solvent atom (ω_1 jumps). For the present case, assuming $p \simeq 1$ and $q_1^* \simeq Q^*_{\mathrm{Au}} = 0.80$ eV and taking $Q^*_{\mathrm{Sb}} - \Delta H_F = -3.00$ eV implies that $q_2^* \simeq -1.40$ eV for the heat of transport associated with the ω_2 jumps alone, in somewhat closer agreement with Gerl's predicted value for Sb in Ag.

ACKNOWLEDGMENTS

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Effect of Hydrostatic Pressure on the Recovery of Electrical Properties of Neutron-Irradiated Molybdenum[†]

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High-purity molybdenum has been irradiated at 40°C to a fluence of 6.2×10^{18} n/cm^2 ($E > 1$ MeV) and subsequently isochronally annealed at two pressures, ≤ 1 and 20 000 bar. At low pressure, the electrical resistance increase recovers in three stages, at 150, 425, and 575°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 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 before any pressure coefficient can be determined. The final 575°C recovery peak is lowered to 375°C under pressure and displays a pressure coefficient of -10°C/kbar.

I. INTRODUCTION

THE recovery of irradiation-produced defects in molybdenum has been studied by many investigators with particular attention being paid to stage-III recovery at ~150°C. Unfortunately, there still is no general agreement on the species migrating in stage III, and the interpretations of the data usually fall into one of two camps. The first group[1–5] feels that interstitials, either free or those released from traps, are migrating to immobile vacancies or adding on to interstitial clusters. The second group[6–11] feels that vacancies are migrating to trapped interstitials, to interstitial clusters, or to small vacancy 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 prove their case conclusively.

Because additional information is needed to identify uniquely the mobile defect, or defects, in the 150°C stage, a new approach which differs radically from that of previous investigators has been utilized. In addition to the customary postirradiation anneals at pressures equal to or less than 1 bar, irradiated Mo specimens have been subjected to isochronal anneals at 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 a crystal containing such defects 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. In 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 and 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

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[1] J. Nihoul, in *Symposium on Radiation Damage in Solids and Reaction Materials, Vienna, 1962* (International Atomic Energy Agency, Vienna, 1963), Vol. 1.

[2] N. F. Pravdyuk and A. M. Ivanov, Atomic Energy Commission Report No. AEC-TR-5263, 1962 (unpublished).

[3] S. Veljkovic and N. Milasin, Atomic Energy Commission Report No. AEC-TR-6227/2, 1964 (unpublished).

[4] M. DeJong and H. B. Afman, Acta Met. **15**, 1 (1967).

[5] J. Moteff and J. P. Smith, in *Flow and Fracture of Metals and Alloys in Nuclear Environments*, Special Technical Publication No. 380 (American Society for Testing Materials, Philadelphia, Pa., 1965), p. 171.

[6] G. H. Kinchin and M. W. Thompson, J. Nucl. Energy **6**, 275 (1958).

[7] D. E. Peacock and A. A. Johnson, Phil. Mag. **8**, 563 (1963).

[8] M. DeJong and B. L. Wensink, Phys. Letters **17**, 200 (1965).

[9] B. L. Eyre and A. C. Roberts, in *Flow and Fracture of Metals and Alloys in Nuclear Environments*, Special Technical Publication No. 380 (American Society for Testing Materials, Philadelphia, Pa., 1965), p. 188.

[10] M. E. Downey and B. L. Eyre, Phil. Mag. **11**, 53 (1965).

[11] A. S. Wronski, G. A. Sargent, and A. A. Johnson, in *Flow and Fracture of Metals and Alloys in Nuclear Environments*, Special Technical Publication 380 (American Society for Testing Materials, Philadelphia, Pa., 1965), p. 69.

as an activation volume and, if it is positive, processes which require an activation energy E at zero pressure require an activation enthalpy of $E+P\Delta V$ 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 an extra dimension capable of distinguishing between defects which act similarly when only thermal energy is considered. Accordingly, the objectives of the present study are to (a) measure the direction in which the third annealing stage in neutron-irradiated molybdenum is shifted with pressure, (b) calculate an over-all activation volume for that annealing stage, and (c) investigate the effect of pressure on the higher-temperature annealing stages.

