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DEFECT FORMATION IN 800-MeV PROTON-IRRADIATED ALUMINUM

by

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ABSTRACT

Transmission electron microscopy was used to investigate the formation of irradiation-induced defects in proton-irradiated high-purity aluminum. The specimens were irradiated by 800-MeV protons to about 0.25 displacements per atom (dpa) in the Los Alamos Meson Physics Facility (LAMPF), producing about 20 atomic ppm helium, 130 atomic ppm hydrogen, and approximately 70 atomic ppm of spallation products. The as-irradiated microstructure mainly consisted of cavities with a mean size of 88 Å, number density of 1×10^{15} cavities/cm³, and volume fraction of about 0.05%. The swelling was comparable to that of high-purity aluminum samples neutron-irradiated to the same displacement level. However, the high production rate of gas atoms during the proton irradiation increased the cavity number density by an order of magnitude relative to neutron irradiation, and reduced the cavity size by a factor of about 3. A postirradiation annealing treatment at 250°C resulted in complete disappearance of the small cavities and formation of gas bubbles on grain boundaries.

I. INTRODUCTION

The LAMPF accelerator offers a beam of 800-MeV protons at a design current of 1 mA. The high proton energy allows uniform damage production in thick (several centimeters) targets. At several locations in the experimental area, the beam is focused to form a beam several millimeters across, allowing very high damage rates to be achieved. These irradiation conditions could make 800-MeV protons a useful tool in studying the effects of radiation on mechanical properties. In addition, such studies would provide information on radiation effects to LAMPF structures such as windows, targets, and

beam stops which are irradiated at lower fluxes for long periods.

A theoretical analysis of displacement damage was made by Coulter *et al.* for 1-cm-thick copper¹ and aluminum² targets irradiated with 800-MeV protons. Only a fraction of the primary beam interacts significantly with the target nuclei, producing secondary charged particles which are mostly absorbed within the target, while the primary beam is not stopped. Nuclear theory was used to calculate the number and energy of secondary particles. The resulting damage energy cross sections and spallation atom cross sections were used to calculate displacement rates and production rates of hydrogen,

helium, and spallation impurity atoms. The calculated displacement rate is large, up to 0.5 displacements per atom (dpa) per day in aluminum at locations where the beam is focused down to its smallest size, i.e., a few millimeters across. And the beam heating per dpa is less than with most simulation techniques. The displacement rate is essentially constant for specimens up to several centimeters thick. The majority of the displacements (98%) are produced by energetic heavy spallation impurity atoms. The spallation nucleus recoil energy spectrum shows a peak at about 50 keV, a high energy tail, and an average energy of 2 MeV in copper.

II. EXPERIMENTAL PROCEDURE

Marz-grade aluminum (99.999% purity) specimens, approximately 0.25 mm thick and 3 mm diameter, were irradiated to a dose of about 0.25 dpa with 800-MeV protons in the Los Alamos Meson Physics Facility (LAMPF). Aluminum samples were chosen rather than copper because even at ambient temperature (20°C) the aluminum would be in the temperature range for void growth. The specimen holder was placed in a water-cooled fixture which centered the specimens in the proton beam. The temperature of the fixture remained 20°C throughout the irradiation. It was not possible to attach a thermocouple directly to the irradiated area of the specimen. Based on the changes in void structure following a 150°C anneal, it is clear that the irradiation temperature was between 20 and 150°C.

Thin foils of these specimens were prepared for transmission electron microscopy in a Fischione electropolishing apparatus by using a solution of 25-ml HNO₃, 25-ml methanol, and 1-ml HCl at room temperature. In order to check on the uniformity of the damage accumulation across the specimen thickness, one foil was prepared by first removing 20 μ m of the irradiated surface layer on one side before thinning the specimen from the other side. It was thus possible to compare the midplane to a plane lying just inside the irradiated surface. The foils were examined in a JEM 200 A transmission electron microscope equipped with a specimen cold finger and 30° tilt-360° azimuth goniometer stage. The microscope was operated at 100 kV during the

examination of microstructures in order to minimize possible damage to the specimen by the electron beam, but was elevated to 200 kV when photographs were taken. No electron damage was noted.

