Ion Irradiation of High Strength, High Conductivity Copper Alloys at Fusion-Relevant Temperatures

S.J. Zinkle, R.A. Dodd and G.L. Kulcinski

November 1984

UWFDM-605

Presented at the First International Conference on Fusion Reactor Materials, Tokyo, Japan, 3-6 December 1984; to be published in J. Nucl. Materials.

FUSION TECHNOLOGY INSTITUTE

UNIVERSITY OF WISCONSIN

MADISON WISCONSIN

Ion Irradiation of High Strength, High Conductivity Copper Alloys at Fusion-Relevant Temperatures

S.J. Zinkle, R.A. Dodd and G.L. Kulcinski

Fusion Technology Institute
University of Wisconsin
1500 Engineering Drive
Madison, WI 53706

http://fti.neep.wisc.edu

November 1984

UWFDM-605

Presented at the First International Conference on Fusion Reactor Materials, Tokyo, Japan, 3-6 December 1984; to be published in J. Nucl. Materials.

ION IRRADIATION OF HIGH STRENGTH, HIGH CONDUCTIVITY COPPER ALLOYS AT FUSION-RELEVANT TEMPERATURES†

S.J. Zinkle, R.A. Dodd and G.L. Kulcinski

Fusion Technology Institute
1500 Johnson Drive
University of Wisconsin-Madison
Madison, Wisconsin 53706

December 1984

UWFDM-605

†Presented at the First International Conference on Fusion Reactor Materials, Tokyo, Japan, 3-6 December 1984. Proceedings to be published in J. Nucl. Mater.

ION IRRADIATION OF HIGH STRENGTH, HIGH CONDUCTIVITY COPPER ALLOYS AT FUSION-RELEVANT TEMPERATURES

S.J. Zinkle, R.A. Dodd and G.L. Kulcinski

Fusion Technology Institute
University of Wisconsin
Madison, Wisconsin 53706, USA

Abstract

The microstructures of two commercial high strength, high conductivity copper alloys have been examined by transmission electron microscopy (TEM) following heavy ion irradiation. Both alloys were found to be resistant to microstructural changes over the temperature range of 100-250°C and peak damage levels of 40 dpa. There is no observable void formation in either of the as-received alloys following single ion irradiation to 40 dpa over a wide temperature range (100-550°C). The absence of voids may be due to the lack of gaseous nucleating agents in these alloys. Black spot damage has been observed for irradiation temperatures of 100-250°C. It is concluded that the high strength of these alloys will be retained following irradiation at temperatures below 250°C, or perhaps even increased due to radiation hardening effects.

Introduction

High strength, high conductivity copper alloys are currently being considered for a variety of applications in proposed fusion reactors, ranging from high magnetic field insert coils for superconducting magnets to divertors, limiters, and r.f. antennas [1]. There are several commercial copper alloys which have unirradiated physical properties that make them suitable for consideration in several fusion reactor applications. However, it is uncertain as to what degree of degradation of material properties, if any, will occur in these alloys following irradiation.

A recent investigation of two high strength, high conductivity copper alloys (AMZIRC and AMAX-MZC) following high temperature (400-550°C) ion irradiation determined that the main radiation effect was an acceleration of the recrystallization process [2]. It was concluded that this irradiation effect might make these alloys unsuitable for fusion reactor applications, since much of their strength is lost upon recrystallization. However, this study [2] only investigated a limited temperature regime, which is at or above the upper limit for fusion reactor applications [1,2]. To date, there are no known irradiation data [3] for any high strength, high conductivity copper alloys at conditions similar to the environment they may experience in a fusion reactor, i.e. 50-400°C, 1-100 dpa. The object of the present study is to investigate the microstructures of two copper alloys following heavy ion irradiation at fusion-relevant conditions: 100-250°C, 40 dpa peak damage level.