II. EXPERIMENTAL

Polycrystalline, high-purity molybdenum containing less than 10-ppm carbon was used in foil form, 0.0075 cm thick. 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 Fig. 1. After degreasing, the samples were etched in an electrolyte of 25-ml HCl, 10-ml H_2SO_4, and 75-ml methyl alcohol cooled to 10°C. The etched samples were vacuum-annealed for 20 min at 1760°C at 10^{-5} Torr. The average grain diameter after this treatment was 19 μ. The ratio of the electrical resistance at 273°K to that at 4.2°K was 42. Irradiation took place in a Hanford reactor to a fast fluence of 6.2×10^{18} n/cm^2 ($E>1$ MeV) at a temperature of about 40°C.

The resistance of samples was measured at 4.2°K on a high-sensitivity (0.01-μV) voltage-measuring system with a current of 20 mA. 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 change in resistivity. Calculation of the absolute resistivity was hampered because the precise length over which the voltage drop was measured was not known (although it is the same each time). If the lines of equal potential are symmetrical, then this length should be measured from the midpoints of the voltage tabs. But rather than let this uncertainty affect the results, only resistance ratios are reported here.

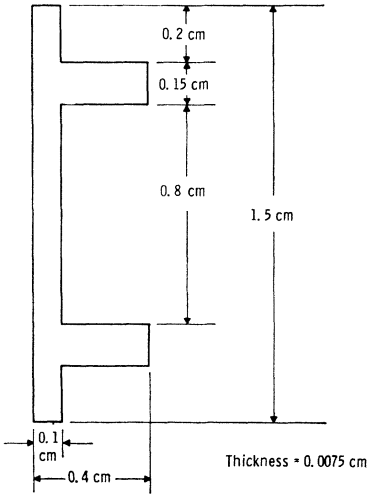

FIG. 1. Schematic of four-probe resistance sample for postirradiation annealing studies.

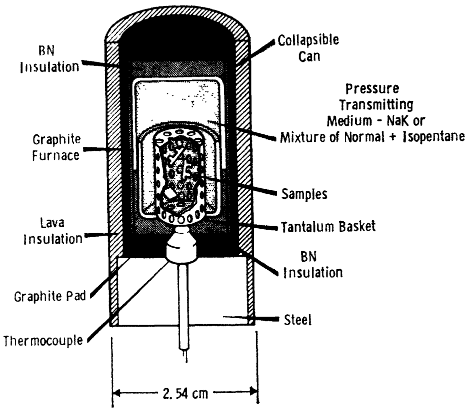

FIG. 2. Pressure-cell assembly for annealing irradiated Mo samples under high hydrostatic pressures and temperatures.

The low-pressure isothermal and isochronal anneals below 200°C were carried out in a silicone oil bath. Temperatures were controlled to within ±0.5°C. At 250°C, a KNO_3-$NaNO_3$ bath was used and from 300 to 1000°C the samples were heated at 10^{-5} Torr with radiant heat lamps. These latter anneals were controlled to within ±3°C. The time of the isochronal anneals was 2 h. Unirradiated control samples were included in each test.

The high-pressure system used has been described elsewhere[12] and is basically a piston-cylinder unit which was calibrated at 25°C by discontinuous electrical resistance changes in Ce at 7.6 kbar[13] and in Bi at 25.4 kbar.[14] The equipment was also calibrated at 100°C by discontinuous volume changes in RbCl at 5.3 kbar[15] and in KI at 17.2 kbar.[16]

The samples were contained in a collapsible can arrangement[12] shown schematically in Fig. 2. Although only one thermocouple was used in most tests, several tests utilized two thermocouples, with one touching

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[12] G. L. Kulcinski, Battelle Northwest Laboratory Report No. BNWL-465, 1967 (unpublished).

