THE EFFECT OF HYDROSTATIC PRESSURE
ON THE RECOVERY OF UNIT CELL DIMENSIONS
IN IRRADIATED MOLYBDENUM

G. L. Kulcinski and H. E. Kissinger

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Physical Metallurgy Section
Metallurgy Research Department

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ABSTRACT

Irradiation of high purity molybdenum to 6.2×10^{18} n/cm² ($E > 1$ MeV) at 40°C results in a 0.22% lattice parameter increase. Isochronal anneals at ≤ 1 bar disclose that the expansion of the material recovers in three stages, 150°C, 400°C, and 750°C. Combination of this data with previously obtained electrical resistance measurements reveals that there are four recovery stages above room temperature. The designation of recovery stages has been modified: stage III (150°C), stage IV-A (400-425°C), stage IV-B (575°C), and stage V (750°C). Because isochronal anneals at 20,000 bars of hydrostatic pressure lower stage III to 90°C, a negative activation volume of migration is implied. The temperature for complete recovery of lattice parameter is lowered by pressure from 750°C to 350°C. Analysis of the data implies a divacancy mechanism for stage III recovery.

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INTRODUCTION

High precision X-ray determinations of lattice parameters provides a useful method of estimating the relative number of free interstitials in irradiated or cold worked metals. This technique can also be used to identify the temperature ranges in which the interstitial concentration is changing. Such information, in conjunction with electrical resistivity, length change, mechanical property, and electron microscopy measurements, is needed to develop a model which will describe the recovery of neutron induced damage in metals.

A metal which has received considerable attention in the bcc system is molybdenum.⁽¹⁻⁵⁾ Adam and Martin⁽¹⁾ showed that lattice expansions of 0.02% result from a fast neutron bombardment of 1.5×10^{19} n/cm². Gray and Cummings⁽²⁾ later found that the lattice parameter increase reaches a maximum value of 0.05% at 5×10^{19} n/cm², and that any further irradiation causes a contraction of a unit cell. It was also shown that the amount of impurities in the Mo apparently affected the lattice parameter increase (hence, interstitial concentration) in irradiated samples.⁽²⁾ The isochronal annealing of Mo irradiated to 6×10^{18} n/cm² has revealed⁽³⁾ that the defects

responsible for the lattice parameter increase anneal in three definite stages; $0.15 T_m$, $0.23 T_m$, and $0.35 T_m$ where T_m is the melting point at 1 bar*. Analysis of the annealing kinetics were complicated and obeyed neither first or second order.⁽³⁾

The progressive broadening of the (400) $K\alpha_1$ X-ray peak with exposures up to 1.2×10^{20} n/cm² is indicative that considerable lattice straining has taken place. This broadening of X-ray peaks was found⁽⁴⁾ to be stable to postirradiation anneals to 600°C and that it is completely removed by anneals at 830°C ($0.37 T_m$).

Prompted by the recent discovery that the application of hydrostatic pressure during postirradiation annealing accelerates the recovery of irradiation-induced electrical resistance increases,⁽⁶⁾ an investigation of the effect of pressure on the recovery of irradiation-induced lattice parameter increases was begun. This report describes the results of that study.

EXPERIMENTAL TECHNIQUES

The sample material, preirradiation heat treatments, irradiation data, and postirradiation low and high pressure annealing techniques have been described previously.⁽⁶⁾ Briefly, polycrystalline high purity molybdenum containing less than 10 ppm of carbon was irradiated to 6.2×10^{18} n/cm² ($E > 1$ MeV) at temperatures of $\sim 40^\circ\text{C}$. The postirradiation annealing of these samples was carried out at two pressures; ≤ 1 bar and 20,000 bars. The time

* 1 bar = 1 atm. = 10^6 dynes/cm²

of the isochronal anneal was 2 hours.

