RECEIVED BY DTIC AUG 19 1968

CONF-680910--2

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OF NEUTRON-IRRADIATED SINGLE-CRYSTAL
AND POLYCRYSTALLINE MOLYBDENUM*

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*This paper is based on work performed under United States Atomic Energy
Commission Contract AT(45-1)-1830.

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SOME OBSERVATIONS ON THE ANNEALING OF NEUTRON-IRRADIATED SINGLE-CRYSTAL AND POLYCRYSTALLINE MOLYBDENUM

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INTRODUCTION

After irradiation with fast neutrons near room temperature, molybdenum shows an increase in lattice parameter with a decrease in density,¹ a higher resistivity,² and an increased hardness.³ Electron microscopy reveals defect clusters in the form of black spots or small loops which interact at sufficiently high fluences to form extended dislocation networks.⁴

Annealing of the neutron-irradiated molybdenum in the temperature range 150 to 250°C, about 0.15 of the absolute melting point, results in the recovery of an appreciable fraction of the irradiation-induced changes and the evolution of stored energy. This annealing stage is commonly known as "Stage III" from its analogy to a similar annealing stage in fcc metals.⁵ The defects responsible for this annealing stage and the mechanisms whereby they interact are not completely understood. While several models for Stage III annealing have been proposed,^{2,5,6} none satisfactorily accounts for all the phenomena observed.

The work described in this paper was undertaken to re-examine the Stage III annealing behavior of molybdenum by simultaneous lattice parameter and length change measurements, together with stored energy release measurements, during annealing of high purity samples.

Single-crystals produced by multiple zone-refining of selected high-purity stock was the source of the very pure sample material used in the studies and allowed very precise measurements of lattice parameter. Parallel

experiments, utilizing samples of the high purity stock without the zone refining treatments provided data on the effects of zone refining on the accumulation of irradiation-induced defects and their subsequent annealing.

EXPERIMENTAL PROCEDURE

The single crystals used in this work were prepared from 3.2 mm diameter sintered rod obtained from the Lamp Metals and Components Division, General Electric Company. The techniques employed in zone-refining have been described earlier.⁷ Analyses of the samples before and after zone-refining are given in Table I. Most crystals were seeded to a $[14\bar{4}]$ axis orientation during the final pass. After three-pass zone-refining, the crystals were cut into 38 mm lengths and the blunt ends were finished into rounded points by grinding, followed by heavy electropolishing. A (011) metallographically prepared face parallel to the rod axis facilitated subsequent lattice parameter measurements. Residual cold-work was again removed by heavy electropolishing followed by annealing at 1300°C. This treatment has been found to produce single crystals having a high degree of crystalline perfection.⁷ Polycrystalline rod samples were processed in the same manner except that a flat face was not utilized.

Single-crystal lattice parameters were measured by a symmetrical back-reflection technique. Lattice parameters for polycrystalline rods were measured by conventional high-angle diffractometry with extrapolation to $2\theta = 180^\circ$. Lengths were measured by the gage-block comparator method. These procedures are described in detail elsewhere.⁷ The estimated precision of all length measurements and single-crystal lattice parameters was 0.001%; for polycrystalline lattice parameters it was 0.003%.

Stored-energy release measurements were made in a calorimeter designed specifically for small single-crystal specimens. Three samples, each 3.2 mm in diameter and 38 mm long, were attached to three junctions of a chromel-alumel thermopile. The emf generated by this thermopile was opposed by that from a similar thermopile to which were attached three reference samples, identical except for the irradiation treatment. The differential emf was amplified and recorded. A bank of quartz infra-red lamps controlled by an electronic programmer comprised the heat source. The heating rate employed in these experiments was 2°C per minute. The melting of measured amounts of lead in hollow molybdenum samples provided a means for calibrating the heat evolved as a function of the amplified differential emf. The combined weight of the three samples was about 10g.

Electron microscopy was performed on sections cut from selected single-crystal and polycrystalline rods. These sections were thinned by standard electropolishing techniques.⁴

For each irradiation, six specimens were housed in cylindrical cavities in a helium-filled aluminum capsule. All capsules were irradiated at 40°C in a Snout Facility in a Hanford reactor.