[13] A. W. Lawson and T. Y. Tang, Phys. Rev. **76**, 301 (1949).

[14] G. C. Kennedy and P. M. LaMori, in *Progress in Very High Pressure Research*, edited by F. P. Bundy (Wiley-Interscience, Inc., New York, 1962), p. 304.

[15] C. W. F. T. Pistorius, J. Phys. Chem. Solids **25**, 1477 (1964).

[16] C. W. F. T. Pistorius, J. Phys. Chem. Solids **26**, 1543 (1965).

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,[17] generally less than 3°C, was applied to the thermocouple readings. It was felt that the temperatures quoted for the high-pressure tests are accurate to ±5°C.

The pressurizing fluid was a 50-50 mixture of isopentane and *n*-pentane for tests 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 significant change in resistance over the range of pressures used.

The chronology of a pressure test was as follows. The pressure on the sample at room temperature was raised to 20 kbar in 5 min and then the temperature was raised to the desired level within 5 min. After a 2-h holding period, the temperature was lowered to below 50°C within 2 min and then the pressure was reduced to ambient in 2 min.

III. METHOD OF ANALYSIS

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 this defect is just[18]

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

where C is the concentration of defects, t is the time, $F(C)$ is the function of C, K_0 is the rate constant, k is Boltzmann's constant, T is the temperature, and H is the activation enthalpy.

Several quantities of interest can be calculated from Eq. (1). The activation enthalpy can be determined by following the approach of Meechan and Brinkman.[19] They find that

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

where Δt is the time of an isochronal anneal at temperature T_i, and $\Delta\tau$ is the elapsed time of an isothermal anneal at temperature T_a, which produces the same defect concentration associated with Δt at T_i. The slope of a $\ln\Delta\tau$-versus-$1/T_i$ plot will then give the activation enthalpy.

The order of the reaction taking place can also be determined[18] from Eq. (1), assuming that the electrical resistance increase ΔR is proportional to the concentration of defects and that $F(C)=(\Delta R)^n$. With these assumptions, one finds that

$$(\Delta R_0/\Delta R)^{n-1}=1+At,\quad \text{for } n\neq 1 \tag{3}$$

where $\Delta R=R_T-R_e$, $\Delta R_0=R_0-R_e$, R_T is the resistance of sample after annealing for time t at temperature T, R_e is the resistance of sample at the end of the annealing stage in question, R_0 is the as-irradiated resistance, and $A=(n-1)K_0\exp(-H/kT)$. When n is chosen properly, a plot of $(\Delta R_0/\Delta R)^{n-1}$ will yield a straight line.

The activation volume of an event can be determined from Eq. (1) by noting that

$$H=E+P\Delta V. \tag{4}$$

Since P is considered positive in compression, the sign of ΔV will determine whether the $P\Delta V$ term will raise or lower the activation enthalpy. 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 isochronal recovery temperatures will be shifted to higher or lower values, respectively.

If a horizontal line is drawn at a fixed fraction of defect recovery on an isochronal plot (a fixed fraction of resistance recovery in our case), and substituting $C=\Delta R$, $F(C)=(\Delta R^n)$, and $H=E+P\Delta V$, one finds that the left-hand side of Eq. (5) will be constant for any T_j and P_j

$$-\frac{1}{K_0}\int_1^{\Delta R/\Delta R_0}\frac{d(\Delta R)}{(\Delta R)^n}=t\exp\left(-\frac{E+P_j\Delta V}{kT_j}\right). \tag{5}$$

In this case, T_j is the temperature at which the resistance recovery reaches $\Delta R/\Delta R_0$ 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, Eq. (5) reduces to Eq. (6) at any $\Delta R/\Delta R_0$, and

$$\exp\left(-\frac{E+P_jV}{kT_j}\right)=\text{const}. \tag{6}$$

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

$$\Delta V=\frac{E(T_{j+1}-T_j)}{P_{j+1}T_j-P_jT_{j+1}}. \tag{7}$$

IV. RESULTS

A. Low-Pressure Anneals

Figure 3 is the isochronal-annealing curve as determined at ≤1 bar. The curve was generated basically from one sample, although several other samples were annealed at temperatures of interest to provide more detail. All the samples showed good agreement when plotted on a reduced scale. Differential annealing-rate

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[17] R. E. Hanneman and H. M. Strong, J. Appl. Phys. **36**, 523 (1965).

