THE EFFECT OF HYDROSTATIC PRESSURE
ON THE RECOVERY OF IRRADIATION
INDUCED HARDNESS IN MOLYBDENUM

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OF IRRADIATION INDUCED HARDNESS IN MOLYBDENUM

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ABSTRACT

Irradiation of high purity molybdenum at $\sim 40^\circ\text{C}$ to $6.2 \times 10^{18} \text{ n/cm}^2$ ($E > 1 \text{ MeV}$) induces a 19% increase in the Vickers hardness of the metal. Post-irradiation isochronal annealing at $\leq 1 \text{ bar}$ results in a steady increase in the hardness which reaches 26% at 600°C . The hardness increase recovers over the $600\text{--}1000^\circ\text{C}$ temperature range and returns to the unirradiated value at 1000°C . Isochronal anneals at 25°C and 20 kbars results in a 40% increase in the hardness over the as-irradiated value. High pressure anneals in the $80\text{--}400^\circ\text{C}$ range do not significantly change the hardness while in the $400\text{--}500^\circ\text{C}$ range rapid recovery occurs. The recovery of irradiation induced hardness appears to be related, in a very complex manner, to the recovery of observable defect clusters. The annealing of electrical resistance, lattice parameter, defect cluster density, and hardness increases are compared and discussed.

I. INTRODUCTION

It has been recently discovered that the application of an external hydrostatic pressure during the postirradiation annealing of molybdenum causes some irradiation induced property changes to recover at lower temperatures.⁽¹⁻³⁾ The electrical resistance increase,⁽¹⁾ lattice parameter increase,⁽²⁾ and defect cluster density⁽³⁾ were completely recovered at temperatures $200\text{--}300^\circ\text{C}$ lower

at 20 kbars* than required at pressures ≤ 1 bar. Furthermore, the stage III recovery peak, which occurs at approximately 0.15 times the melting point, was also lowered by annealing under pressure.

Neutron irradiation normally causes a hardening of metals by the introduction of defects which impede the motion of dislocations through the solid. An effective barrier is the defect cluster which is on the order of 10-100 Å or more in diameter. In view of the pressure induced recovery of the defect clusters in Mo,⁽³⁾ it was postulated that the hardness of this metal should show approximately the same pressure dependence. This paper summarizes the results of the hardness measurements made on the same samples used for the earlier electron microscopy study.⁽³⁾

Previous work with respect to the neutron induced hardness changes in Mo has shown a 5% increase at 7×10^{18} n/cm²,⁽⁴⁾ a 33% increase at 5×10^{19} n/cm²,⁽⁵⁾ 40% for 1.8×10^{20} n/cm²,⁽⁴⁾ and 73% for 2×10^{20} n/cm².⁽⁶⁾ When the irradiated samples are isochronally annealed at low ambient pressures (≤ 1 bar), the hardness recovers at $0.15 T_m$,^(6,7) $0.37-0.39 T_m$,^(4,7-9) and $0.48-0.50 T_m$,^(6,9) where T_m is the melting temperature in °K. The above data indicate that the defects responsible for hardening anneal in a rather complex fashion and are quite stable with respect to temperature.

II. EXPERIMENTAL

The sample material, preirradiation heat treatments, irradiation conditions, and postirradiation annealing procedures have been previously described.⁽¹⁾

*1 kbar $\approx$ 1000 atmospheres

Briefly, polycrystalline high purity molybdenum containing less than 10 ppm carbon was irradiated to 6.2×10^{18} n/cm² ($E > 1$ MeV) at temperatures of about 40°C. The postirradiation annealing of these samples was carried out at two pressures: ≤ 1 bar and 20 kbar. The time of the isochronal anneals was two hours.

Specimens used for the hardness tests were identical to those used for the lattice parameter measurements⁽²⁾ and the transmission electron microscopy studies.⁽³⁾ They were 0.0075 cm thick foils, 1 cm long and 0.5 cm wide.

The hardness was measured on a Vickers Microhardness Tester with a 50 gram load. Ten measurements were made on each sample and an average value was determined.

III. RESULTS

The experimental data from these tests is listed in Table I and presented in graphical form in Figure 1.

For the sample annealed at low pressure the hardness gradually increases over the as-irradiated value up to 600°C temperature range. At 1000°C the hardness value is completely returned to the unirradiated, as-annealed value.

The application of 20 kbars pressure at 25°C apparently further increases the hardness, from a value of 19% for the as-irradiated case to 27% after the anneal. There is a slight increase in hardness on annealing at 80°C after which the hardness is essentially constant to 400°C. Above 400°C the hardness recovers rapidly and only 7% remains at 500°C.

Figure 2 is a replot of the data curves in Figure 1 expressed as a percent recovery of the as-irradiated hardness. Figure 2 discloses a 40% increase in the hardness after a room temperature 20 kbar anneal. The hardness further

increases to 160% of the as-irradiated value when the samples are annealed at 80°C and 20 kbars pressure for two hours. Annealing at 20 kbars to temperatures of 400°C produces essentially no hardness change while annealing above 400°C results in rapid recovery. At 500°C there is still ~ 40% of the irradiation induced hardness increase remaining.

IV. DISCUSSION

It is advantageous at this point to divide the discussion into two parts, one covering the low pressure results and the other covering the high pressure data.

A. Low Pressure Results

The irradiation induced hardness increase of 19% over the as-annealed condition for 6.2×10^{18} n/cm² is somewhat larger than would be expected from previous work.⁽⁴⁻⁶⁾ This might be explained by the fact that the material in this study was annealed at a higher temperature (1760°C) than the Mo used by other investigators, and therefore was 'softer' before irradiation than that used by others.

