 2 to 3 µm in the z direction.

Analysis

A quantitative prediction of the shift in the recrystallization temperature (ΔT_R) during irradiation may be made by assuming that the acceleration of recrystallization kinetics is solely due to radiation-enhanced diffusion (RED) as discussed below. The radiation-enhanced diffusion coefficient is given by $D = D_v C_v + D_i C_i$, where $D_{v,i}$ is the diffusivity of vacancies or interstitials and $C_{v,i}$ is the corresponding point defect concentration [13]. This neglects the small contribution of higher order defect configurations such as divacancies to the overall diffusion coefficient. The term $D_v C_v$ is the irradiation analog of the thermal self-diffusion coefficient ($D_v C_v^e$) for diffusion via a vacancy mechanism. It is called the radiation-enhanced self-diffusion coefficient in this paper.

The value of D was determined from a calculation of the steady-state point defect concentration during irradiation of copper using standard rate theory equations [14]. The material parameters of pure copper [15] were used in the calculation. The steady-state point defect concentrations are dependent on the strength of the various sinks present in the matrix, such as dislocations. The present calculation used temperature-dependent dislocation densities that have been observed in pure copper [16,17] following neutron or ion irradiation (Table 1). Figure 3 shows the calculated temperature-dependent self diffusion coefficient (D_vC_v or $D_vC_v^e$) of copper for conditions appropriate to ion irradiation (2×10^{-3} dpa/s), neutron irradiation (1×10^{-6} dpa/s), and thermal annealing. Only the vacancy contribution to the radiation-enhanced diffusion coefficient (i.e., D_vC_v) is given in this figure.

The predicted shift in recrystallization temperature during irradiation, as applied to copper alloys, may be obtained as follows: The recrystallization temperature of AMZIRC and AMAX-MZC for a 1 h thermal anneal is about 475°C [11]. The thermal self-diffusion coefficient of copper at this temperature is about 3×10^{-19} m^2/s (Fig. 3). During ion irradiation at 2×10^{-3} dpa/s, the calculations in Fig. 3 show that the radiation-enhanced self-diffusion coefficient equals 3×10^{-19} m^2/s when the irradiation temperature is about 300°C. The shift in the recrystallization temperature of the two copper alloys due to ion irradiation is therefore predicted to be $\Delta T_R \simeq 180$°C.

Neutron irradiation at 1×10^{-6} dpa/s has no effect on the self-diffusion coefficient for irradiation temperatures above 420°C due to a low vacancy supersaturation at high temperatures for this dose rate (Fig. 3). The recrystallization temperature of AMZIRC and AMAX-MZC for a 2-year anneal is estimated to be <350°C [11], which corresponds to a thermal self-diffusion coefficient of about 4×10^{-22} m^2/s. From Fig. 3, the predicted recrystallization temperature of these alloys during a 2-year neutron irradiation at 10^{-6} dpa/s is about 250°C (ΔT_R = 100°C).

The results of a recent study suggest that interstitials may also have an effect on grain boundary migration [18]. The inclusion of interstitial diffusion in the RED calculation increases the radiation-enhanced diffusion coefficient by about a factor of 2. This leads to a predicted shift in the recrystallization temperature during irradiation that is ~50°C larger than shown in Fig. 3 for both neutron and ion irradiation conditions.

Discussion

The microstructural changes that occur during high-temperature annealing of a cold-worked metal are generally divided into four (or more) overlapping stages: Recovery (dislocation rearrangement), subgrain nucleation, subgrain coalescence (formation of high-angle grain boundaries), and grain growth [10,19,20]. Despite the fundamental importance of recrystallization, the physical mechanisms that control its behavior are still not well known [20]. However, certain isolated steps in the recrystallization process have been characterized.

It is well established that recrystallization requires a sufficiently large driving force in combination with adequate atomic mobility in order to proceed [7,8,10]. Irradiation tends to increase the nucleation driving force of recrystallization by creating defect clusters in the lattice. The atomic mobility is also increased during irradiation due to a supersaturation of point defects (radiation-enhanced diffusion). Recent research using electric current pulses has shown that an increase in the mobility of dislocations (which is also enhanced during irradiation) causes an appreciable enhancement in the recrystallization rate of metals [21]. In addition, theoretical studies indicate that the kinetics of dislocation absorption by subgrain boundaries (i.e., subgrain nucleation) is controlled during irradiation by the radiation-enhanced diffusion coefficient, D, as opposed to the thermal self-diffusion coefficient, $D_vC_v^e$, [22,23]. All of the preceding processes, which taken together comprise the initial stages of recrystallization, are therefore enhanced in the presence of irradiation as a direct consequence of radiation-enhanced diffusion.