[18] A. C. Damask and G. J. Dienes, *Point Defects in Solids* (Gordon and Breach Science Publishers, Inc., New York, 1963).

[19] C. J. Meechan and J. A. Brinkman, Phys. Rev. **103**, 1193 (1956).

analysis from Fig. 3 shows a large recovery peak at $0.15T_m$,[20] a rather small one at $0.24T_m$, and another at $0.29T_m$.

Isothermal-annealing data for three samples annealed at 135, 149, and 164°C are plotted in Fig. 4. Combining these data with those in Fig. 3 produces a Meechan-Brinkman plot [see Eq. (2)] shown in Fig. 5. The slope of these plots yields an activation energy of 1.25 ± 0.09 eV.

In order to determine the reaction order of the $0.15T_m$ 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 Nihoul[1] and of Moteff and Smith,[5] 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 [Eq. (3)] to be dependent on temperature in the following fashion:

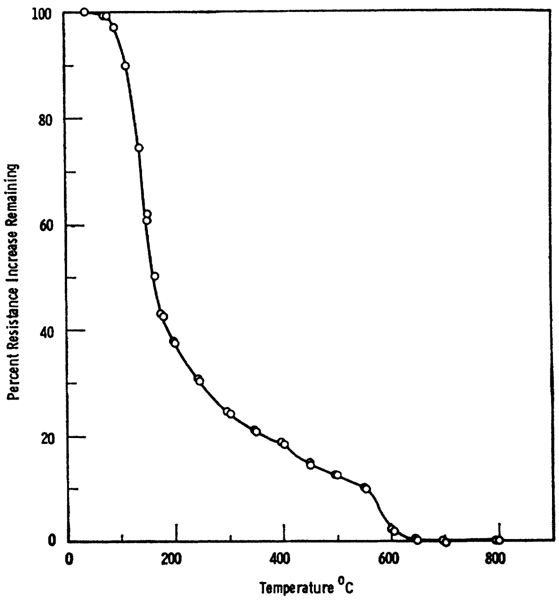

Fig. 3. Isochronal recovery of electrical resistance in irradiated Mo annealed at ≤1 bar.

T (°C)	Order
135	3.4
149	2.0
164	1.7

Figure 6 shows the plot of $(\Delta R_0/\Delta R)^{n-1}$ versus t and verifies that the above orders are correct.

B. High-Pressure Anneals

Figure 7 is a comparison between the isochronal curve obtained at 20 kbar and that obtained at low pressures. Obviously, both the major and final recovery temperatures are lowered by pressure. The data are not detailed enough to allow a definite statement about the $0.24T_m$ peak. The differential annealing rates for both the low- and high-pressure anneals are plotted in Fig. 8, where it can be seen that the major recovery temperature is lowered from 150 to 90°C under pressure, while the final recovery stage of electrical resistance is lowered from 575 to 375°C.

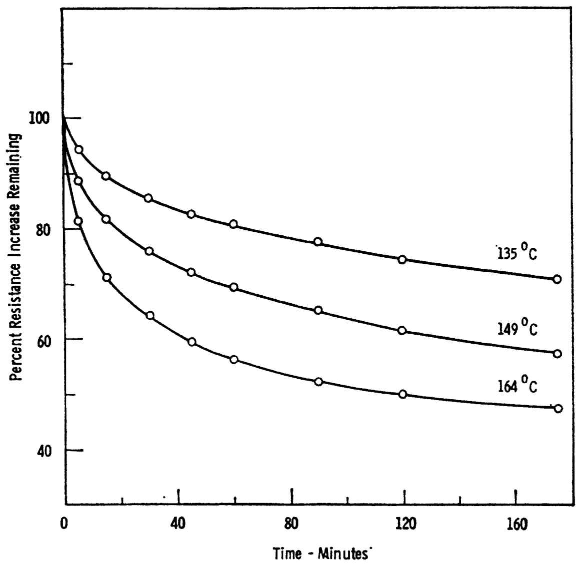

Fig. 4. Isothermal recovery of irradiated Mo annealed at ≤1 bar.

