THE EFFECT OF HYDROSTATIC
PRESSURE ON THE RECOVERY OF
ELECTRICAL PROPERTIES OF
IRRADIATED MOLYBDENUM

G. L. Kulcinski

JULY, 1968

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PACIFIC NORTHWEST LABORATORY

RICHLAND, WASHINGTON

operated by

BATTELLE MEMORIAL INSTITUTE

for the

UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

PRINTED BY/ FOR THE U. S. ATOMIC ENERGY COMMISSION

3 3679 00061 1535

BNWL-844

UC-25, Metals, Ceramics, and Materials

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by

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July, 1968

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

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INTRODUCTION

The effect of irradiation on the electrical resistivity of molybdenum has been studied in great detail by many investigators.¹⁻⁹ In general, the resistivity increase is proportional to the fast fluence although Moteff¹⁰ has recently shown that the increase reaches a maximum at 10^{20} n/cm² after which it begins to decline. In an effort to determine what defect, or defects, are responsible for this property change, scientists have usually used post-irradiation annealing techniques at 1 bar* or less. Such experiments reveal that the damage recovers in several distinct stages. In Mo, which has been irradiated at room temperature, it has been found that the most prominent recovery temperatures occur at approximately $0.15 T_m$, $0.22 T_m$, and $0.31 T_m$, where T_m is the melting temperature in °K.

The $0.15 T_m$ stage has been studied more intensively than the others and it seems generally accepted that the activation energy for this stage is 1.2-1.3 eV.^{1-3, 8, 11-12} Considerable difficulty has been encountered by investigators in determining the order of the reaction in this stage. Apparently it is close to second order,^{1, 8, 13} analogous to results found in W⁹ and Nb¹⁴, but the extreme sensitivity to temperature and time make any conclusive statement impossible.

*1 bar $\approx$ 1 atmosphere

The $0.22 T_m$ stage is very weak in lightly irradiated samples and for that reason has not been studied in any great detail. Moteff¹⁵ has examined the reaction order for the $0.31 T_m$ stage and finds that it starts out with second order kinetics, but approaches first order as the time increases.

Investigators who make interpretations of the species migrating in the $0.15 T_m$ stage generally fall into one of two camps. The first group^{1, 6-9} feels that interstitials, either free or those released from traps, are migrating to immobile vacancies or adding on to interstitial clusters. Both groups use supporting arguments concerning length and lattice parameter change, defect cluster observation, or the recovery of hardness and mechanical properties to fortify their position, but neither has been able to conclusively prove their case.

In an effort to provide information which might uniquely identify the mobile defect, or defects, in the $0.15 T_m$ stage, we have undertaken a radically new approach from that of previous investigators. In addition to performing the customary postirradiation anneals at pressures equal to less than 1 bar, we have isochronally annealed irradiated Mo specimens while they were subjected to high hydrostatic pressures. The reason for this approach is briefly outlined in a qualitative fashion below.

Since any defect, whether it is a vacancy, interstitial, or cluster of either type, increases the specific volume of a crystal, the application of a hydrostatic pressure will raise the energy of an irradiated crystal more than that of an identical crystal with no defects. This extra strain energy will then provide a driving force for the elimination or annealing of the defect.

However, the defect must migrate to be removed and pressure also affects that process. Consider the simple case of a migrating vacancy. The atom jumping into the vacancy must pass through a ring of lattice atoms. At its saddle point,

this ring of atoms is forced outward which causes a volume increase ΔV . To do this when a pressure P is pushing on the crystal requires an extra amount of energy, $P\Delta V$. The term ΔV is commonly referred to as an activation volume and, if it is positive, processes which require an activation energy E at zero pressure require $E + P\Delta V$ at high pressure.

It is reasonable to expect that each type of defect (interstitial, vacancy, or cluster) will have a unique ΔV associated with it. Given this situation, the application of pressure during annealing at any temperature should then provide a third dimension capable of distinguishing between defects which act similarly when only thermal energy is considered. Accordingly, the objectives of the present experiments are to:

1. measure the direction in which the $0.15 T_m$ annealing peak is shifted with pressure,
2. measure the magnitude of the shift in number 1,
3. calculate an overall activation volume for stage $0.15 T_m$ annealing, and
4. investigate the effect of pressure on the higher temperature annealing stages ($0.22 T_m$, $0.31 T_m$).