Experimental Procedure

The composition and measured physical properties [2,4] of AMZIRC and AMAX-MZC are given in Table 1. The base material for the alloys is oxygen free, high conductivity (OFHC) copper [5]. The alloy preparation consisted of a solution anneal at 900°C for 1 hr, followed by 90% cold-rolling and then aging for 0.5 hr at 375°C for the AMZIRC alloy and 400°C for the MZC alloy. Prior to their irradiation, specimens from both alloys were mechanically polished and then electropolished at an applied potential of 5 V in a solution of 33% HNO_3/67% CH_3OH cooled to -45°C. The alloys were irradiated with 14-MeV Cu^{3+} ions using the University of Wisconsin tandem Van de Graaf accelerator. All samples were irradiated to a fluence of 3×10^{20} ions/m^2 with an ion flux of 6×10^{16} ions/m^2-s. The BRICE code [6] was used to calculate the depth-dependent displacement damage. Table 2 lists the irradiation conditions for the samples. A damage efficiency of K = 0.8 was used in the dpa calculations, although recent work indicates that $K \approx 0.3$ is more appropriate for fast neutrons and heavy ions [7].

Following irradiation, the samples were prepared for cross-section analysis using techniques which are described in detail elsewhere [8]. The cross-section specimens were jet-electropolished in a solution of 33% HNO_3/67% CH_3OH cooled to -20°C at an applied voltage of 15-20 V, and were examined in a JEOL TEMSCAN-200CX electron microscope.

Results

Radiation-enhanced recovery, but not recrystallization, was observed in both AMZIRC and AMAX-MZC over the entire temperature range of 100-250°C. Figure 1 shows the effect of 250°C irradiation on the microstructure of AMAX-MZC. The cross-section micrograph at the top allows the scale of the radiation damage region to be noted, with both irradiated and non-irradiated portions of the foil observable. The bottom two micrographs show the irradiated and non-irradiated regions of the foil at higher magnification. Partial recovery of the cold-worked dislocation structure has occurred in the irradiated region of the foil, while the unirradiated microstructure remains similar to that of the as-received alloy. Subgrain development is observed to be more advanced in the damage region compared to the control. A third feature is the appearance of small "black spots" in the irradiated regions of the foil. Similar results were obtained for the AMZIRC alloy irradiated under the same conditions.

The irradiated microstructures of both alloys showed very little temperature dependence for 250°C > T_{irr} > 100°C. Figure 2 shows the microstructures of AMZIRC and AMAX-MZC following irradiation at 100°C. Once again, some of the cold-worked dislocation structure has recovered during irradiation. Indications of subgrain nucleation are visible in both micrographs. Both alloys contain a high density of small black spots. There was no observable void formation in either alloy for the irradiation conditions used in this study (Table 2).

The subgrain size in the longitudinal direction for the irradiated copper alloys (determined by TEM) is given in Fig. 3 as a function of irradiation temperature. Data from previous high-temperature irradiations [2] have been included in this figure. The subgrain size is independent of irradiation temperature over the interval 100-300°C for both AMZIRC and AMAX-MZC, and is equal to the measured non-irradiated value (0.4 μm, 0.34 μm for AMZIRC and AMAX-MZC, respectively). The AMZIRC alloy has a slightly larger subgrain size than MZC and it recrystallizes at a lower irradiation temperature (400°C vs. 500°C). There was no apparent dependence of subgrain size on fluence for damage levels of 1-40 dpa. Representative microstructures of AMAX-MZC following ion irradiation to 10 dpa at three different temperatures are shown in Fig. 4.

Discussion

AMZIRC and AMAX-MZC appear to have quite similar responses to moderately high ion irradiation doses over the temperature range of 100-250°C. This is in contrast to their high temperature irradiation behavior, where AMAX-MZC exhibited more pronounced microstructural changes as compared to AMZIRC [2]. The microstructures of both alloys are quite stable against ion radiation-induced changes for irradiation temperatures of 100-250°C. It is seen from Fig. 3 that the irradiated subgrain size of both alloys is constant over this temperature range, with a value equal to the non-irradiated size. It is therefore concluded that there are no radiation-enhanced recrystallization processes occurring in the present case even though some recovery of the dislocation structure has occurred following irradiation for both AMZIRC and AMAX-MZC.