Previous studies have suggested that grain boundary mobility in the absence of irradiation is directly related to the vacancy concentration in the matrix [5,7,10]. On the other hand, the driving force for grain boundary migration is apparently due to the difference in the chemical potential across the boundary [24,25]. Irradiation increases the point defect chemical potentials on both sides of a grain boundary by equal amounts in the absence of stress effects. This implies that subgrain growth may not be strongly affected by radiation-enhanced diffusion (RED). In summary, it appears that RED should enhance recrystallization kinetics during the initial stages, whereas it may not have a strong effect on the latter stages of recrystallization.

The predicted shift in the recrystallization temperature of AMZIRC due to ion irradiation (Fig. 3) is in reasonable agreement with the actual observations (Fig. 2). In particular, the predicted and observed recrystallization temperatures for AMZIRC during ion irradiation are both about the same, 300°C. The results for AMAX-MZC are not in as close agreement; the predicted and observed recrystallization temperatures are 300 and 400°C, respectively. The discrepancy between the predicted and observed radiation-enhanced recrystallization temperature of AMAX-MZC is probably due to the neglect of solute/precipitate effects in the recrystallization calculations. For example, the radiation-enhanced diffusion calculations do not take into account point defect-solute trapping effects, which would increase recombination and lessen the effect of irradiation on diffusion. This results from the lowering of the free defect concentrations C_v and C_i by recombination of free defects with a large population of trapped defects of the opposite type. Vaidya and Ehrlich [9] found that slight variations in the composition of irradiated stainless steel resulted in a spectrum of recrystallization stages that ranged from unrecrystallized to completely recrystallized. In the present case, AMZIRC is a simple binary alloy containing 0.15% Zr, whereas AMAX-MZC is a quaternary alloy containing 0.65% Cr, 0.15% Zr, and 0.04% Mg. If solute-defect trapping effects were taken into account in the calculation, it is possible that the shift in recrystallization temperature might be better correlated with the total radiation-enhanced diffusion coefficient, $D_vC_v + D_iC_i$, instead of the vacancy component D_vC_v.

Examination of the damage microstructure of the two alloys following irradiation at different temperatures indicated that recrystallization is initiated in both AMZIRC and AMAX-MZC at temperatures of ~300°C (i.e., subgrain nucleation occurs). However, the coalescence and growth of these subgrains during irradiation occurs at a slower rate in AMAX-MZC than in AMZIRC (Fig. 2). This results in a sluggish recrystallization response of AMAX-MZC that is maintained up to irradiation temperatures of 500°C. Chromium and magnesium are both oversized solutes in copper [26] and are expected to migrate away from vacancy sinks such as grain boundaries during irradiation (vacancy inverse Kirkendall effect). It has been observed that solutes which segregate away from grain boundaries act to strongly retard grain growth [10,27]. Therefore, it appears that irradiation enhances the recovery stage in AMAX-MZC (subgrain formation), but retards subgrain coalescence and subsequent grain growth.

Thermal annealing studies of AMZIRC and AMAX-MZC have shown that the yield strength of these alloys decreases by about 50% (from 450 to 200 MPa) when recrystallization occurs [11]. Neutron irradiation studies of AMZIRC and AMAX-MZC have found that their yield strengths decreased by 25 to 40% compared to thermal-annealed control specimens following irradiation to 10 to 15 dpa at temperatures of 450°C [28] and 385°C [29]. Recent microhardness measurements have indicated that ion irradiation of AMZIRC at 400°C produces a substantial (~40%) decrease in its yield strength as a direct result of radiation-enhanced recrystallization [30]. Many of the proposed applications for high-strength copper alloys in fusion devices require operation at irradiation temperatures of 100 to 350°C for several years. The predicted recrystallization temperature of AMZIRC and AMAX-MZC for a 2-year neutron irradiation (10^{-6} dpa/s) is about 250°C, according to Fig. 3. The softening effects associated with recrystallization in these two alloys may prohibit their use in fusion reactor components that operate at temperatures of >250°C. Radiation hardening effects will be important in copper-base alloys for irradiation temperatures <250°C [31], and this may offset any strength decrease due to recrystallization in this temperature regime.

Conclusions

The shift in the recrystallization temperature of AMZIRC and AMAX-MZC during ion irradiation may be qualitatively explained by considering the effect of radiation-enhanced diffusion. The recrystallization temperature of these alloys under long-term neutron irradiation conditions is predicted to be <250°C. This may limit their applicability in fusion devices to rather low temperatures, since their high strength is not retained following recrystallization. The solutes and/or precipitates in irradiated AMAX-MZC tend to retard the growth of subgrains and grains, which leads to a higher recrystallization temperature than that observed for AMZIRC during irradiation.