SUMMARY

High purity molybdenum has been irradiated at 40°C to $6.2 \times 10^{18} \text{ n/cm}^2$ ($E > 1 \text{ MeV}$) and subsequently isochronally annealed at two pressures, $\leq 1 \text{ bar}$ and $20,000 \text{ bars}$. The electrical resistance increase recovers in three stages at low pressure, 150°C , 425°C , and 575°C . The activation energy for the 150°C recovery peak is $1.25 \pm 0.09 \text{ eV}$ and the order of the reaction varies from 3.4 at 135°C to 1.7 at 164°C . The effect of pressure is to lower the 150°C recovery peak to 90°C ; this shift implies a negative activation volume of migration of -0.9 molar

volumes for the migrating defect. The final recovery peak is lowered to 375°C under pressure and displays a pressure coefficient of -10°C/kbar. The 425°C peak is apparently also lowered by pressure, but because of its small magnitude and uncertainty in its position, more detailed data are required for analysis.

EXPERIMENTAL

SAMPLES

Polycrystalline, high purity, 0.0075 cm-thick molybdenum foil containing less than 10 ppm carbon was used. Because of the number of times each specimen was to be handled, as well as limitations imposed on specimen size by the high pressure apparatus, the foils were machined into the four-probe type specimens pictured in Figure 1. After degreasing, the samples were etched in an electrolyte of 25 ml HCl, 10 ml H₂SO₄ and 75 ml methyl alcohol cooled to 10°C. The applied voltage between the specimen and the electrodes was 18 V and the current density was 0.9A/cm². The etched samples were vacuum annealed at 1760°C for 20 minutes at 10⁻⁵ torr. The average grain diameter after this treatment was 19 microns. The ratio of the electrical resistance at 273°K divided by that at 4.2°K was 42.

Irradiation took place in a Hanford Production Reactor to a fast fluence (> 1 MeV) of 6.2×10^{18} n/cm² at temperatures of about 40°C.

RESISTANCE MEASURING EQUIPMENT

The resistance measurements were made on a high sensitivity (0.01 microvolt) voltage measuring system with a current of 20 milliamps. All measurements reported here were taken at 4.2°K.

The four probe samples were placed in a special Micarta holder such that each tab was resting on an individual copper disk through which current was introduced and the voltage drop measured. In this way the geometry factor was

constant for each test and the data on any individual sample reflect changes in resistivity. Calculation of the absolute resistivity was hampered by not knowing the precise length over which the voltage drop was measured (although it is the same each time). If the lines of equipotential are symmetrical, then this length should be measured from the mid-points of the voltage tabs. But rather than let this uncertainty affect the results, only resistance ratios will be reported here.

LOW PRESSURE ANNEALS

The low pressure isothermal and isochronal anneals below 200°C were carried out in a silicone oil bath. Temperatures were controlled to within $\pm 0.5^\circ\text{C}$. At 250°C a $\text{KNO}_3\text{-NaNO}_3$ bath was used and from 300-1000°C the samples were heated at 10^{-5} torr with radiant heat lamps. These latter anneals were controlled to within $\pm 3^\circ\text{C}$. The time of the isochronal anneals was 2 hours. Unirradiated control samples were included in each test.

HIGH PRESSURE ANNEALS

Four probe samples were isochronally annealed for 2 hours under a hydrostatic pressure of 20 ± 1 kbars from 25 to 490°C. The high pressure system used has been described elsewhere¹⁹ but is basically a piston-cylinder unit which was calibrated at 25°C by discontinuous electrical resistance changes in Ce at 7.6 kbars²⁰ and Bi at 25.4 kbars.²¹ The equipment was also calibrated at 100°C by discontinuous volume changes in RbCl at 5.3 kbars²² and in KI at 17.2 kbars.²³

The samples were contained in a collapsible can arrangement¹⁹ such as that shown in the schematic in Figure 2. Although only one thermocouple was used on most tests, several tests with two thermocouples were made: one touching the bottom and one touching the side of the can. It was found that the temperature difference between thermocouples was less than 3°C. A pressure

correction generally less than 3°C was applied to the thermocouple readings.²⁴

At the present time it is felt that the temperatures quoted for the high pressure tests are accurate to $\pm 5^{\circ}\text{C}$.