V. DISCUSSION

It is advantageous at this point to break the discussion into two parts, one covering the low-pressure

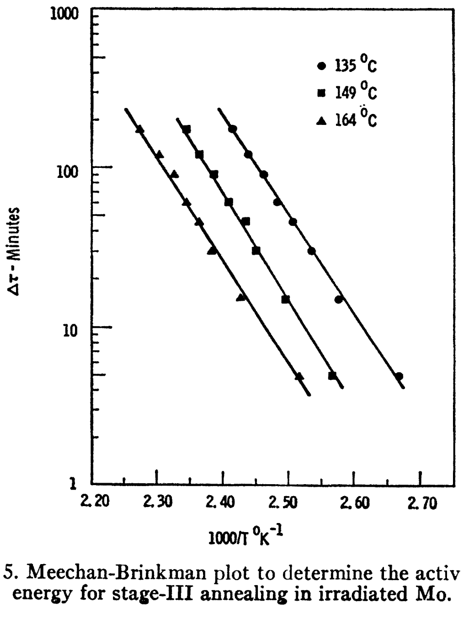

Fig. 5. Meechan-Brinkman plot to determine the activation energy for stage-III annealing in irradiated Mo.

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[20] T_m is melting temperature at 1 bar.

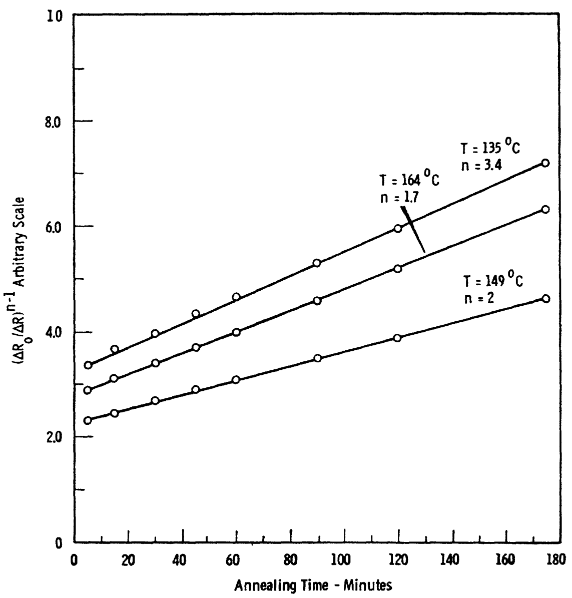

FIG. 6. Confirmation of the correct order of reaction for temperatures near stage-III recovery in irradiated Mo.

work and the other covering the high-pressure results. The low-pressure work will be briefly discussed relative to previous studies on Mo in order to show that this material was not unique in any way, except perhaps for its low carbon content.