There was no observable void formation in either of the as-received copper alloys following single ion irradiation at 100-250°C. A previous single ion irradiation study of these alloys in their as-received condition at higher temperatures also did not detect any voids [2]. Therefore, no voids have been observed in as-received AMZIRC or MZC specimens following single ion irradiation to peak damage levels of 40 dpa over the wide temperature range of 100-550°C (0.28-0.61 T_m). On the other hand a recent investigation of copper alloys irradiated at 450°C with fast neutrons has found that 1% swelling occurs in MZC following irradiation to 16 dpa, compared with 6.5% swelling in pure annealed copper [9]. One possible reason for the lack of observable void formation in these alloys following ion irradiation is the absence of gaseous nucleating agents (both alloys are fabricated from oxygen free copper in a carefully controlled environment). Previous charged particle irradiation studies on pure copper have shown that degassed, low oxygen content foils exhibit a substantial reduction in void swelling compared to non-degassed foils, and the peak swelling temperature is decreased [10,11].

Elasticity [12] and molecular dynamics [13] calculations on the morphology of small vacancy clusters in copper have found that stacking fault tetrahedra (SFT) and small faulted dislocation loops are more stable configurations than voids. Vacancy clusters in the form of SFT have recently been observed in copper following a 100°C electron irradiation [14]. Therefore, it is possible that gas may be required for void formation to occur in copper. Additional dual ion or gas preinjection irradiation experiments are needed to address this possibility. McLaurin has recently demonstrated that high purity aluminum does not form voids over a wide range of experimental conditions, while aluminum containing as little as 0.1 appm He swells readily [15].

A second possible explanation for the lack of voids in the as-received copper alloys is that the high dislocation density which is initially present may be delaying the onset of void formation. To investigate this issue, samples of both alloys that were solution annealed and aged without any cold-working were irradiated with 14 MeV Cu ions at temperatures 100-400°C. No void formation was observed for peak damage levels of 40 dpa [16].

A review of the literature reveals that copper alloys exhibit either enhanced or suppressed void swelling compared to pure copper, depending on the identity of the solute [3]. For example, no void formation has been observed in Cu-Be containing greater than 0.1 at % Be following electron or ion irradiation (dose levels up to 100 dpa). It is possible that the solutes and precipitates present in AMZIRC and AMAX-MZC (Table 1) are extending the incubation fluence for void formation to high values in the absence of gas. Since injected interstitial effects may suppress void nucleation and growth in the peak damage region for ion irradiations [17], only damage regions which are distant from the damage peak are suitable for quantitative investigations of void swelling. In the present case (14 MeV ions), one may use with confidence only the void data obtained at depths $\lesssim 1$ μm (i.e. 1 μm away from the peak damage region). The maximum damage level applicable to quantitative void swelling analysis in this investigation is therefore about 10 dpa. In summary, we have determined that the incubation fluence for observable void swelling in AMZIRC and AMAX-MZC in the absence of gas is at least 10 dpa.

Microhardness and tensile measurements on as-received and annealed AMZIRC and AMAX-MZC have shown that both alloys suffer a severe loss in strength when recrystallization occurs [4]. Therefore, these alloys are unsuitable for any high strength fusion reactor applications that may result in recrystallization. We have recently estimated the long-term recrystallization temperature of AMZIRC and MZC to be 320°C [4]. Irradiation and applied stress are known to decrease the recrystallization temperature [2]. However, the present results (Fig. 3) indicate that there is no radiation-enhanced recrystallization in AMZIRC or MZC at damage levels up to 40 dpa for irradiation temperatures below 300°C. It may therefore be concluded that, in the absence of large stress effects, both of these alloys are structurally suitable as a high strengh fusion reactor material for irradiation temperatures less than 300°C.

Irradiation of copper and copper alloys below 300°C results in the creation of small defect clusters (black spots) [3], similar to those visible in Figs. 1 and 2. These defect clusters are believed to be responsible for the hardening that occurs in copper and its alloys following irradiation at temperatures $\lesssim$ 300°C [18]. Previous TEM studies of ion and neutron irradiated copper found that the cluster density is constant for irradiation temperatures of 50-250°C, with a much lower density at higher irradiation temperatures [19]. Measured defect cluster densities following low-temperature ion or neutron irradiation to high doses range from $10^{22}/m^3$ to greater than $10^{25}/m^3$ [3,20,21]. Our observations are in agreement with these literature results--the density ($\gtrsim 10^{23}/m^3$) and size (3 nm diameter) of the black spots found in the ion-irradiated AMZIRC and AMAX-MZC specimens are roughly constant over the temperature range 100-250°C.