The pressurizing fluid was a 50-50 mixture of isopentane and n-pentane below 300°C while the eutectic mixture of NaK was used above 350°C . Unirradiated control specimens were included in each run and showed no change over the range of pressures used. Figure 3 shows a typical can before and after the test. Obviously the samples were designed to easily fit into the collapsed volume to avoid any damage due to bending.

The chronology of a pressure test was as follows. The pressure was raised to 20 kbars in five minutes at room temperature and the temperature was then raised to the desired level within five minutes. After operating for two hours, the temperature was lowered to below 50°C within two minutes and then the pressure released to ambient in two minutes.

METHOD OF ANALYSIS

ACTIVATION ENERGY

It is well known that if the annealing of a defect takes place with a single activation energy, then the rate of change of the concentration of defect is just²⁵

$$\frac{dC}{dt} = -F(C)K_0 \exp\left(-\frac{H}{kT}\right) \quad (1)$$

where C = concentration of defects

t = time

$F(C)$ = function of C

K_0 = rate constant

H = activation enthalpy of the process

k = Boltzman's constant.

There are at least four different methods of determining H in equation 1 and one of the most widely used is the technique of Meechan and Brinkman.²⁶ Their method combines both isothermal and isochronal data. The relation between the elapsed time of the isothermal anneal, $\Delta\tau$, and the time of the temperature pulses in the isochronal plot, Δt , taken at the same level of defect concentration is just

$$\ln(\Delta\tau/\Delta t) = \frac{H}{k} \left(\frac{1}{T_a} - \frac{1}{T_i} \right) \quad (2)$$

where T_a = temperature of isothermal anneal

T_i = temperature in the isochronal plot which produces the same defect concentration associated with $\Delta\tau$ at T_a .

The activation enthalpy can be determined by plotting $\ln\Delta\tau$ versus $1/T_i$ and equating the slope equal to $-H/k$.

ORDER OF REACTION

The order of a reaction can be calculated by measuring a physical property which is proportional to the number of defects remaining after time t at temperature T . Assuming the electrical resistance to be such a property and substituting ΔR for C in equation 1 and $(\Delta R)^n$ for $F(C)$, one finds

$$\Delta R_o \int \frac{\Delta R d(\Delta R)}{(\Delta R)^n} = -K_o \exp -H/kT \int_0^t \quad (3)$$

where n = order of the reaction

$$\Delta R = R_T - R_e$$

$$\Delta R_o = R_o - R_e$$

R_T = resistance of sample after annealing for time t at temperature T

R_e = resistance of sample at the end of the annealing stage in question

R_o = as-irradiated resistance.

Integrating equation 3 one finds for $n \neq 1$,

$$\left(\frac{\Delta R}{\Delta R_0}\right)^{n-1} = 1 + At \quad (4)$$

where $A = (n-1)K_0 \exp(-H/kT)$.

When n is chosen properly, a plot of $(\Delta R_0/\Delta R)^{n-1}$ versus time will give a straight line.

ACTIVATION VOLUME

The activation enthalpy of an event is the sum of the activation energy E , and the pressure-volume relation of the process.

$$H = E + P\Delta V \quad (5)$$

Hence if isochronal annealing is performed at different pressures the number of defects annealed out at any temperature T for a fixed time t will be a very sensitive function of $P\Delta V$. Since P is always positive in compression, the sign of ΔV will determine whether the $P\Delta V$ term will raise the activation enthalpy or lower it. If it is raised, fewer defects will anneal in time t at temperature T , and if it is lowered, more defects will anneal. As a consequence, the position of the recovery temperatures will be shifted to higher or lower values respectively.