The geometry of the foil samples used for the lattice parameter studies was 1 cm long, 0.5 cm wide, by 0.0075 cm thick. The lattice parameters were determined with Cu K α and Cu K β radiation and extrapolated in the usual manner by means of the Nelson-Riley function, $1/2 (\cos^2 \theta / \theta + \cos^2 \theta / \sin \theta)$.⁽⁷⁾ Lonsdale's⁽⁸⁾ wave length values were used, namely

$$\text{Cu K}\alpha_1 = 1.54051 \text{ \AA}$$

$$\text{Cu K}\alpha_2 = 1.54433 \text{ \AA}$$

$$\text{Cu K}\beta = 1.39217 \text{ \AA}$$

RESULTS

The extrapolated value of the lattice parameter of the molybdenum samples after annealing, but before irradiation, was $3.1472 \pm 0.0001 \text{ \AA}$. The corresponding as-irradiated value of the molybdenum was $3.1479 \text{ \AA}$, equivalent to a 0.022% increase for an exposure of $6.2 \times 10^{18} \text{ n/cm}^2$. Table I lists the values of the lattice parameters after annealing at low pressures along with the widths of the (400) K α_1 X-ray peak at half intensity. Figure 1 presents these results in graphical form and shows that the annealing takes place in three distinct stages, 150°C (0.15 T_m), 400°C (0.24 T_m), and 750°C (0.35 T_m); these stages are more clearly shown in the differential annealing curve in Figure 2. It should also be noted from Table I that there is no noticeable change in the X-ray peak width either due to irradiation or low pressure annealing up to at least 1000°C.

The results of the 20 kbar anneals are listed in Table II and shown graphically in Figures 1 and 2 where they can be compared to the low pressure results. It is obvious that annealing under pressure induces the damage to

T A B L E I

SUMMARY OF LATTICE PARAMETER MEASUREMENTS OF
IRRADIATED MOLYBDENUM ISOCHRONALLY ANNEALED AT PRESSURES OF ≤ 1 BAR

Annealing Temperature* °C	Lattice Parameter _o <u>± 0.0001 A</u>	<u>% Lattice Parameter Increase Remaining</u>	Half Width of (400) $K\alpha_1$ Peak ($^{\circ}2\theta$)
As Annealed	3.1472		0.21
As Irradiated	3.1479	100	0.23
75	3.1479	100	0.21
133	3.1478	86	0.23
150	3.1476	59	0.20
200	3.1475	43	0.21
300	3.1475	43	0.20
400	3.1474	29	0.21
500	3.1473	14	0.21
605	3.1473	14	0.23
650	3.1473	14	0.20
700	3.1473	14	0.22
800	3.1472	0	0.21
900	3.1472	0	0.20
1000	3.1472	0	0.22

*2 hours at each temperature

T A B L E II

SUMMARY OF LATTICE PARAMETER MEASUREMENTS OF IRRADIATED
MOLYBDENUM ISOCHRONALLY ANNEALED AT 20 KBAR

<u>Annealing Temperature*</u> °C	<u>Lattice Parameter</u> <u>+ 0.0001 Å</u>	<u>% Lattice Parameter Increase Remaining</u>	<u>Half Width of (400) Kα₁ Peak (°2θ)</u>
As Annealed	3.1472		0.21
As Irradiated	3.1479	100	0.23
25	3.1479	100	0.23
80	3.1478	86	0.24
90	3.1477	71	0.23
110	3.1475	43	0.23
175	3.1474	29	0.23
205	3.1474	29	0.22
300	3.1474	29	0.22
350	3.1473	14	0.24
400	3.1472	0	0.23
430	3.1472	0	0.25
490	3.1472	0	0.25

* 2 hours at each temperature

anneal out at lower temperatures. The shift from 150 to 90°C represents a pressure coefficient of -3°C/kbar and the shift from 750°C to 350°C for final recovery represents -20°C/kbar reduction. No indication of the original 400°C low pressure peak is found in the high pressure data. It should be noted again that the half width of the (400) $K\alpha_1$ X-ray peak is not significantly affected by the high pressure anneals.

It should be pointed out that the error limits of ± 0.0001 Å^o are indicative of the absolute error while the relative error between samples X-rayed in the same equipment is somewhat smaller.

DISCUSSION

A brief analysis of the low pressure anneals is in order prior to the analysis of the high pressure results.

The lattice parameter increase of 0.022% for 6.2×10^{18} n/cm² is in fair agreement with the results of Gray⁽³⁾ who found 0.032% increase that exposure. However, our results indicate a considerably larger increase than the 0.003% increase found by Adam and Martin.⁽¹⁾ As Gray and Cummings⁽²⁾ point out, the lattice parameter increase at any fluence varies directly with impurity level. Since our material is known to be purer than Gray's⁽³⁾ but probably less pure than that of Adam and Martin's,⁽¹⁾ the results are consistent with the proposed impurity effect.