Acknowledgments

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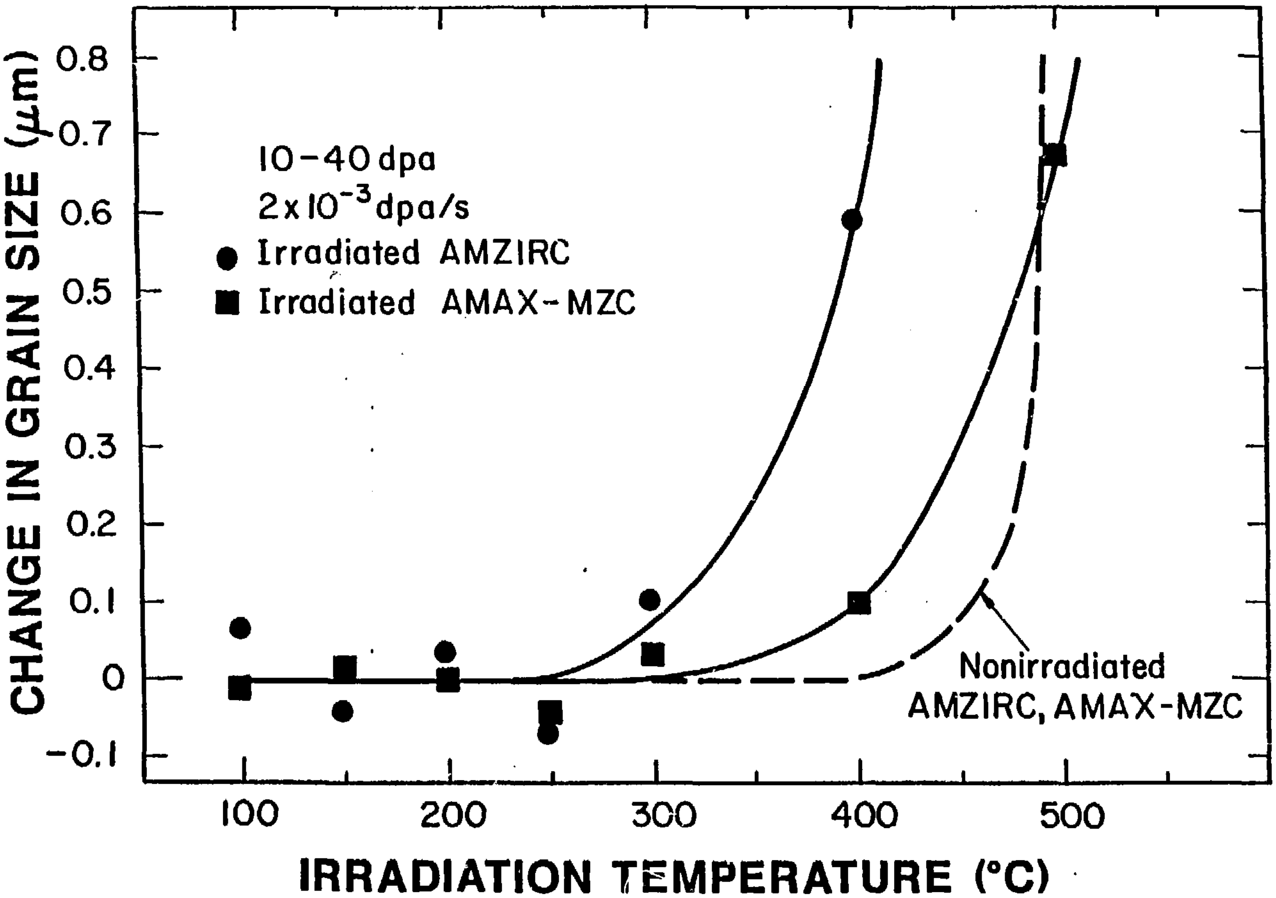
Table 1. Temperature-dependent sink strengths used to calculate radiation-enhanced diffusion in copper (from refs. [16,17])