If a horizontal line is drawn at a fixed amount of defect recovery on an isochronal plot (a fixed amount of resistivity recovery in our case) then the quantity

$$-\frac{1}{K_0} \int_{\Delta R_0}^{\Delta R} \frac{d(\Delta R)}{(\Delta R)^n} = t \exp\left(-\frac{E + P_j \Delta V}{kT_j}\right) \quad (6)$$

will be constant for any T_j and P_j . In this case T_j is the temperature at which the resistance recovery reaches ΔR in an annealing time t under a pressure P_j . It is assumed that the activation energy, the pre-exponential term, and the order of the reaction are not changed by the applied pressure.

Since the time of the isochronal anneal is constant by definition, equation 6 reduces to equation 7 at any ΔR , and

$$\exp\left(-\frac{E + P_j \Delta V}{kT_j}\right) = \text{constant} \quad (7)$$

If the isochronal annealing is carried out at two different pressures P_j and P_{j+1} , then the activation volume of the process can be calculated by noting the temperatures T_j and T_{j+1} at which the annealing curves intersect the line of fixed resistance recovery, or

$$\Delta V = \frac{E(T_{j+1} - T_j)}{P_{j+1}T_j - P_jT_{j+1}} \quad (8)$$

WAITE'S ANALYSIS

According to Waite²⁷ a diffusion limited bimolecular recovery process in which one of the defects is essentially immobile can be described by

$$C_o/C - 1 = k_o t \exp(-H_m/kT) + k_1 t^{1/2} \exp(-H_m/2kT) \quad (9)$$

where C_o = the total concentration of defects annealed in the recovery stage of interest

C = the concentration at time t and temperature T

$$k_o = 4\pi N r_o C_o D_{om}$$

$$k_1 = 8\pi^{1/2} N r_o^2 C_o (D_{om})^{1/2}$$

N = number of atoms/cc

r_o = capture radius, i.e., distance within which defects have to approach each other to react chemically.

D_{om} = pre-exponential constant for migration

H_m = activation enthalpy of migration.

Assuming that C_o/C is proportional to $\Delta R_o/\Delta R$, one can estimate the quantity

$r_o C_o D_o$ from equation 9 by plotting $\Delta R_o/\Delta R$ versus t and $t^{1/2}$. The slope of the

straight line curves at any temperature then is equal to $k_o \exp(-H_m/kT)$ for a linear time dependence and to $k_l \exp(-H_m/2kT)$ for a square root time dependence.

RESULTS

LOW PRESSURE ANNEALS

Figure 4 is the isochronal annealing curve as determined at ≤ 1 bar. It represents data from seven different samples which all show good agreement when plotted on a reduced scale. Figure 5 is the differential annealing curve from Figure 4 showing a large recovery peak at $0.15 T_m$, a rather small one at $0.24 T_m$ and another one at $0.29 T_m$.

Isothermal annealing data for three samples annealed at 135, 149, and 164°C are plotted in Figure 6. Combining these data with that in Figure 4 produces a Meecham-Brinkman plot (see equation 2) shown in Figure 7. The slope of these plots yields an activation energy of 1.25 ± 0.09 eV.

In order to determine the reaction order of the $0.15 T_m$ stage one must know the well annealed resistance ratio at the end of that stage. A sample which was annealed at 149°C for 2190 min. gave a value of 0.408, whereas, using the method of Nihoul¹ and Moteff,⁹ namely designating the resistance at the minimum of the differential annealing curve as the well-annealed resistance, gave a resistance ratio of 0.413. If 0.410 is assumed to be the correct ratio, the order of the reaction is calculated (equation 4) to be dependent on temperature in the following fashion:

<u>T°C</u>	<u>Order</u>
135	3.4
149	2.0
164	1.7

Figure 8 shows the plot of $(\Delta R_o / \Delta R)^{n-1}$ versus t and verifies that the above orders are correct.

The isothermal data was plotted versus $\sqrt{t}$ and t to compare with Waite's²⁷ analysis; Figures 9 and 10 show the results. The 135° annealing data show a $\sqrt{t}$ annealing dependence, whereas the 149°C data show good second order behavior. The 164°C anneal did not give a straight line for either time scale. Using the slopes of the 135 and 149°C curves in Figures 9 and 10 along with equation 9 one can obtain two independent equations containing C_o , r_o , and D_o .