The annealing of the molybdenum takes place at almost exactly the same temperatures as reported by Gray;⁽³⁾ this agreement indicates that purity does not have a significant effect on the recovery temperatures

at this fluence. The complete recovery of the lattice parameter increase at 800°C is also in agreement with Gray⁽²⁾ and Butra.⁽⁴⁾

The lattice parameter recovery can be compared with the electrical resistance recovery in the same material in Figure 3. The two curves coincide fairly well up to $\sim 500^{\circ}\text{C}$ except for the 200-300°C range where the lattice parameter change is less than the error limits and causes a "step" in the curve. Above this temperature, the resistance anneals out with no noticeable recovery in lattice parameter at $\sim 575^{\circ}\text{C}$ while the lattice parameter shows its final annealing stage at 750°C. This behavior is emphasized in Figure 5a where the differential annealing curves for resistance recovery can be compared with lattice parameter recovery.

The fact that there are at least four detectable annealing stages above room temperature makes the use of normal stage III, IV, and V notation rather awkward. To avoid confusion with the work of others who refer to the annealing in terms of stages, we have arbitrarily decided to label the 400-425°C recovery peak as stage IV-A and that at 575°C as stage IV-B. This will leave the highest annealing stage as stage V while that at 150°C will still be referred to as stage III.

From considerations of both the lattice parameter and electrical resistance measurements (Figure 5) it can be inferred that interstitial migration or annihilation is taking place in stages III and IV-A while a defect other than interstitials is responsible for stage IV-B. The final lattice parameter recovery at a temperature higher than that at which the electrical resistance increase is completely recovered suggests that the interstitials

are in a configuration which does not contribute to resistivity. This would be the case if the interstitials were clustered and the last annealing stage corresponded to the annealing of the clusters.

The information obtained in the present tests shows that any model describing the pressure induced stage III annealing must include annihilation of free interstitials. This could be accomplished by:

1. Migration of free interstitials to vacancies, to interstitial clusters, or traps where they could contribute very little to the lattice parameter increase.
2. Release of interstitials from traps to participate in the process in number 1.
3. Migration of divacancies to isolated or trapped interstitials.
4. Migration of vacancies to isolated or trapped interstitials.

The fact that interstitials participate in both stages III and IV-A indicates that processes 1 and 2 are rather unlikely because if the interstitial migrated in stage III there would be no free or trapped interstitials to annihilate in stage IV-A. Processes 3 and 4 could account for lattice parameter decreases in both stages if one type of vacancy migrated in stage III, and the other migrated in stage IV-A. Since divacancies are slightly more mobile than single vacancies,⁽⁹⁾ a logical order might be divacancies migrating at the lower temperature stage and single vacancies in the $0.24 T_m$ stage.

At this point one would hope that the pressure experiments might distinguish between the two possibilities. It has been shown⁽¹⁰⁾ that pressure retards diffusion by vacancies in most metals and Emrick⁽¹¹⁾

has measured the activation volume of vacancies to be positive in Au. These observations indicate that if the stage III were due to single vacancies migrating to interstitials, then this annealing stage should occur at higher temperatures under pressure. Unfortunately, no measurements have been made on the diffusion of divacancies or interstitials for that matter, and it remains for future experiments to solve this question.

The pressure induced lowering of the annealing temperature shown in Figures 1 and 2, is almost identical to that found in resistivity studies⁽⁶⁾ and indicates that whatever process is taking place, interstitials are still involved as they were at low pressures. Figure 4 shows the recovery of both the electrical resistance and lattice parameter at 20 kbars. Because they display the same recovery peaks (Figure 5b), they must be closely related.

One can calculate an activation volume of migration for the mobile defect in stage III from the shift with pressure of the isochronal annealing curves.⁽⁶⁾ This calculation shows that the activation volume of the defect migrating at stage III is $-0.9V^*$, where V^* is the atomic volume. The implications of this value were discussed in the electrical resistance studies⁽⁶⁾ on the same material and the lattice parameter measurements confirm that interstitials are involved. Whether an interstitial is migrating or whether a vacancy type defect is migrating to a trapped interstitial is not evident from these studies. In view of the previous observations⁽⁶⁾ and the fact that point defect type interstitials are still present above stage III at low pressure, it is felt that the migrating divacancy is the most likely defect responsible for stage III.