RESULTS AND DISCUSSION

Both the single-crystal rods and the polycrystalline rods showed changes in length and lattice parameter as a result of irradiation, as shown in Figure I. The length change $\Delta L/L$ approached a saturation value with increasing fluence while the lattice parameter disclosed an initial increase and then a decrease with increasing fluence. The two sample types differed,

however, in that the relative lattice parameter increase of the polycrystalline rods was greater than the relative length increase for exposures up to $4 \times 10^{19} \text{ n/cm}^2$ ($E > 1 \text{ MeV}$), while the relative lattice parameter increase for the single crystals was less than the relative length increase for all the fluences studied.

Electron microscopy of the irradiated samples also showed differences between single-crystal and polycrystalline molybdenum after irradiation. Micrographs of the two sample types are compared in Figure II. In both cases the irradiation-induced defects appear as black spots. These defect clusters, or small dislocation loops, believed to be interstitial in nature,⁸ are smaller, 50-60 Å, in the polycrystalline samples as compared to 90-100 Å in the single crystals after a neutron fluence of $1 \times 10^{19} \text{ n/cm}^2$. The defect configuration is presumed to consist of molybdenum interstitials which exist as clusters and as isolated defects in traps of varying strengths, as well as vacancy defects which exist as isolated defects or very small clusters.

The greater lattice parameter change and the smaller clustered defects observed in the polycrystalline samples, as compared to similarly irradiated single-crystal samples, leads to a tentative conclusion that a much higher concentration of isolated interstitials exists in the polycrystalline samples. At the irradiation temperature, 40°C, interstitial defects are mobile. The high isolated interstitial concentration must therefore be a result of some trapping process.

The results of annealing studies and stored energy release measurements further confirmed the existence of dissimilar defect configurations in the two sample types. In Figure III, typical isochronal annealing data to 900°C are shown for a single crystal rod and a polycrystalline rod. The as-irradiated length changes $\Delta L/L$ were identical for the two samples and length-change recovery with annealing was very similar. Recovery of lattice parameter changes were, however, quite different up to 400°C. A partial recovery of the lattice expansion took place between 100 and 200°C in the irradiated polycrystalline rod, but no such recovery was observed in the single-crystal rod. Stored-energy-release measurements showed a comparatively large release of stored energy at 150-200°C upon heating the irradiated polycrystalline rods while the single-crystals showed but a small release. Typical stored energy release curves are shown in Figure IV. The lattice parameter recovery and the stored energy release in the polycrystalline samples are apparently directly related.

From the equation given by Simmons and Balluffi,⁹

$$C_V - C_I = 3(\Delta L/L - \Delta a/a)$$

where C_V and C_I are the concentrations of single vacancies and interstitials respectively, it is apparent that the interstitial concentration exceeds the vacancy concentration in the irradiated polycrystalline samples while the opposite is true in the single crystals. The difference $\Delta L/L - \Delta a/a$ does not remain constant upon annealing, so the annealing is not entirely a result of mutual annihilation of isolated defects. From the similarity of the length change annealing data and the completely dissimilar nature of the lattice parameter annealing below 400°C, it follows that the lattice

parameters and lengths anneal independently of one another. From the annealing curve of the polycrystalline sample irradiated to 1×10^{19} n/cm² of Figure IV, and from the Simmons and Balluffi relationship, it can be shown that the concentration of excess interstitials is reduced from 3.3×10^{-4} to almost zero with the evolution of 0.48 cal/gm, which is equivalent to the evolution of 1.25×10^{19} eV/gm during the loss of 2.1×10^{18} defects/gm. This evolution of 6 eV per defect is probably too low for mutual annihilation of isolated vacancies and interstitials, but is compatible with the expected energy evolved by an interstitial upon absorption at some alternative sink such as an interstitial cluster. Because some length change recovery occurs also, some mutual annihilation may be indicated.

The same analysis applied to the single-crystal annealing data shows about 0.1 cal/gm, or 2.5×10^{18} eV/gm, is evolved by the loss of 1.8×10^{18} excess vacancies/gm, or roughly 1.4 eV per vacancy. This is almost certainly the result of vacancies moving to vacancy clusters or to sinks other than interstitials. In the single-crystal annealing data shown in Figure III, an increase in unit cell volume of 1.05×10^{-4} is observed to occur simultaneously with the length change recovery. This is equivalent to 0.37 atomic volume per vacancy if the interstitial concentration is assumed to be unchanged. Prior estimates¹⁰ have placed ΔV_V , the relaxation about a vacancy in cubic metals, in this range. The length change is not completely recovered at 400°C, so that only a fraction of the total vacancy defects are involved. The fraction annealed out represents one-fourth to one-third of the total, a fraction which corresponds fairly closely to the relative concentration of divacancies in irradiated iron calculated by Beeler.¹¹ If

these calculations apply to other bcc metals as well, the low temperature length change annealing could result from the annealing out of the comparatively mobile divacancy complex, leaving the less mobile vacancy configurations in the crystal lattice.