The value of C_o was estimated in the following manner. Lucasson and Walker⁴ found that the resistivity contribution per atomic percent defects in Mo is 4.5 micro-ohm-cm. By noting the resistance ratios ($R_{273}/R_{4.2}$) before and after irradiation, one calculates that the resistivity increase in this experiment was 0.65 micro-ohm-cm. This would then imply that there are 0.144 atomic percent defects in the samples due to irradiation. Since 59% of those defects anneal at the 0.15 T_m stage, $C_o \approx 8.5 \times 10^{-4}$. Using this value of C_o one finds that

$$r_o = 9-10 \text{ \AA}$$

if D_o is between $3-8 \times 10^{-3} \text{ cm}^2/\text{sec}$.

HIGH PRESSURE ANNEALS

Figure 11 shows the isochronal curve obtained by annealing at 20 ± 1 kbars and Figure 12 shows its corresponding differential annealing curve. The annealing temperature is now 90°C as opposed to 150°C at low pressure (Figure 4). The recovery peaks are lowered to 0.13 T_m and 0.22 T_m , where T_m is again the one atmosphere melting temperature. To be strictly correct these recovery peaks should be stated in terms of the melting temperature at 20 kbars. Although this information is not available at the present time, it is most likely that the melting temperature is increased with pressure.

Figure 13 shows the isochronal recovery of both the low and high pressure anneals on the same curve, emphasizing the fact that pressure has lowered both

the $0.15 T_m$ and $0.29 T_m$ recovery stages. Insufficient points are available to make any definite statements about the $0.24 T_m$ peak at this time.

DISCUSSION

It is advantageous at this point to break the discussion into two parts, one covering the low pressure work and the other covering the high pressure results. The low pressure work will be briefly discussed in view of previous studies on Mo in order to show that this material was not unique in any way except perhaps its low carbon content.

LOW PRESSURE RESULTS

A summary of the previous electrical resistance studies of irradiated and cold worked Mo is shown in Table I. It can be seen that the present work agrees quite well with that of other investigators with respect to the recovery stages and energy of migration for the $0.15 T_m$ stage.

The variation of reaction order in the $0.15 T_m$ annealing stage, similar to that reported by Nihoul¹, DeJong⁸, and Gray¹³ indicates that the annealing process is indeed complex. This work along with Nihoul's¹ and DeJong's⁸ shows that the reaction order decreases as temperature increases while Gray¹³ states that it actually approaches first order kinetics. However, there is no reason that n should be two even if the reaction is bimolecular, i.e., even if the annealing takes place by the migration of interstitials to vacancies or vice versa. Second order kinetics can only be expected from a bimolecular reaction when the initial concentrations of the reactants are equal.²⁵ It is highly unlikely that the number of free or trapped interstitials exactly equals the number of free or trapped vacancies (or divacancies for that matter). Electron microscopy studies^{16,17,29-32} have shown that there is a high density of defect clusters observed in Mo after irradiation and that these clusters are predominantly interstitial in character. Since equal numbers of vacancies and interstitials

TABLE I.
Summary of Previous Electrical Resistance Studies
of Irradiated and Cold Worked Molybdenum

<u>Reference</u>	<u>Purity, %</u>	<u>T/T_m</u>			<u>E eV</u>	<u>Fast Fluence</u>	<u>Irradiation Temperature, °C</u>
This work	99.99	0.15	0.24	0.29	1.25	6.2x10 ¹⁸	40
Kinchin & Thompson ²	99.9	0.15	0.22	(a)	1.3	1.5x10 ¹⁸	30
Nihoul ¹	99.9	0.15	0.21	(a)	1.23	2x10 ¹⁷	-196
Peacock & Johnson ³	99.99	0.15	0.19	(a)	1.25	3x10 ¹⁹	40
Martin ¹²	99.99	0.15	0.22	(a)	1.26	Cold Worked	
DeJong ⁸	99.98	0.15	(a)	(a)	1.23	2x10 ¹⁸ (b)	50
Veljovic & Milasen ⁷	99.9	0.15	(a)	(a)	-	4x10 ¹⁹	60
Ibragimov ⁵	-	0.16	-	0.31	-	1.8x10 ²⁰	40-70
Pravdyuk ⁶	-	0.16	-	0.30	-	2.9x10 ²⁰	40
Moteff & Smith ⁹	99.98	0.15	-	0.31	-	1.3x10 ¹⁹	Reactor Ambient
Laidler & Wheeler ²⁸	99.9	0.15	0.20	0.30	-	1.5x10 ²⁰	40