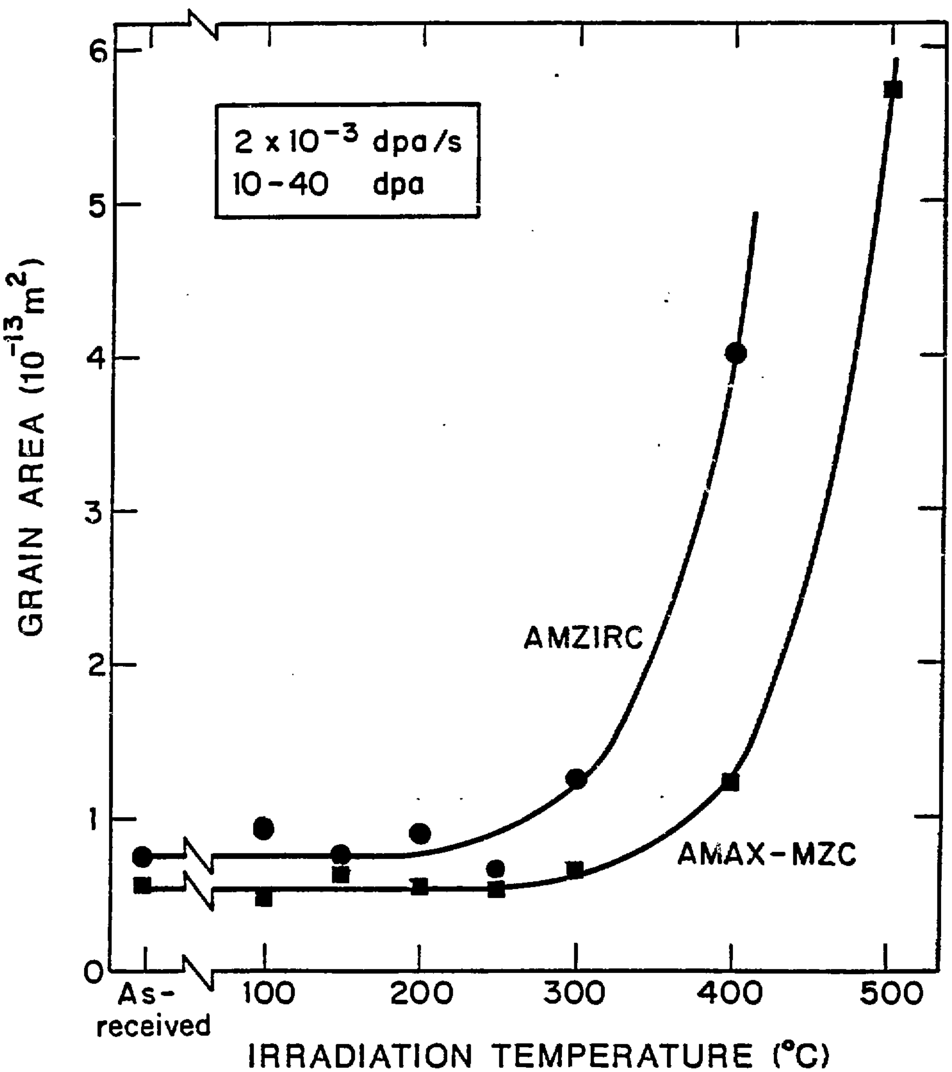
Temperature (°C)	Dislocation density (m^{-2})	
	2×10^{-3} dpa/s	1×10^{-6} dpa/s
50–200	2×10^{15}	1×10^{15}
250	1×10^{15}	4×10^{14}
300	7×10^{14}	6×10^{13}
350	3×10^{14}	3×10^{13}
400	1×10^{14}	3×10^{13}
450	3×10^{13}	3×10^{13}
500	1.5×10^{13}	1.5×10^{13}
550	1×10^{13}	1×10^{13}

Fig. 1. Longitudinal grain size of cold-worked-and-aged copper alloys versus irradiation temperature. The initial grain sizes were 0.4 and 0.34 μm for AMZIRC and AMAX-MZC, respectively.

Fig. 2. Area of an average grain ~~area~~ (including subgrains) in cold-worked-and-aged copper alloys versus irradiation temperature. Note that the grain/subgrain area is constant for irradiation temperatures below 300°C, with a value equal to that of the as-received material.

Fig. 3. Predicted shift in the recrystallization temperature of copper alloys due to radiation-enhanced diffusion.


10-40 dpa
2x10^-3 dpa/s
Irradiated AMZIRC
Irradiated AMAX-MZC
Nonirradiated
AMZIRC, AMAX-MZC
CHANGE IN GRAIN SIZE (μm)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
100
200
300
400
500
IRRADIATION TEMPERATURE (°C)


2 x 10^-3 dpa/s
10-40 dpa
AMZIRC
AMAX-MZC
GRAIN AREA (10^-13 m^2)
0
1
2
3
4
5
6
As-received
100
200
300
400
500
IRRADIATION TEMPERATURE (°C)

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