Neutron irradiation of copper and its alloys to fluences greater than $10^{23} n/m^2$ ($\sim 10^{-2}$ dpa) results in a saturation of radiation hardening [22-24]. The increase in yield strength due to irradiation of pure copper is about 300 MPa, and the total yield strength at saturation is about 350 MPa. In general, single phase copper alloys exhibit a smaller radiation-induced increase in yield strength at saturation, but their total yield strength ($\sigma_y \sim$ 350-450 MPa) is greater than that for irradiated pure copper [23,24]. Therefore the strength of irradiated AMZIRC and AMAX-MZC may be expected to increase over the non-irradiated values for irradiation below 250°C.

Cold work prior to irradiation reduces the amount of radiation-induced strengthening in copper, but the total yield strength can be substantially larger than that for irradiated annealed copper [22,25]. For modest cold work levels, the measured yield strength has been proposed to be of the form [25]

$$\sigma_y = (\sigma_{irr}^2 + \sigma_{cw}^2)^{1/2} \quad (1)$$

where σ_{irr} and σ_{cw} are the yield stress levels due to irradiation and cold work, respectively. At very high cold work levels, it is possible that the yield strength may decrease slightly following irradiation [26]. Hence, this cold work effect can cause either an increase or decrease in the yield strength.

Conclusions

No voids have been observed in cold worked plus aged AMZIRC and AMAX-MZC copper alloys following single ion irradiation to calculated peak damage levels of 40 dpa at temperatures of 100-550°C (0.28-0.61 T_m). The absence of void formation is attributed to a lack of gaseous nucleating agents.

Both alloys are resistant to microstructural changes for irradiation temperatures of 100-250°C, but we cannot conclusively determine from our microstructural observations whether the strength of AMZIRC and MZC will increase, stay the same, or decrease following low temperature irradiation.

Acknowledgements

This work was performed under appointment to the Magnetic Fusion Technology Fellowship Program and with funds supplied by the Office of Fusion Energy, United States Department of Energy.

References

1. F.W. Wiffen and R.E. Gold (Eds.), Copper and Copper Alloys for Fusion Reactor Applications, DOE-OFE Workshop Proceedings (Oak Ridge National Laboratory, CONF-830466, June 1984).

2. S.J. Zinkle, R.A. Dodd and G.L. Kulcinski, "Comparison of Thermal and Irradiated Behavior of High Strength, High Conductivity Copper Alloys", 12th Intern. Symp. on the Effects of Radiation on Materials, June 1984, Williamsburg, VA, F.A. Garner and J.S. Perrin, Eds., ASTM STP 870.

3. S.J. Zinkle and R.W. Knoll, "A Literature Review of Radiation Damage Data for Copper and Copper Alloys", University of Wisconsin Fusion Technology Institute Report UWFDM-578, June 1984.

4. S.J. Zinkle, D.H. Plantz, A.E. Bair, R.A. Dodd and G.L. Kulcinski, "Correlation of the Yield Strength and Microhardness of High Strength, High Conductivity Copper Alloys", First Intern. Conf. on Fusion Reactor Materials, Tokyo, Dec. 1984.

5. Interim Publications on AMZIRC and AMAX-MZC Copper Alloys, AMAX Copper Inc., New York, NY (1982).

6. D.K. Brice, Sandia National Laboratory Report SAND75-0622, July 1977, Albuquerque, NM.

7. R.S. Averback, R. Benedek and K.L. Merkle, Phys. Rev. B 18 (1978) 4156-4171 and J.H. Kinney, M.W. Guinan and Z.A. Munir, J. Nucl. Mater. 122/123 (1984) 1028-1032.