(a) Did not carry annealing to required temperature

(b) 2.5 MeV electrons

must be produced initially, this would mean that the free vacancy concentration will greatly outnumber the free or trapped interstitial concentration. Given this situation, one might expect the annealing behavior to be complex and it appears that little weight can be placed on the failure to meet second order kinetics.

The calculation of a capture radius r_0 , and pre-exponential factor using Waite's²⁷ analysis is subject to question considering that Waite's analysis is only good for the case of equal defect concentrations. It is possible that this uncertainty could explain why the calculated capture radius of 9-10 Å is lower than DeJong's¹¹ value of 15-36 Å for Mo and 20-43 Å for Nb obtained by Stals and Nihoul.³³

The calculated pre-exponential factor of $3-8 \times 10^{-3} \text{ cm}^2/\text{sec.}$ can be compared to experimentally measured values for vacancy diffusion if it is multiplied by $\exp(S_f^v/k)$ where S_f^v is the entropy of formation of a vacancy, or,

$$D_{OD}^v = D_{om} \exp(S_f^v/k) \quad (10)$$

where D_{OD}^v is the pre-exponential self diffusion coefficient for single vacancies. According to Kraftsmaker³⁴ the value of S_f^v/k for Mo is 5.8 which would give a $D_{OD}^v = 0.94-2.5 \text{ cm}^2$. This is a factor of 3-8 larger than that found for self diffusion of a single vacancy ($0.3 \text{ cm}^2/\text{sec.}$).³⁵

It is interesting to calculate the self diffusion coefficient of divacancies, D_{OD}^{2v} , from D_{om} by

$$D_{OD}^{2v} = D_{om} \exp(S_f^{2v}/k) \quad (11)$$

where S_f^{2v} is the entropy of formation of a divacancy. Peart and Askill³⁵ have calculated that $S_f^{2v}/S_v^v = 1.8$ so that $S_f^{2v}/k = 10.4$. Equation 11 then gives $D_{OD}^{2v} = 100-260 \text{ cm}^2/\text{sec.}$, close to the value of $350 \text{ cm}^2/\text{sec.}$ predicted by Peart and Askill³⁵ for divacancy migration.

While the above numbers must be regarded with caution because of the unequal amount of participating defects, they do indicate that the defect migrating in the $0.15 T_m$ stage has a rather large pre-exponential factor. Such a large factor could be indicative of divacancy migration in the $0.15 T_m$ stage.

HIGH PRESSURE RESULTS

$0.15 T_m$ Stage

From the data in Figure 14 and from equation 8 the activation volume for the process occurring in the $0.15 T_m$ stage of annealing is calculated to be approximately $-0.9V^*$. This is particularly startling from two standpoints, the negative sign of the activation volume and its magnitude.

Experiments which have measured the activation volume for vacancy diffusion have shown that in practically all cases the measured volume is positive.³⁶ At this point it should be pointed out that the activation volume for diffusion is really the sum of two terms, the activation volume for formation and the activation volume for migration of a defect. In most cases it has been shown that ΔV_f is positive³⁶ and roughly equal to $(1/2 \text{ to } 3/4)V^*$ while the only direct measurement of ΔV_m has yielded a value of $+ 0.15 V^*$ for Au.³⁷ It has also been found³⁸ that the recrystallization of Cu is slower under pressure indicating a positive activation volume, presumably for vacancies. Hilliard, et.al.,³⁹ have found that dislocation motion is retarded under pressure and Norris⁴⁰ has found that prismatic loops in Al require a higher temperature to anneal under pressure than at 1 atmosphere.