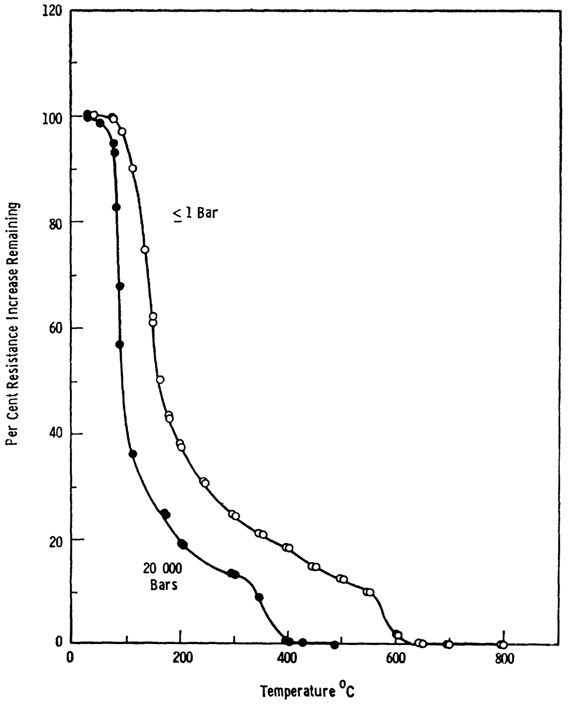

FIG. 7. Comparison of the isochronal recovery of electrical resistance in irradiated Mo as a function of annealing pressure.

A. Low-Pressure Results

A review of the previous electrical-resistance studies of irradiated and cold-worked Mo reveals that the present work agrees quite well with that of other investigators with respect to the recovery temperatures[1–7,21,22] and the migration energy for the $0.15T_m$ stage.[1,4,6,7,21] Therefore, the relatively high purity of the present material and the relatively low fast-neutron exposure do not seem to affect the energetics of the recovery process significantly.

The variation of reaction order in the $0.15T_m$ annealing stage, similar to that reported by Nihoul,[1] by DeJong and Afman,[4] and by Gray,[23] indicates that the annealing process is indeed complex. This work along with that of Nihoul[1] and of DeJong and Afman[4] shows that the reaction order decreases as temperature increases, while Gray[23] states that it actually approaches first-order kinetics. However, there is no reason that n should be 2 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.[18] It is highly unlikely that the number of

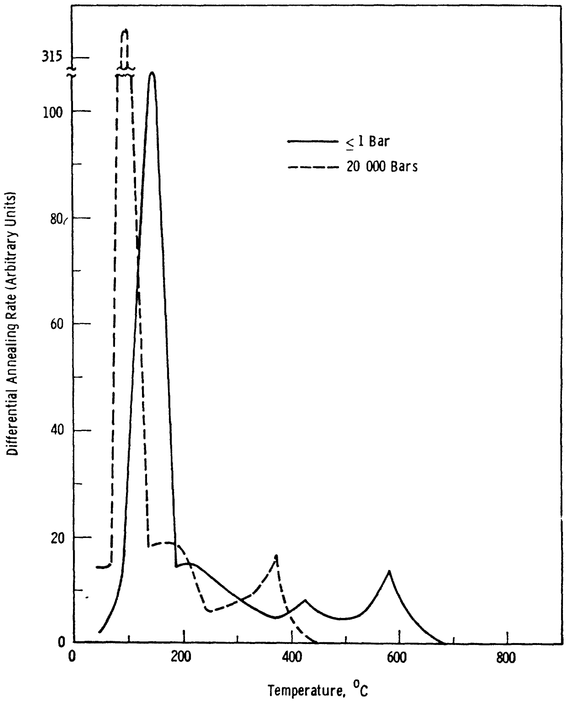

FIG. 8. Comparison of the differential annealing rates for irradiated Mo as a function of annealing pressure.

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[21] D. G. Martin, Acta Met. 5, 371 (1957).

[22] S. S. Ibragimov and V. S. Lyashenko, Fiz. Metal. i Metalloved. 10, 183 (1960).

[23] D. L. Gray, Acta Met. 7, 432 (1959).

free or trapped interstitials exactly equals the number of free or trapped vacancies (or divacancies, for that matter). Electron microscopy studies[9,10,24–26] 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 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.

B. High-Pressure Effects on the $0.15T_m$ Stage

From the data in Fig. 7 and from Eq. (7), the activation volume for the process occurring in the $0.15T_m$ 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.[27] 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 vacancy. In most cases, it has been shown that ΔV_f is positive[27] and roughly equal to $\frac{1}{2}$–$\frac{3}{4}$ V^*, while the only direct measurement of ΔV_m has yielded a value of $+0.15V^*$ for Au.[28] It has also been found[29] that the recrystallization of Cu is slower under pressure, indicating a positive activation volume, presumably for vacancies. Hilliard *et al.*[30] have found that dislocation motion is retarded under pressure, and Norris[31] has found that prismatic loops in Al require a higher temperature to anneal under pressure than at 1 atm. These latter experiments can also be interpreted as evidence for a positive activation volume of migration for vacancies.

