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POINT DEFECT PRODUCTION AND ANNIHILATION
IN NEUTRON-IRRADIATED ZIRCONIUM*

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High-purity Zr has been irradiated to a dose of $2.2 \times 10^{21} \text{ n/m}^2$ ($E < 0.1 \text{ MeV}$) using the pulsed spallation source at IPNS. Electrical resistivity was monitored continuously during irradiation. The saturation resistivity, found from a linear extrapolation of the damage-rate curve between four and five $\text{n}\Omega\cdot\text{m}$, is found to be $35 \text{ n}\Omega\cdot\text{m}$. However, comparison with data from the literature shows that the normalized damage-rate curves from five experiments at different temperatures ($< 77 \text{ K}$) and with different neutron spectra, all fall on the same common curve. A saturation resistivity of $100 \text{ n}\Omega\cdot\text{m}$ is found from the high-dose, linear part of this curve. A spontaneous recombination volume in the range 280 to 400 atomic volumes is found using the theory of Dettmann, Leibfried and Schroeder and the saturation resistivity of $100 \text{ n}\Omega\cdot\text{m}$. Post-irradiation annealing has been done up to 300 K using stepped, isochronal anneals. The recovery spectrum is in reasonable agreement with previous work, showing a large peak near 100 K , and two smaller peaks at 160 K and 250 K .

1. INTRODUCTION

Irradiation of crystalline solids by energetic particles produces vacancies and interstitials in pairs known as Frenkel defects. For low energy particles, such as electrons, isolated Frenkel pairs are produced randomly; with heavy ion or neutron irradiation the defects are produced in cascades with high concentrations of defects. Each point defect is characterized by a volume surrounding it in which a point defect of the opposite sign is unstable and spontaneously recombines without thermal activation. Experimentally, the spontaneous recombination volume, V_r , can be determined by measuring electrical resistivity, ρ , as a function of irradiation dose, ϕt , at temperatures where neither the vacancy nor the interstitial is mobile. The parameter of interest is the saturation resistivity, $\Delta\rho_s$, which is commonly found from an extrapolation of the damage rate $d\rho/d\phi t$, to zero.

Saturation resistivities for neutron-irradiated Zr have been reported previously from four experiments: Rosenbaum et al.¹ give $\Delta\rho_s = 24 \text{ n}\Omega\cdot\text{m}$ for Zr irradiated at 77 K , Vialaret et al.² report $\Delta\rho_s = 100 \text{ n}\Omega\cdot\text{m}$ for irradiation at 24 K , while Nakagawa et al.³ and Klabunde and Coltman⁴ give values of $200 \text{ n}\Omega\cdot\text{m}$ and $47 \text{ n}\Omega\cdot\text{m}$, respectively, for irradiation at 4.5 K . It has been suggested³ that the large range of $\Delta\rho_s$ measured (and thus of V_r calculated) may originate from differences in irradiation temperature. Other possible sources for the discrepancy could be trace impurities, spectrum effects, or simply the difficulty in extrapolating the damage-rate curves. The last would be most significant for experiments done to low total dose, and thus one might question the low values of $\Delta\rho_s$ reported by Rosenbaum et al.¹ and by Klabunde and Coltman⁴. However, the experiments of Vialaret et al.² and Nakagawa et al.³ extended to high doses

and both report linear damage-rate curves after an initial transient, yet the values of $\Delta\rho_0$ reported differ by a factor of two.

The objective of this work is to obtain damage-rate curves for high purity Zr at low temperature (5 K) using two different neutron spectra, and thus to clarify the effects of irradiation temperature and neutron energy on $\Delta\rho_0$. This paper will report only the results obtained at the Radiation Effects Facility at IPNS; data from an experiment at KTHS are given in a comparison paper by Guinan et al.⁵.

2. EXPERIMENTAL TECHNIQUE

Marz-grade Zr, obtained from the Materials Research Corporation, was further purified using the electrotransport process⁶. Samples were cold-rolled to a thickness of 0.05 mm, and then cut into 0.25 mm wide strips, 30 mm long. The wire was chemically cleaned before annealing in a vacuum of 10^{-5} Pa for 1 h at 1000 K. The initial resistivity of the sample, ρ_0 , (at 5.2 K) was 2.6 n Ω m, and its resistivity ratio was 162.

Irradiation was carried out at the Intense Pulsed Neutron Source (IPNS) at the Argonne National Laboratory. The specimen was maintained at 5.2 K in a target chamber that was surrounded by liquid helium and filled with helium exchange gas to ensure effective heat transfer between the specimen and the cryogenic liquid. A calibrated Cu-Au 0.2% Fe thermocouple was used to monitor the temperature of the specimen. The sample was irradiated to a total dose of 2.2×10^{21} n/m², with an average flux of 1.27×10^{16} n/m².s; the neutron spectrum has been reported previously⁷.

Stepped, post-irradiation, isochronal annealing was conducted up to 300 K, with the specimen held at each annealing temperature for 300 s. All resistivity measurements were made at 5.2 K.

3. RESULTS

The change in resistivity induced by irradiation as a function of neutron dose is given in Figure 1. Failure of the data-logging system resulted in the loss of data from 6×10^{19} to 4.3×10^{20} n/m², and a perturbation of unknown origin produced a small fluctuation in the damage rate near 1.5×10^{21} n/m². The damage-rate vs. damage curve, Figure 2, was obtained by smoothing a cubic spline fit to the data, eliminating the points near the perturbation. As seen in Figure 2, the damage-rate initially decreased very rapidly, however this transient lasted for only ~ 0.2 n Ω m. Thereafter, the curve was slightly concave.