There have been a few notable exceptions to the above statements. Beyeler and Adda⁴¹ show that the self diffusion coefficients in bcc U and fcc Ag were first increased at low pressures (indicating a negative activation volume), then reduced at higher pressures. Gertsriken and Pryanishnikov^{42,43} have also found a similar anomaly in polycrystals of iron and iron-titanium alloy. Pines and Syrenko⁴⁴

have discovered that the application of hydrostatic pressure on LiF near its melting point causes dislocations to anneal out faster than a similar high temperature treatment at low pressure. Studies on the thermal annealing of irradiation damage in chemical compounds, such as $\text{NH}_4\text{H}_2\text{PO}_4$,⁴⁵ K_2CrO_4 ,⁴⁶ $\text{Pb}(\text{NO}_3)_2$,^{47,48} KH_2AsO_4 ,⁴⁹ and KBrO_3 ⁵⁰ have shown that pressure accelerates the recovery.

From the theoretical standpoint, the situation is also somewhat confused. Johnson⁵¹⁻⁵³ has calculated the activation volumes for migration of both vacancies and interstitials and his results are summarized in Table II. Obviously no clear trend is established.

TABLE II.

Summary of Activation Volumes of Migration
as Calculated by Johnson⁵¹⁻⁵³

	<u>Vacancy</u>	<u>Interstitial</u>
Cu (fcc)	+0.25V*	-0.01V*
γ -Fe (fcc)	-0.05V*	+0.10V*
α -Fe (bcc)	0.00V*	+0.10V*

Because the calculation of the volume change associated with a migrating defect is a many bodied problem, it is difficult to pursue this line of approach until such time as reliable computer models are established.

POSSIBLE MECHANISMS FOR THE 0.15 T_m RECOVERY STAGE

There are at least three possibilities that might explain the pressure induced recovery.

- Divacancy migration.
- Effect of pressure on the binding energy of interstitial atoms to traps.
- The increased potential energy which an interstitial acquires as a result of being forced closer to its nearest neighbors.

Beeler^{54,55} has calculated that in irradiated metals there are as many, if not more, vacancies in a di- or multi-configuration than there are single vacancies. Furthermore, he has calculated that as a solid is "heated", the relative concentration of the divacancies actually increases. The mobility of divacancies in bcc metals has been calculated by Johnson,⁵⁶ who finds that divacancies have slightly lower activation energies for migration than single vacancies. This latter observation, coupled with the high pre-exponential factor for divacancies, would mean that divacancies may migrate to sinks at a lower temperature than single vacancies leaving the latter to migrate at higher temperatures.

The fact that ΔV_m for vacancies has been measured to be positive tends to discount single vacancy migration for the $0.15 T_m$ recovery stage (although the situation may be considerably different in bcc metals than in fcc metals). Measurements of the activation volume of migration for divacancies have never been made so that one cannot support or disprove the idea of divacancy migration in the $0.15 T_m$ from the pressure tests. It is more plausible to think of the entire region around a divacancy contracting as the migration takes place than in the case of a single vacancy but more definite statements must await further work with computer models.

Another possible explanation for the $0.15 T_m$ recovery stage is that the interstitial atoms are trapped at impurity sites and that the effect of pressure is to lower the binding energy between the trap and the interstitial. Such a situation might exist between a substitutional Fe atom and a Mo interstitial. Since the iron atom is slightly smaller than a molybdenum atom, a Mo interstitial could be accommodated more easily at the impurity site compared to a similar position in a perfect lattice. Recent computer calculations of this situation⁵⁷ have indicated that a considerable binding energy does exist between an Fe atom and an interstitial Mo atom, but the effect of pressure on this type of defect has yet to be investigated.

When an interstitial atom is in a split or crowdion configuration, it is so close to its nearest neighbor that slight changes in the interatomic spacing will have a large effect on its potential energy. For example, using Bridgeman's⁵⁸ compressibility data for Mo, one finds that there is a 0.23% lattice parameter decrease at a pressure of 20 kbars. This does not greatly affect the atoms which are in their equilibrium conditions surrounded by a perfect lattice because they are in the "trough" of the potential well. But an interstitial in a $\langle 100 \rangle$ or $\langle 110 \rangle$ split configuration is much closer than the normal nearest neighbor distance and small changes in its position will drastically change its potential energy. This difficulty with using this argument to explain the enhanced migration is that at the same time that the interstitial would be acquiring potential energy, it would also need more energy to migrate as its "windows" of escape are becoming smaller. Again, a computer simulation of the problem is required.