There have been a few notable exceptions to the above statements. Beyeler and Adda[32] 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.

TABLE I. Summary of activation volumes of migration as calculated by Johnson.[a]

	Vacancy	Interstitial
Cu (fcc)	$+0.25V^*$	$-0.01V^*$
γ-Fe (fcc)	$-0.05V^*$	$+0.10V^*$
α-Fe (bcc)	$0.00V^*$	$+0.10V^*$

[a] References 42–44.

Gertsriken and Pryanishnikov[33,34] have also found a similar anomaly in polycrystals of iron and iron-titanium alloy. Pines and Syrenko[35] 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[36–41] have shown that pressure actually accelerates the recovery.

From a theoretical standpoint, the situation is also somewhat confused. Johnson[42–44] has calculated the activation volumes for migration of both vacancies and interstitials; his results are summarized in Table I. Obviously no clear trend is established.

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

There are at least three possible explanations for the pressure-induced recovery in the $0.15T_m$ recover stage: divacancy migration; effect of pressure on the binding energy of interstitial atoms to traps; and the increased potential energy which an interstitial atom acquires as a result of being forced closer to its nearest neighbor.

Beeler[45,46] has calculated that in irradiated metals there are as many, if not more, vacancies in a di- or multiconfiguration than there are single vacancies. The mobility of divacancies in bcc metals has been calculated by Johnson,[47] who finds that divacancies have slightly lower activation energies for migration than single vacancies. This latter observation would mean that divacancies may migrate to sinks at a lower

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[24] P. R. B. Higgins and A. C. Roberts, J. Less-Common Metals 6, 472 (1964).

[25] P. Rao and G. Thomas, Acta Met. **15**, 1153 (1967).

[26] J. L. Brimhall, B. Mastel, and T. K. Bierlein, J. Appl. Phys. **36**, 8 (1965); **36**, 2585 (1965).

[27] D. Lazarus and N. H. Nachtreib, *Solids Under Pressure* (McGraw Hill Book Co., New York, 1963), p. 43.

[28] R. M. Emrick, Phys. Rev. **122**, 1720 (1961).

[29] L. E. Tanner and S. V. Radcliffe, Acta Met. **10**, 1161 (1962).

[30] J. E. Hilliard, J. M. Lommel, J. B. Hudson, D. F. Stein, and J. D. Livingston, Acta Met. **9**, 787 (1961).

[31] D. I. R. Norris, Acta Met. **14**, 291 (1966).

[32] M. Beyeler and Y. Adda, in *Physics of Solids at High Pressures*, edited by C. T. Tomizuka and R. M. Emrick (Academic Press Inc., New York, 1965), p. 349.

[33] S. D. Gertsriken and M. P. Pryanishmkov, Ukr. Fiz. Zh. **3**, 651 (1958).

[34] S. D. Gertsriken and M. P. Pryanishmkov, Fiz. Metal. i Metalloved. **2**, 297 (1960).

[35] B. Y. Pines and A. F. Syrenko, J. Mater. Sci. **3**, 80 (1968).

[36] T. Andersen, Trans. Faraday Soc. **59**, 2625 (1965).

[37] T. Andersen and A. G. Maddock, Trans. Faraday Soc. **59**, 1641 (1963).

[38] S. R. Mohanty and S. R. Upadhyay, Nature **199**, 169 (1963).

[39] S. R. Mohanty and S. R. Upadhyay, Nature **201**, 921 (1964).

[40] V. Kacena and A. G. Maddock, in *Symposium on Radiation Damage in Solids and Reactor Materials, Vienna, 1962* (International Atomic Energy Agency, Vienna, 1963), Vol. 1, p. 255.