Quantitative TEM data were obtained by using a TGZ 3 Zeiss particle-size analyzer, and the specimen thickness was determined by stereomicroscopy using the following relationship.

$$t = \frac{P}{2M \sin \phi} \quad (1)$$

where

$$\begin{aligned} t &= \text{specimen thickness} \quad , \\ P &= \text{parallax} \quad , \\ M &= \text{magnification} \quad , \end{aligned}$$

and

$$\phi = \text{one-half of the total tilting angle.}$$

The parallax, P, was measured at several different areas of the micrograph by using a mirror stereoscope (stereoviewer) equipped with a micrometer head and floating mark units. The cavities which appeared to be on or near the surfaces of the specimen were chosen as reference points in measuring the parallax, and the average value of the measurements was used to calculate the specimen thickness.

Postirradiation annealing treatments were carried out on two separate specimens in a vacuum of 2×10^{-6} torr for 1 h at 150 and 250°C, respectively. The specimens were then thinned for the TEM examination. The thinned foil obtained from the 250°C anneal treatment was subsequently reannealed at 425°C for 20 h in the same vacuum system.

Results

The as-irradiated specimens were found to contain a high concentration of cavities, joggy dislocations, black spots, and dislocation loops. A typical

cavity structure is shown in Fig. 1. The cavities appeared to be bounded by (111) crystallographic planes with their projections in the form of squares, and were distributed fairly uniformly throughout the grain interiors. The size of the cavities varied from 40 to 180 Å, and the average size was 88 Å, as shown in Fig. 2. The cavity data in this figure represent about 700 cavities measured with the aid of a Zeiss particle-size analyzer on micrographs at a magnification of 150 000 X. The calculated cavity concentration was 1.0×10^{18} cavities/cm³, and the resultant volume fraction was 0.05%. The cavity distribution did not appear to be altered near the loops associated with dislocations, as shown in Figs. 3(a) and (b). On the other hand, regions adjacent to grain boundaries were denuded of cavities by about 0.2 μm, as shown in Fig. 3(c). The cavity size and population immediately adjacent to the denuded zones seemed to be consistent with those in regions away from the grain boundaries. Also, the overall cavity structure, i.e., size, density, and shape obtained from the regions 20 μm below the

Fig. 1.

A typical cavity microstructure in Marz-grade aluminum irradiated by 800-MeV protons to 0.25 dpa at 20°C.

irradiated surface were seemingly identical with those obtained from the midplane of the specimen as described above.

Joggy network dislocations, which seemingly developed by agglomeration and growth of radiation-induced point defects, varied remarkably in their number density from one region of the specimen to another, as shown in Figs. 4(a) and (b). The average dislocation density, determined by the random line intercept method, was about 3×10^9 cm/cm². Figure 4(c) shows dislocation loops of various sizes and black spots. The black spots were considered to be unresolvable dislocation loops, and their number density, combined with that of the resolvable loops, was about 2×10^{18} loops/cm². Dislocation loop-denuded zones near grain boundaries were not evident, as shown in Fig. 4(d).

Postirradiation anneal at 150°C for 1 h resulted in a reduction in the dislocation density from 3×10^9 cm/cm² to 1×10^9 cm/cm², but almost no changes in

Fig. 2.

Size distribution of cavities formed in proton-irradiated aluminum.

Fig. 3.

As-irradiated microstructures of proton-irradiated aluminum. (a) Small black spots in the background are overfocused cavities, and the cavity distribution is not altered near the loops; (b) cavities are underfocused in this micrograph, and are not associated with the dislocations; and (c) cavity-denuded zone adjacent to a grain boundary.

Fig. 4.

Typical dislocation structures in proton-irradiated aluminum; (a) and (b) show a large variation in dislocation density from one area of the specimen to another, (c) dislocation loops of various sizes, and (d) dislocation structures near a grain boundary.

the cavity structures, as shown in Figs. 5(a) and (b). After the anneal at 250°C for 1 h, all the small cavities were annealed out, and the microstructure consisted of large cavities newly formed during the

annealing treatment and coarse network dislocations, as shown in Figs. 5(c) and (d), respectively. The cavities were faceted and were observed preferentially at or near grain boundaries. The size

Fig. 5.