8. S.J. Zinkle and R.L. Sindelar, "Preparation of Ion-Irradiated Foils for Cross-Section Analysis", DAFS Quarterly Progress Report DOE/ER-0046/18, (August 1984) 133-141.

9. H.R. Brager, H.L. Heinisch and F.A. Garner, "Effects of Neutron Irradiation at 450°C and 16 dpa on the Properties of Various Commercial Copper Alloys", these proceedings.

10. L.D. Glowinski, J. Nucl. Mater. 61 (1976) 8-21.

11. L.D. Glowinski and C. Fiche, J. Nucl. Mater., 61 (1976) 22-28.

12. J.A. Sigler and D. Kuhlmann-Wilsdorf in The Nature of Small Defect Clusters, Vol. 1 (Consultants Symp.), M.J. Makin, Ed., Harwell Report AERE R5269, July 1966 pp. 125-143.

13. N.V. Doan, in Point Defects and Defect Interactions in Metals, J-I Takamura, M. Doyama and M. Kiritani, Eds. (University of Tokyo Press, 1982), p. 722.

14. H. Fujita, T. Sakata and H. Fukuyo, Jap. J. Appl. Physics 21 (1981) L235-6.

15. S.K. McLaurin "Radiation Damage from Heavy Ion Bombardment in High Purity Aluminum", Ph.D. Thesis, University of Wisconsin-Madison, Jan. 1984.

16. S.J. Zinkle and G.L. Kulcinski, to be published.

17. B. Badger Jr., et al., "Experimental Investigation of the Effect of Injected Interstitials on Void Nucleation, 12th Intern. Symp. on Effects of Radiation on Materials, Williamsburg, VA, 1984, ASTM STP 870, F.A. Garner and J.S. Perrin, Eds.

18. N.M. Ghoniem, J. Alhajji and F.A. Garner, in Effects of Radiation on Materials: Eleventh Conf., ASTM STP 782, H.R. Brager and J.S. Perrin, Eds. (ASTM, 1982) 1054-1072.

19. B.L. Eyre and C.A. English, in Point Defects and Defect Interactions in Metals (University of Tokyo Press, 1982) 799.

20. B.L. Eyre, J. Phys. F: Metal Phys 3 (1973) 422.

21. J. Narayan, O.S. Oen and T.S. Noggle, J. Nucl. Mater. 71 (1977) 160-170.

22. M.J. Makin, in Radiation Effects, Metallurgical Society Conf. 37, Asheville, N.C., W.F. Sheely, Ed. (Gordon and Breach, 1967) 627.

23. I.A. El-Shanshoury, J. Nucl. Mater. 45 (1972/73) 245-257.

24. H.G. Mohamed, A.M. Hammad and F.H. Hammad, Trans. Indian Inst. Metals 35 (1982) 258-262.

25. T.J. Koppenaal and D. Kuhlmann-Wilsdorf, Appl. Phys. Lett. 4 (1964) 59-61.

26. M.J. Makin and F.J. Minter, J. Inst. Metals 85 (1957) 397.

Table 1. Composition and Measured Physical Properties of As-received AMZIRC and AMAX-MZC

Alloy	Cr (%)	Zr (%)	Mg (%)	Electrical Conductivity @ 20°C[2]	Yield Strength 0.2% Offset [4]
AMZIRC	--	0.10	--	75% IACS*	440 MPa
AMAX-MZC	0.80	0.15	0.04	59% IACS*	490 MPa

* IACS = International Annealed Copper Standard

Table 2. Irradiation Parameters of Ion-Irradiated AMZIRC and AMAX-MZC

Alloy	Irradiation Temperature	Calculated Damage (dpa)	
		1 µm	peak (2 µm)
AMZIRC,MZC	100°C	10	40
AMZIRC,MZC	150°C	10	40
AMZIRC,MZC	200°C	10	40
AMZIRC,MZC	250°C	10	40

Figure Captions

Fig. 1. Microstructure of as-received AMAX-MZC irradiated with 14 MeV Cu ions at 250°C to a peak damage level of 40 dpa. The top micrograph shows the irradiated and non-irradiated regions of the foil in cross-section. The bottom two micrographs are higher magnifications of the damage (left) and control (right) regions.