[41] T. Andersen, Nature **200**, 1094 (1963).

[42] R. A. Johnson, Phys. Rev. **195**, 423 (1966).

[43] R. A. Johnson and E. Brown, Phys. Rev. **127**, 446 (1962).

[44] R. A. Johnson, Phys. Rev. **134**, 1329 (1964).

[45] J. R. Beeler, J. Appl. Phys. **37**, 3000 (1966).

[46] J. R. Beeler, Phys. Rev. **150**, 470 (1966).

[47] R. A. Johnson, *Diffusion in Body Centered Cubic Metals* (American Society for Metals, Cleveland, Ohio, 1965), p. 357.

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 $0.15T_m$ 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 $0.15T_m$ from the pressure tests. It is more plausible to envision a contraction of the region around a divacancy as the migration takes place than for a similar contraction around a single vacancy, but more definite statements must await further work with computer models.

Another possible explanation for the $0.15T_m$ 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 Fe atom is slightly smaller than a Mo 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 situation[48] 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 Bridgman's[49] compressibility data for Mo, one finds that there is a 0.23% lattice parameter decrease at a pressure of 20 kbar. This does not greatly affect the atoms which are in their equilibrium positions 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. A 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, since its "windows" of escape are becoming smaller.

C. Pressure Effects on Higher-Temperature Stages

Because of the smallness of the $0.24T_m$ peak, one cannot speculate about the defect responsible for recovery in that temperature range at this time.

In reality, the negative shift of the $0.29T_m$ stage is larger than that of the $0.15T_m$ stage. Unfortunately, Eq. (7) cannot be used, because E for that stage is unknown. A reasonable estimate of E might be the self-diffusion energy of a vacancy,[50] 1.5 eV. Equation (7) then yields $\Delta V = -1.9V^*$. This large volume decrease might signify the collapse of three-dimensional clusters of defects into two-dimensional loops. The calculated value of 1.9 at. volumes could represent the volume difference between the defects in the three-dimensional configuration and the stable geometry under stress. In any case, the large negative pressure coefficient (-10°C/kbar) is more likely to be connected with clustered defects than point defects. Future study of this effect should be most revealing.

VI. CONCLUSIONS

For high-purity Mo irradiated to a fluence of 6.2×10^{18} n/cm^2 ($E>1$ MeV), it has been shown that: (a) The electrical-resistance increase recovers in three distinct stages, at 0.15, 0.24, and $0.29T_m$, under low pressures; (b) the activation energy of the $0.15T_m$ stage is 1.25 ± 0.09 eV; (c) the reaction order is not uniform over the $0.15T_m$ stage, being greater than 2 at $T<149$°C and less than 2 above 149°C; (d) the application of 20 kbar of hydrostatic pressure causes the damage to anneal out at a lower temperature, the shift being -60°C for the original $0.15T_m$ stage and -200°C for the $0.29T_m$ stage; and (e) the pressure shift indicates that the activation volume for the defect, or defects, migrating in the $0.15T_m$ stage is negative and 0.9 of the at. volume.

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[48] D. G. Doran (private communication).

[49] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. 72, 45 (1937).

[50] J. D. Meakin, A. Lawley, and R. C. Koo, Appl. Phys. Letters 5, 133 (1964).

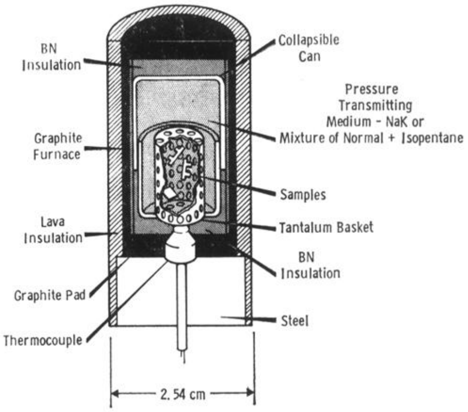

FIG. 2. Pressure-cell assembly for annealing irradiated Mo samples under high hydrostatic pressures and temperatures.