Postirradiation-annealed microstructures of proton-irradiated aluminum; (a) and (b) cavities and dislocations after an anneal at 150°C for 1 h, (c) and (d) large cavities formed near grain boundaries and coarsened network dislocations after an anneal at 250°C for 1 h.

of the cavities varied from about 1 to 5 μm , and the larger ones were cut by the foil surfaces. Upon further annealing this foil at 425°C for 20 h, some of

the smaller cavities disappeared, but the larger ones persisted.

Using the production cross section, it was calculated that irradiation of aluminum to 0.25 dpa

would generate about 20-ppm helium. To check the calculations, samples were analyzed using vacuum extraction by H. Farrar on a contract basis. Helium concentrations were observed at levels from 13 to 30 appm on 1 mg samples taken from an irradiated foil. The experimental variation was due to the location of the samples relative to the center of the irradiated area. This was confirmed in that measurements of the $\beta + \gamma$ activity from each of the small samples correlated closely with the concentration of helium measured for that sample.

III. DISCUSSION

A. The Nature of the Cavities

As shown in Table I, the 800-MeV protons produce about 600 times the helium and 900 times the hydrogen per unit of displacement damage of a fission reactor. (Since helium is almost completely insoluble in aluminum,³ it can be considered that the helium atoms will form equilibrium gas bubbles and probably reside in radiation-induced voids, because the voids are frequently assumed in the literature to be nucleated on embryonic gas bubbles and stabilized by the gas pressure.) The amount of helium produced during the present irradiation is 15-20 atomic ppm as calculated by the reaction rates, and 30 atomic ppm as determined by a

vacuum extraction method on an as-irradiated specimen. If all these helium atoms reside in the cavities observed in the as-irradiated specimen, each cavity will contain about 1100 ~ 1800 helium atoms. On the other hand, the number of helium atoms contained in an equilibrium gas bubble can be estimated from the simplified Van der Waals' equation as follows:

$$p(\nu - \eta b) = \eta kT \quad ,$$

where

$$p = 2\gamma/r \quad ,$$

$$\eta = \text{number of helium atoms} \quad ,$$

$$r, \nu = \text{bubble radius and volume, respectively} \quad ,$$

$$\gamma = \text{surface tension (=1140 dynes/cm for aluminum⁴)} \quad ,$$

and

TABLE I.

REACTION RATES FOR HIGH-ENERGY PROTONS, EBR-II AND UWMAK-I IN ALUMINUM

Facility	Displacements $\times 10^4 \text{ dpa s}^{-1}$	Helium at. ppm He/dpa	Hydrogen at. ppm H/dpa
LAMPF ^a	2.5	70.	520.
EBR-II ^b	4.2	0.12	0.6
UWMAK-I, First Wall ^c	0.9	15.	12.

^a800-MeV protons at $250 \mu\text{A cm}^{-2}$ (this experiment).

^b $\phi_T = 2.7 \times 10^{14} \text{ n/cm}^2 \text{ s}$.

^c $\phi_T = 4.7 \times 10^{14} \text{ n/cm}^2 \text{ s}$.

k = Boltzman's constant ,

b = constant ($=3.9 \times 10^{-23}$ cm³/atom for helium⁵) .

For a bubble size of 95 Å, η is calculated to be about 9400 helium atoms at 20°C. This suggests that the cavities observed in the as-irradiated specimen probably contain helium atoms up to about 10 ~ 20% (1100 ~ 1800 vs 9400) of the equilibrium amount. For bubbles containing 1100 and 1800 helium atoms, the equilibrium bubble sizes at 20°C are 44 and 54 Å, respectively (see Table II).

Similar calculations presented in Table II have been made for the large cavities observed in the postirradiation-annealed specimens. At the annealing temperature of 250°C, the equilibrium helium bubble size is 4.5 and 5.9 μ m for the helium concentration of 17.5 and 30 atomic ppm, respectively, while the observed cavity size is about 3.1 μ m. Even though these numbers are only approximate because of the insufficient number of cavities observed and their large sizes and preferential occurrence at grain boundaries, it is suggestive that the large cavities are helium bubbles. At 425°C, the calculated helium bubble size increases, while the observed cavity size is slightly reduced, as compared to 250°C. This may be due to a loss of helium atoms during the thin-foil annealing carried out on this specimen.