The present analyses have not been extended to samples exposed to neutron fluences higher than 1×10^{19} n/cm². After 1×10^{19} n/cm² ($E > 1$ MeV), it appears that postirradiation annealing of single crystals and polycrystalline samples involves appreciably different recovery processes. Some characteristic of polycrystalline samples must inhibit the clustering of interstitial defects. Whether the interstitials are trapped at impurities or are perturbed by differences in crystal perfection is a question not readily answered at present. The difference in purity after zone-refining is slight (Table I) and it is difficult to ascribe the observed annealing behavior to this cause. The distribution of impurities, however, could well be altered by the zone-refining treatment. The impurities which normally segregate at grain boundaries or dislocations would of necessity remain dispersed or form a unique complex in the single crystals.

Experiments intended to extend and clarify the above results are in progress. For example, the effect of carbon and iron on the normal behavior of irradiated molybdenum single crystals is being investigated. In another series of experiments, irradiated polycrystalline rods, prepared from zone-refined crystals by torsional deformation alternated with annealing for very short periods will be compared to single-crystal samples. The results of these experiments, which are currently in progress, should do much to explain

the inconsistent annealing behavior of single-crystal and polycrystalline molybdenum after neutron irradiation.

SUMMARY

Single-crystal rods and polycrystalline rods of molybdenum, exposed to high-energy neutron irradiation at 40°C , exhibit very dissimilar annealing behavior at temperatures below 400°C . The polycrystalline samples exhibit simultaneously a large lattice parameter recovery and stored energy release at $150\text{--}200^{\circ}\text{C}$, while length change recovery is relatively slight. Single crystals, on the other hand, show almost no lattice parameter recovery and very little evolution of stored energy in the same temperature range. The interstitial defects and vacancies appear to anneal independently without appreciable mutual annihilation. Accordingly, the so-called Stage III annealing in irradiated molybdenum may consist of both reactions proceeding simultaneously.

From the behavior of the interstitial defects in the polycrystalline samples, a higher concentration of trapping sites is postulated. Whether these are a result of differences in impurity content or a difference in the distribution of impurities is not clear. Additional irradiation experiments, on carbon-doped and iron-doped single-crystals and on polycrystalline rods made from zone-refined single crystals, are underway. Results of these experiments should make possible a more definite assignment of recovery mechanisms in neutron irradiated molybdenum.

ACKNOWLEDGMENT

The assistance of J. M. Leahy and H. A. Flaherty in preparing the single crystals, of Mr. Leahy and M. L. Sorick in measuring the lengths and lattice parameters, and of K. H. Thomas in preparing samples for electron microscopy, is gratefully acknowledged.

TABLE I

ANALYSIS OF ZONE-REFINED SINGLE CRYSTALS OF MOLYBDENUM

<u>Element</u>	<u>Vendor's Analysis</u>	<u>Before Z.R.</u>	<u>After Z.R.</u>	<u>Gas Fusion</u>
		<u>BNW</u> <u>(Mass Spectograph)</u>	<u>BNW</u> <u>(Mass Spectograph)</u>	
W	100	60	60	
Fe	10	13	2	
Ni	< 10	2	< 2	
K	-	6	40	
Si	10	10	12	
C	< 10	9	3	12.8
H ₂	1-2	-	-	
O ₂	6-11	-	-	3-3.5
N ₂	4-8	-	-	1.2

Impurities in parts per million by weight

FIGURE CAPTIONS

- Figure I. Changes in length $\Delta L/L$ and lattice parameter $\Delta a/a$ for neutron-irradiated single-crystal and polycrystalline molybdenum.
- Figure II. Transmission electron micrographs of (a) single-crystal and (b) polycrystalline molybdenum showing differences in defect cluster sizes after exposure to a fast neutron fluence of $1 \times 10^{19} \text{ n/cm}^2$.
- Figure III. Recovery of length and lattice parameter during isochronal annealing of neutron-irradiated single-crystal and polycrystalline molybdenum. Annealing time was two hours at each temperature.
- Figure V. Release of stored-energy from irradiated single-crystal and polycrystal molybdenum

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0.5M

Property Change, Percent

Property Change, Percent

Annealing Temperature