The fact that there are only two recovery stages at 20 kbar for both electrical resistance and lattice parameter/could mean several things. It increases could mean that stages IV-A, IV-B, and V are all reduced proportionately to give a single recovery stage under pressure. This is deemed highly unlikely unless the choice of 20 kbars was extremely fortunate. Another possibility is that the stage V recovery is reduced while IV-A and IV-B are retarded or unaffected. This would change the order in which the defects anneal and would thus allow complete annihilation to take place without the intermediate stages of annealing. One other possibility is that the application of pressure eliminates stage V recovery of the lattice parameter increase and allows only stage III and stage IV-B recovery to occur. This would require stage IV-B to have a negative pressure coefficient which would result in the premature recovery. More definite statements about the mechanism of annealing under pressure must await further results at lower pressure and the results of other measurements (electron microscopy and hardness).

Finally, it should be noted that the absence of any significant X-ray peak broadening introduced by the pressure treatments (Tables I and II) indicates that the pressure was truly hydrostatic at all times. This information substantiates previous observations⁽⁶⁾ that the electrical resistance of unirradiated control specimens was not changed over the range of pressures and temperatures used in this experiment.

CONCLUSION

It has been found that

- ° the lattice parameter increases by 0.022% as a result of

- irradiation to a fast fluence of $6.2 \times 10^{18} \text{ n/cm}^2$,
- during low pressure annealing, the lattice parameter increase recovers in three distinct stages: $0.15 T_m$, $0.24 T_m$, and $0.35 T_m$,
 - lattice parameter recovery and electrical resistance recovery can best be described by a new system of stage designations: $0.15 T_m$ as stage III, $0.24 T_m$ as stage IV-A, $0.29 T_m$ as stage IV-B, and $0.35 T_m$ as stage V,
 - annealing under 20 kbars pressure lowers the stage III peak by 60°C ,
 - under 20 kbars pressure, the activation volume of migration for stage III is $-0.9V^*$,
 - the temperature for complete lattice parameter recovery is lowered by 400°C under 20 kbars of pressure or -20°C/kbar ,
 - a migrating divacancy is the most likely defect responsible for stage III recovery.

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REFERENCES

1. J. Adam and D. G. Martin, Phil. Mag., 3, 1329, 1958.
2. D. L. Gray and W. V. Cummings, Acta Met., 8, 446, 1960.
3. D. L. Gray, Acta Met., 7, 432, 1959.
4. F. P. Butra, Phys. Met. and Metal, 10, 223, 1960.
5. V. A. IL'Yina, V. K. Kritskaya, and B. V. Sharov, Phys. Met. and Metal, 19, 301, 1965.
6. G. L. Kulcinski, BNWL-844, 1968.
7. J. B. Nelson and D. P. Riley, Proc. Phys. Soc., 57, 160, 1945.
8. K. Lonsdale, Acta Cryst., 3, 400, 1950.
9. R. A. Johnson, "Diffusion in Body Centered Cubic Metals", ASM, p. 357, 1965.
10. D. Lazarus and N. H. Nachtreib, "Solids Under Pressure", p. 43, McGraw-Hill, 1963.
11. R. M. Emrick, Phys. Rev., 122, 1720, 1961.

FIGURE 1
The Effect of Pressure on the Isochronal Annealing of Unit
Cell Dimensions in Irradiated Molybdenum

FIGURE 2
Comparison of the Differential Annealing Curves for the
Recovery of Unit Cell Dimensions in Figure 1

FIGURE 3
Comparison of the Isochronal Recovery of Electrical
Resistance and Lattice Parameter Increase in Irradiated
Molybdenum which is Annealed at Low Pressure

FIGURE 4
Thermal Recovery of Electrical Resistance
after Increase in Irradiated Molybdenum
under 20 kbars of Pressure

FIGURE 5
Comparison of the Differential Annealing Curves for
Electrical Resistance and Lattice Parameter Increases in
Irradiated Molybdenum. a) ≤ 1 Bar. b) 20,000 Bars

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