The steady hardening over the 25-600°C temperature range is slightly different than that reported by Downey and Erye,⁽⁶⁾ but similar to that reported by Moteff.⁽⁹⁾ There is no immediate explanation for this behavior except perhaps cluster growth. It is difficult to verify this hypothesis as the extremely small cluster size (25-35 Å) does not allow detection of small changes in cluster size (the experimental error of the measurement is $\sim \pm 5$ Å).

The lack of hardness recovery at stages III, IV-A, and IV-B* is

*See reference 2 for stage terminology

TABLE I

SUMMARY OF THE MICROHARDNESS DATA FOR BOTH HIGH AND
LOW PRESSURE ISOCHRONALLY ANNEALED IRRADIATED MOLYBDENUM

<u>Annealing Temperature (a) °C</u>	<u>Vickers Hardness (b)</u>	<u>% Increase (c)</u>	<u>% Remaining (d)</u>
<u>At ≤ 1 bar</u>			
As-annealed	186	0	0
As-irradiated	221	19	100
75	223	20	106
150	225	21	111
200	228	23	117
300	228	23	117
400	232	25	128
500	234	26	134
605	235	26	137
700	223	20	106
700	223	20	106
800	201	8	48
900	190	2	11
1000	186	0	0
<u>At 20 kbar</u>			
25	230	27	143
80	242	30	160
110	242	30	160
205	240	29	154
300	242	30	160
350	240	29	154
400	242	30	160
430	223	20	106
490	213	14	77
500	199	7	37

(a) 2 hr. isochronal anneals; (b) 50 g load; (c) using unirradiated value as base state; (d) using as-irradiated values as base state.

emphasized in Figure 3 where the differential annealing rates for the hardness recovery is plotted together with those obtained from electrical resistance,⁽¹⁾ lattice parameter,⁽²⁾ and cluster density studies.⁽³⁾ As shown in Figure 3, the final recovery of hardness corresponds to the stage V recovery of both the observable defect clusters and the lattice parameter increase. This indicates that the hardening is related to the observable cluster density, but in a rather complex manner. The hardness values do not start to decrease until almost 50% of the observable clusters are annealed and 50% of the original hardness is left after all the resolvable clusters are removed. Furthermore, the hardness values do not reflect the decrease in cluster density during stage III, or the large drop in point defect concentration at that temperature.

The insensitivity of hardness to the point defect concentration is also dramatized by the fact that the electrical resistance increase, which is a measure of point defect concentration alone,⁽³⁾ is completely recovered before the hardness values start to decrease. It therefore would appear that a defect larger than one or two atoms (or lattice spacings) but smaller than $25 \text{ \AA}$ in diameter is responsible for a large amount of the hardness increase.

B. High Pressure Anneals

Both Figures 1 and 2 show that the hardness recovers at lower temperatures when the samples are annealed under pressure than when they are annealed in a vacuum. The initial increase in hardness due to a 25°C , 20 kbar anneal is rather striking in view of previous electron microscopy observations on the same material.⁽³⁾ These latter studies showed that

the observable defect cluster density had increased some 15% after the 25°C, 20 kbar anneals. Although this is less than the 40% (Figure 2) in hardness increase, the results are not too surprising in view of previous observations on the samples at low pressure.

As was the case for the low pressure annealed samples, more than half of the observable clusters have annealed in the high pressure anneals specimens before the hardness begins to change. Similarly almost half of the as-irradiated hardness increase remains after the observable clusters have been completely removed. This implies that the same type of 'unresolvable' defect that is responsible for the hardness increase at low pressures is also responsible for the hardening at high pressure. That this defect behaves similarly during both low and high pressure anneals is rather surprising.

The differential annealing rate, plotted in Figure 3, shows that the hardness recovery peak is at $\sim 450^\circ\text{C}$ which again corresponds to stage V recovery as indicated by the recovery of defect clusters. At the present time there is no satisfactory explanation for the mixed dependence of hardness increase on both the observable and unresolvable defects. Future studies at higher fluences may shed some light on this problem.

V. CONCLUSIONS

From the low pressure tests it is concluded that:

- . The hardness increases by 19% after an exposure of $6.2 \times 10^{18} \text{ n/cm}^2$ ($E > 1 \text{ MeV}$).
- . The hardness increases during isochronal anneals up to 600°C .
- . The recovery of the hardness increase is centered around 750°C

(stage V) but is not directly correlatabale to changes in the observable defect clusters.

From the 20 kbar anneals it is concluded that:

- . A 2 hour anneal at 25°C increases the hardness of the as-irradiated sample by 40%.
- . Annealing between 25-80°C under pressure increases the hardness of the as-irradiated sample by 60%.
- . The hardness is relatively constant between 80-400°C at 160% of the as-irradiated value.
- . The recovery of the hardness increase is centered around 450°C which coincides with the recovery of observable defect clusters under pressure although ~50% of the increase still remains after the observable clusters are removed.

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FIGURE 1
The Effect of Hydrostatic Pressure on the Isochronal
Annealing of Irradiation Induced Hardness in Molybdenum

FIGURE 2
Comparison of the Data in Figure 1 Plotted on a Reduced Scale Using the As-Irradiated Hardness Increase as a Base

FIGURE 3
Comparison of the Differential Annealing Rates for the
Recovery of Irradiation Induced Electrical Resistance,
Lattice Parameter, Cluster Density and Hardness Increases

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