HIGHER TEMPERATURE STAGES

Because of the smallness of the $0.24 T_m$ peak, it is difficult at this time to speculate about the defect responsible. Further tests using electron microscopy and lattice parameter results should help to clarify the situation.

In reality the negative shift of the $0.29 T_m$ stage is larger than that of the $0.15 T_m$ stage. Unfortunately equation 8 cannot be used because E is unknown. A reasonable estimate of E might be the self diffusion energy of a vacancy,⁵⁹ 1.5 eV, equation 8 then yields

$$\Delta V = -1.9V^*.$$

This large volume decrease might signify the collapse of three-dimensional clusters of defects into two-dimensional loops. In this case the value of 1.9 atomic volumes could represent the volume difference between the defects in the three-dimensional configuration and the stable geometry under stress.

Since it is felt by most investigators that this stage is connected with clustered defects, further analysis should wait for electron microscopy analysis.

CONCLUSIONS

For high purity Mo irradiated to 6.2×10^{18} n/cm² ($E > 1$ MeV), it has been shown that

1. The electrical resistance increase recovers at three distinct stages, $0.15 T_m$, $0.24 T_m$, and $0.29 T_m$ under low pressures.
2. The activation energy of the $0.15 T_m$ stage is 1.25 ± 0.09 eV.
3. The reaction order is not uniform over the $0.15 T_m$ stage, being greater than 2 at $T > 149^\circ\text{C}$ and less than 2 above 149°C .
4. The application of 20 kbars of hydrostatic pressure causes the damage to anneal out at a lower temperature, the shift being -60°C for the original $0.15 T_m$ stage and -200°C for the $0.29 T_m$ stage.
5. The pressure shift indicates that the activation volume for the defect, or defects, migrating in the $0.15 T_m$ stage is negative and ~ 0.9 of the atomic volume.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the assistance of P. K. McDaniel during the high pressure tests and electrical resistance measurements.

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FIGURE 1
Schematic of Four-Probe Resistance Sample for Post-Irradiation
Annealing Studies

FIGURE 2
Pressure Cell Assembly for Annealing Irradiated Molybdenum
Samples under High Hydrostatic Pressures and Temperatures

FIGURE 3
A Comparison of Collapsible Can Assemblies Before (Left) and After (Right) a
High Pressure, High Temperature Test

FIGURE 4
Isochronal Recovery of Electrical Resistance in Irradiated
Molybdenum Annealed at ≤ 1 Bar

FIGURE 5
Differential Annealing Rate for the Isochronal Recovery in
Figure 4

FIGURE 6
Isothermal Recovery of Irradiated Molybdenum Annealed at
 ≤ 1 Bar

FIGURE 7
Meechan-Brinkman Plot to Determine the Activation Energy for
Stage III Annealing in Irradiated Molybdenum

FIGURE 8
Confirmation of the Correct Order of Reaction for
Temperatures Near Stage III Recovery in Irradiated Molybdenum

FIGURE 9
The Inverse of Isothermal Recovery Versus $\sqrt{t}$ used to
Determine $k_1 \exp(-E_m/2kT)$ in Waite's⁽²⁷⁾ Analysis

FIGURE 10
The Inverse of Isothermal Recovery Versus Time used to
Determine $k_0 \exp(-E_m/kT)$ in Waite's⁽²⁷⁾ Analysis

FIGURE 11
Isochronal Recovery of Electrical Resistance in Irradiated
Molybdenum Annealed under 20 Bars of Hydrostatic Pressure

FIGURE 12
Differential Annealing Rate for the Isochronal Recovery in
Figure 11

FIGURE 13
Comparison of the Isochronal Recovery of Electrical
Resistance in Irradiated Molybdenum as a Function of
Annealing Pressure

FIGURE 14
Comparison of the Differential Annealing Rates for Irradiated
Molybdenum as a Function of Annealing Pressure

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