Figure 3 shows the results of the post-irradiation annealing. Three annealing peaks are evident: a large one at ~ 100 K, and two smaller ones at ~ 160 K and ~ 250 K. The total amount of recovery up to 300 K was 76%.

4. DISCUSSION

The general shape of the damage-rate curve, Figure 2, is in agreement with curves reported for other hcp and bcc metals³. The very rapid initial transient is generally attributed to a deviation from Matthiessen's rule and typically lasts for $\Delta\rho \approx 0.1 \rho_0$. An initial damage rate has been determined from Figure 2 from a smooth extrapolation of the damage-rate curve, after the initial fast transient, back to $\Delta\rho = 0$. Linear extrapolation of the data between 4 and 5 n Ω m to zero damage-rate gives a saturation resistivity of 35 n Ω m. For comparison, Figure 2 and damage-rate curves taken from the literature have been normalized by their initial damage rates. Table I lists the relevant parameters and the normalized curves are shown in Figure 4.

Within the uncertainty of the determination of the initial damage rates ($\approx 10\%$) all data with the exception of those of Nakagawa et al.³ fall within a single band. All show a transient

TABLE I IRRADIATION DAMAGE FOR ZIRCONIUM

AUTHOR	TEMP. (K)	ρ_0 (n/cm)	INITIAL DAMAGE RATE (10^{-31} n/cm ³)	$\Delta\rho$ (n/cm) (a)	DOSE (n/cm)
Rosenbaum et al.	77	-	18.0	24	5
Vialaret et al.	24	1.8	35.0	100	22
Nakagawa et al.	4.5	5.6	24.1	200	50
Klabunde et al.	4.5	3.0	25.0	47	34
Guinan et al.	4.2	2.5	63.5	100	10
This work	5.2	2.5	23.5	35	5

(a) from linear extrapolation of the data at the highest dose of the experiment.

which lasts for $\Delta\rho \approx 2\rho_0$, followed by a linear region, if the experiment was continued to a sufficiently high dose. It is significant that the data of Vialaret et al.² (which extends to twice the dose shown in Figure 4) and those of Guinan et al.⁵ have the same final, linear slope, even though the initial damage rates differ by about a factor of two. Table I shows that Nakagawa's experiments were done using Zr that was significantly less pure, as evidenced by the ρ_0 value, than that employed by other workers. Thus, it may be that the effect of trapping or clustering has lowered the final slope of the damage curve (see Averbach et al.⁸).

If one applies the theory of Dettmann, Leibfried and Schroeder⁹ for neutron-irradiated solids, it is found that $\ln 2 \leq C_S V_F \leq 1$, where C_S is the concentration of Frenkel pairs at saturation. The range for $C_S V_F$ is determined by the concentration of defects in a cascade. Burger, Meissner and Schilling¹⁰ have proposed that the transient part of the normalized damage-rate curve results from a focussing mechanism that is sensitive to the presence of dislocations and impurity atoms. They claim as well that the linear portion observed for most metals is independent of microstructure. With this interpretation, a value of $\Delta\rho_S = 100$ n/cm found from an extrapolation of the high dose data of Figure 4 should be the most appropriate for high purity Zr. With $C_S = \Delta\rho_S/\rho_{FP}$ and $\rho_{FP} = 4 \times 10^4$ n/cm as used in previous work¹⁻⁴ one finds $C_S = 2.5 \times 10^{-3}$ and $280 \leq V_F \leq 400$

atomic volumes. The alternative interpretation of the data, that the initial slope of the normalized damage-rate curve is representative of the spontaneous recombination process, leads to unreasonably high values for V_F (1300 to 1900 atomic volumes), and necessitates interpretation of the subsequent large decrease in slope in terms of some new mechanism, such as clustering.

The results of post-irradiation annealing, Figure 3, are in general agreement with previous studies^{1,2,11}. The large peak at ~ 100 K is generally attributed to the migration of free interstitials, as suggested by Heely¹¹. The origin of the other two peaks is less certain. Hood¹² has suggested that the lower limit for the migration energy of free vacancies in Zr to be 1 eV, which implies that vacancies are immobile below 300 K. Thus, the two peaks observed in the range 150 K to 260 K are probably associated with the dissociation of interstitial clusters or interstitial-solute complexes.

5. CONCLUSIONS

1. The normalized damage-rate curves for neutron-irradiated, high-purity Zr are independent of irradiation temperature and neutron spectrum for temperatures up to 77 K.
2. The upper limit for the spontaneous recombination volume in Zr is 400 atomic volumes.
3. Annealing peaks in the range 150 K to 260 K are most likely caused by the decomposition of interstitial complexes.

FIGURE 1

Change in resistivity as a function of neutron fluence in zirconium irradiated at 5.2K at IPNS.

FIGURE 2

Damage rate versus change in radiation-induced resistivity for zirconium.

FIGURE 3

Post-irradiation annealing results showing recovery peaks at 100 K, 150 K and 250 K.

FIGURE 4

Normalized damage rate curves for various neutron irradiation studies.

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