B. Comparison with Neutron Data

The proton data of the present investigation are compared in Table III to the fission neutron data obtained from the literature on high-purity aluminum irradiated at similar temperatures and damage levels. The swelling is nearly the same, though the void density and size distribution differ. In particular, the void density is higher and the void size smaller than for the neutron irradiation. Figure 6 shows the proton swelling data on the same plot as neutron swelling data for high-purity aluminum. In Fig. 7, the void density from this study is plotted together with the data of Packan^{6,7} for neutron-irradiated aluminum.

Several factors influence the differences in void density between the proton- and the neutron-irradiated samples. Proton irradiation results in

Fig. 6.

Void swelling is shown as a function of neutron fluence from the data of Packan⁶ and Jostsons et al.¹⁰ An additional point shows that the proton-induced swelling of this experiment lies on the same curve.

substantially higher helium and hydrogen production rates than does neutron irradiation, which

Fig. 7.

Variation of void number density in proton- and neutron-irradiated high-purity aluminum as a function of dose. The neutron data are from Packan.^{6,7}

TABLE II
CAVITY AND HELIUM BUBBLE PARAMETERS IN PROTON-IRRADIATED ALUMINUM

Experimental Cavity Parameters							Calculated Helium Bubble Parameters			
Temp °C	N_c Cavities/cm ³	$\bar{d}_c$	$\bar{D}_c$ ^b	$\Delta V/V$ %	n^c Helium Atoms/ Cavity	Helium Content ^d at. ppm	for 17.5 at. ppm Helium		for 30 at. ppm Helium	
							n, Helium Atoms/ Bubble	Size, D_b	n	$\bar{D}_b$
20	$1. \times 10^{16}$	89 Å	95 Å	0.05	9.4×10^8	157.	1.1×10^8	44 Å	1.8×10^9	54 Å
250	1.6×10^{10a}	2.6 μm	3.1 μm	~0.26	3.1×10^9	~8.2	$\sim 6.6 \times 10^9$	~4.5 μm	$\sim 1.1 \times 10^{10}$	~5.9 μm
425	1.3×10^{10a}	2.6 μm	3.0 μm	~0.19	2.2×10^9	~4.8	$\sim 8.1 \times 10^9$	~5.7 μm	$\sim 1.4 \times 10^{10}$	~7.5 μm

^aRepresents the upper limit; the overall average value was assumed to be two orders of magnitude lower than this.

$$\bar{D}_c = (\sum \bar{d}_i^3 n_i / \sum n_i)^{1/3}$$

^cMaximum number of helium atoms that can be contained in equilibrium.

^dAmount of helium necessary to fill the cavities with equilibrium gas.

TABLE III
IRRADIATION EFFECTS IN HIGH-PURITY ALUMINUM

Purity Weight %	Irradiation Temperature °C	Type of Irradiation	Flux $n/cm^2 s$	Fluence n/cm^2	dpa	N_v Voids/cm ³	$\bar{d}_v$, Å	$\Delta V/V$ %	Reference
99.999	20 ~ 150	P			0.25	1.0×10^{18}	88	0.05	This study
99.9999	55	n	1.1×10^{14}	1.3×10^{20}	0.2	1.9×10^{18}	323	0.04	5,6
99.9999	55	n	10.9×10^{14}	1.6×10^{20}	0.2	3.8×10^{18}	244	0.03	5,6
99.99996	55	n	1.4×10^{14}	2.4×10^{20}	0.17	7.8×10^{18}	305	0.11	9
99.994	55	n	1.4×10^{14}	2.4×10^{20}	0.17	$1. \times 10^{18}$	285	0.014	9

should increase the void density. The displacement rates are about the same for the proton-irradiated aluminum as for the neutron-irradiated material. Higher displacement rates generally result in a larger homogeneous void nucleation rate. In addition, impurities are known to reduce the void density, requiring consideration of the spallation impurities introduced.