Fig. 2. Microstructures of AMZIRC (left) and AMAX-MZC (right) following 14 MeV Cu ion irradiation at 100°C to a peak damage level of 40 dpa.

Fig. 3. Subgrain size in as-received copper alloys following irradiation at various temperatures.

Fig. 4. Effect of irradiation temperature on the microstructure of AMAX-MZC.

FIGURE 1

RADIATION–ENHANCED RECOVERY IN AMAX–MZC

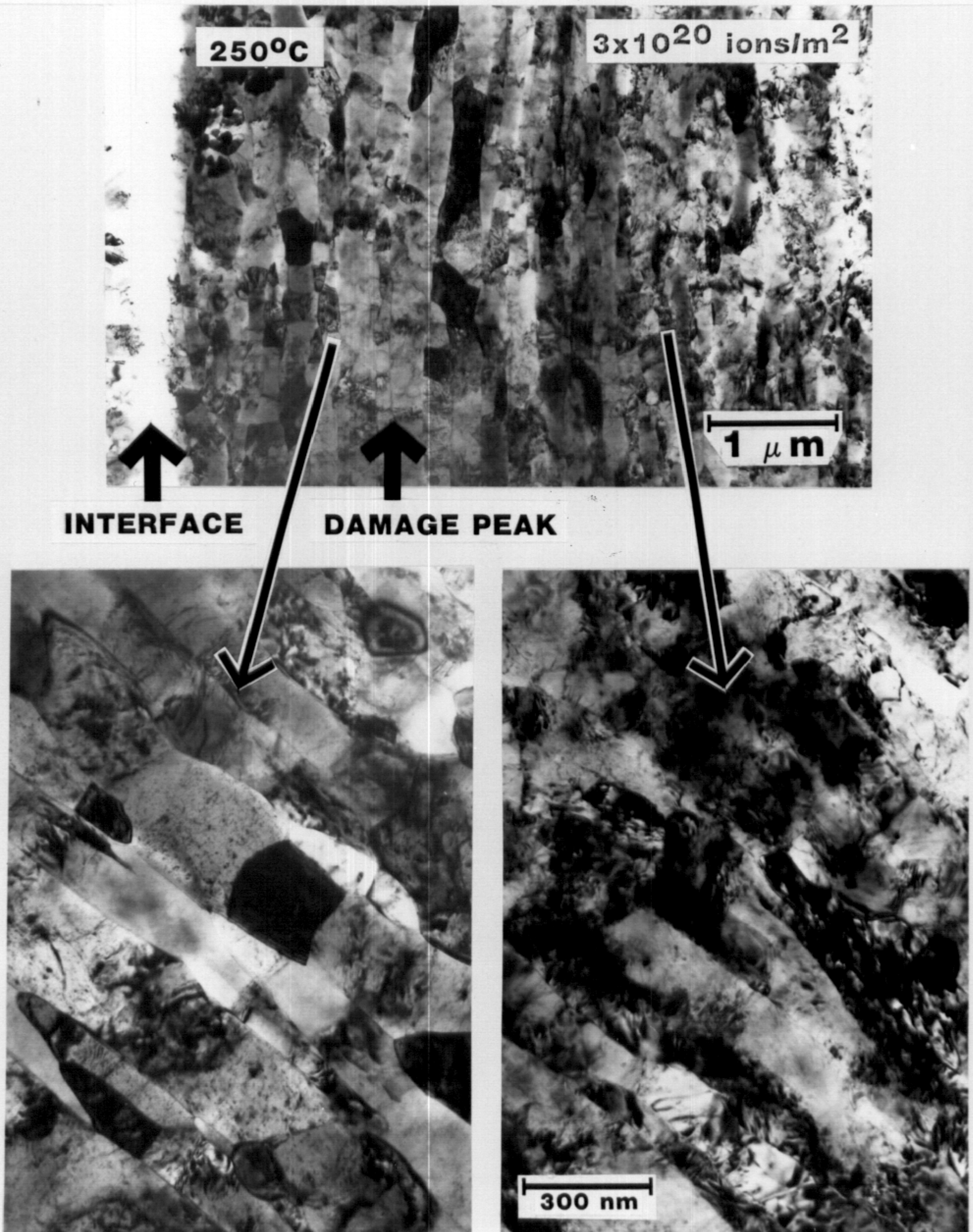

FIGURE 2

MICROSTRUCTURE OF COPPER ALLOYS IRRADIATED AT 100°C