The larger void density in proton-irradiated aluminum can be primarily attributed to the higher production rate of gaseous atoms in the proton irradiation, as shown in Table I. Farrell *et al.*⁸ observed an increase of void concentration in neutron-irradiated aluminum samples preinjected with helium and hydrogen, and also found that helium is more effective than hydrogen. Packan⁶ observed no profound effect of hydrogen on void formation in high-purity neutron-irradiated aluminum. Therefore, it is suggestive that the higher void number density observed in the present investigation is primarily due to the high helium production rate.

The void size of this study is smaller than the neutron data by a factor of about 3; however, the void volume fraction is almost the same. This implies that the same number of vacancies is involved in the voids both in the neutron and the proton irradiation, suggesting that the gaseous atoms influence only the void nucleation process. Therefore, for a constant vacancy supersaturation, the void growth rate will be reduced by a higher void nucleation rate which increases the competition between voids for the vacancies.

As mentioned previously, the void size distribution can also be altered by high fluxes⁶ and impurities.⁹ The high flux effect is not comparable to the results of this study because even an order of magnitude higher flux only reduces the size by a factor of 2.⁶ Impurities are known⁹ to reduce both void size and swelling. Thus, the fact that the swelling was the same for this experiment and for neutron irradiation to the same damage level suggests the spallation products generated during the proton irradiation have little effect on void formation at the damage levels reached in this study.

Finally, the void-annealing behavior of this study is consistent with that of Jostons *et al.*¹⁰ who observed, in high-purity aluminum specimens irradiated to 1.6×10^{21} n/cm² at 55°C, little or no void annealing at temperatures below about 200°C, and a complete disappearance of all the smaller voids with

sizes less than 200 Å in diameter at temperatures of 250 to 275°C.

IV. CONCLUSIONS

1. Cavities are formed in Marz-grade aluminum (99.999% purity) irradiated by 800-MeV protons to 0.25 dpa at 20°C, and the cavities are probably filled with helium gas up to 10 ~ 20% of the equilibrium amount.

2. High production rate of gas atoms during proton irradiation increases the cavity number density by an order of magnitude, and decreases the cavity size by a factor of about 3, resulting in a degree of swelling comparable to neutron irradiation.

3. Gas atoms produced during proton irradiation seem to behave like preinjected gases in neutron irradiation in terms of influencing the void formation behavior.

4. Spallation products produced during proton irradiation seem to have little effect on the void formation behavior.

5. An irradiation with 800-MeV protons produces a uniformly damaged region through a bulk specimen.

6. No observable precipitates are formed during the proton irradiation.

7. Annealing behavior of the proton-irradiation-induced cavities is consistent with that of neutron-produced voids.

8. Helium atoms produced during the proton irradiation form equilibrium gas bubbles on grain boundaries after a postirradiation anneal at 250°C and above.

REFERENCES

1. C. A. Coulter, D. M. Parkin, and W. V. Green, *J. Nucl. Mater.* **67**, 140 (1977).
2. C. A. Coulter, private communication.
3. R. Blackburn, *Met. Rev.* **11**, 159 (1966).
4. K. H. Westmacott, R. E. Smallman, and P. S. Dobson, *Met. Sci. J.* **2**, 177 (1968).

5. *Handbook of Chemistry and Physics*, 54th ed. (1973-74), D-157 (Ed. R. C. Weast, Chemical Rubber Co., Cleveland, Ohio).
6. N. H. Packan, *J. Nucl. Mater.* **40**, 1 (1971).
7. J. O. Stiegler, "Radiation-Induced Voids in Metals," AEC Symp. Series **26**, 292 (1972).
8. K. Farrell, A. Wolfenden, and R. T. King, *Rad. Eff.* **8**, 107 (1971).
9. A. Risbet, G. Brebec, J. M. Lanore, and V. Levy, *J. Nucl. Mater.* **56**, 348 (1975).
10. A. Jostsons, E. L. Long, Jr., J. O. Stiegler, K. Farrell, and D. N. Braski, "Radiation-Induced Voids in Metals," AEC Symp. Series **26**, 363 (1972).