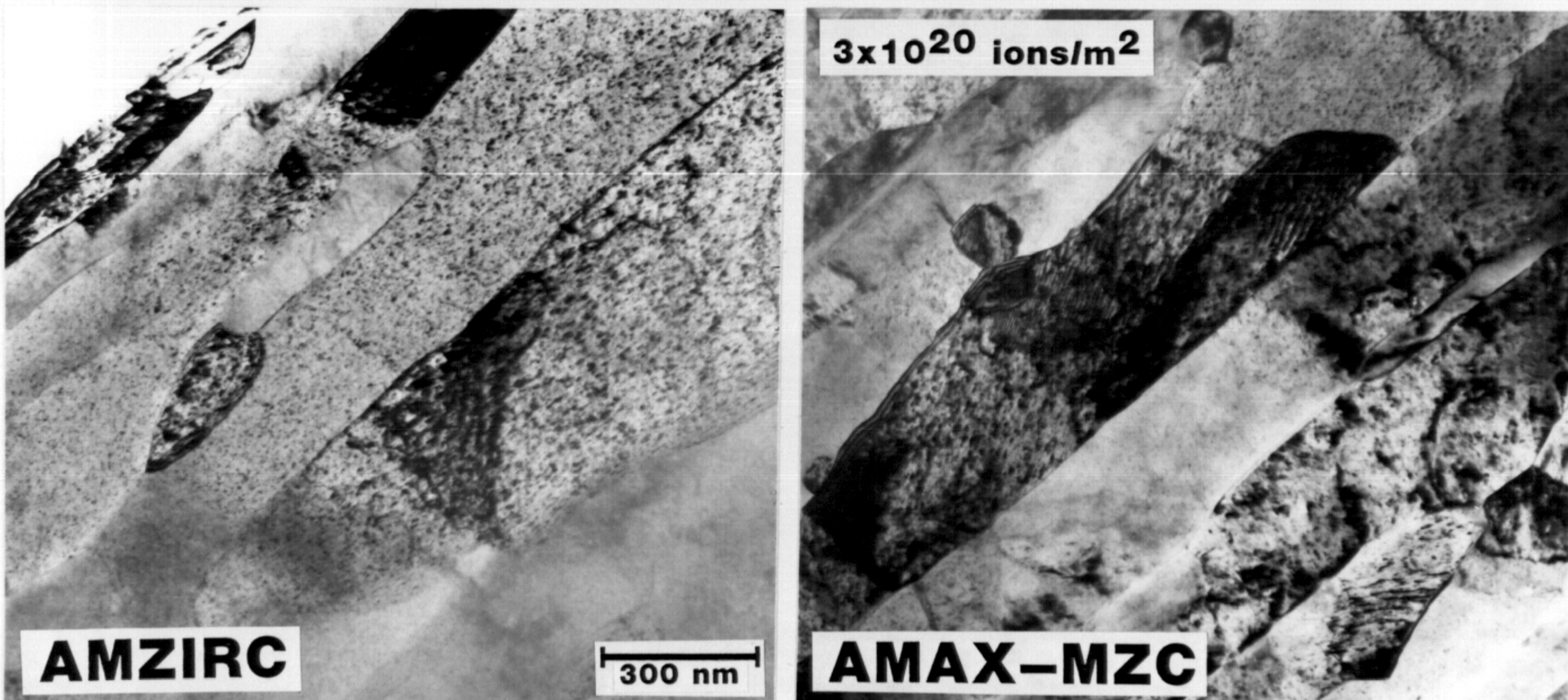

FIGURE 3

LONGITUDINAL SUBGRAIN SIZE vs. IRRADIATION TEMPERATURE

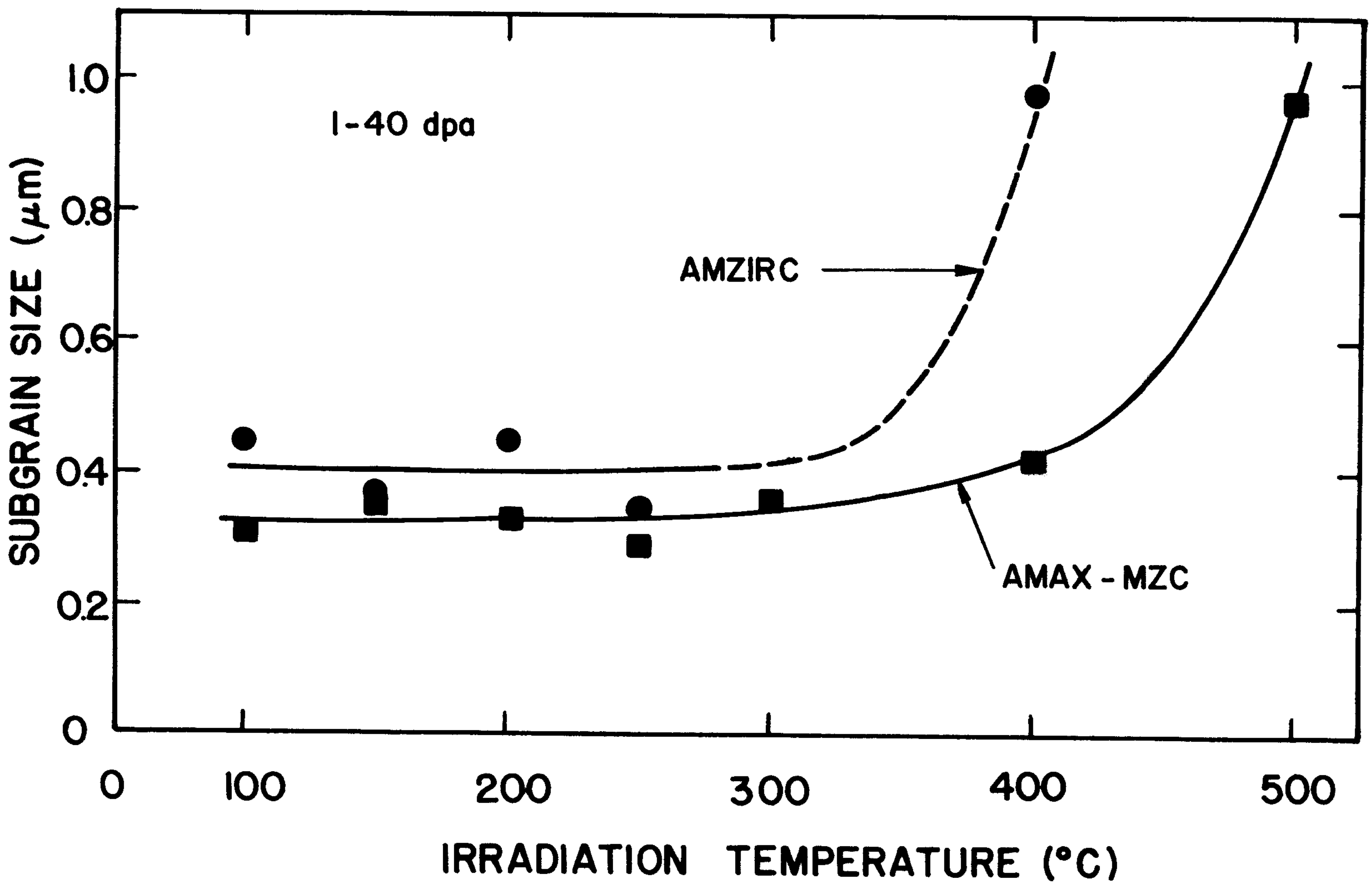

FIGURE 4

EFFECT OF IRRADIATION TEMPERATURE ON GRAIN SIZE IN AMAX-MZC