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**A Summary Report of the Compressive
Creep Properties of Irradiated and
Unirradiated Molybdenum**

Ronald E. Zielinski

April 15, 1977

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Table of Contents

	<u>Page</u>
Abstract.	4
Introduction.	5
Material Selection.	5
Literature Review	6
1. Radiation Damage	6
Displacement of Atoms.	6
Transmutation Reactions.	8
Radiation Damage State	9
Irradiation Damage in Molybdenum	9
Annealing of Irradiated Molybdenum	13
Voids in Neutron Irradiated Molybdenum	14
Swelling of Molybdenum	15
Irradiated-Strained Molybdenum	15
Physical Property Alterations	16
Annealing Recovery in Irradiated Molybdenum.	16
Radiation Hardening.	17
Radiation Anneal Hardening	23
Temperature Dependence of the Yield Stress	23
2. Neutron Irradiation Effects on Mechanical Properties	24
Hardness	24
Ductile-Brittle Transition Temperature	24
Tensile Tests.	24
Creep Rupture.	25
3. Creep of Unirradiated Molybdenum	26
Creep of Molybdenum in the Temperature Range of 600 to 1000°C.	26
Creep Structure.	27
4. Cold Working and Irradiation	28
Experimental Procedures	29
1. Material	29
2. Creep Test Procedures.	29
3. Transmission Electron Microscopy	31
4. Scanning Electron Microscopy	32
5. Optical Microscopy	32
6. Microhardness Determination.	32

TABLE OF CONTENTS (Continued)

	<u>Page</u>
Observations and Results.	32
1. Creep Tests.	32
2. Metallographic Examination	37
3. Transmission Electron Microscopy	43
4. Scanning Electron Microscopy	52
5. Microhardness Measurement.	56
Discussion of Results	58
Conclusions	70
Recommendations for Future Work	70
Acknowledgement	71
References.	72
Appendices	
A. Determination of the Solubility of Helium in Molybdenum at at 1000°K.	82
B. Quantitative Microscopy Techniques	86

Abstract

Compressive creep tests were performed on molybdenum samples exposed to four different pre-test conditions: (1) Annealed; (2) annealed and neutron irradiated at 480°C to a fluence of $5 \times 10^{19} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$); (3) stress-relieved; and (4) stress-relieved and neutron irradiated at reactor ambient temperature to a fluence of $1 \times 10^{19} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$). The tests were performed in the temperature range of 600 to 900°C with an initial applied stress of 176.5 MPa. Both pre- and post-test specimens were examined using electron microscopy and the relationship between substructure and mechanical properties is discussed. Possible controlling mechanisms of deformation are proposed and activation energies for creep are determined.

Introduction

The creep of refractory metals and alloys, in elevated temperature regimes, must be considered in the design of advanced concept SNAP (Space Nuclear Auxiliary Power) systems, Liquid Metal Fast Breeder Reactors (LMFBR) and Controlled Thermo-nuclear Reactors (Fusion Reactors) since dimensional changes of these structural materials may affect both the performance and the integrity of the system. The influence of radiation damage (especially neutron irradiation) on the creep properties of these materials should, therefore, be known for optimum design. Although tensile creep testing is the most common method for obtaining creep data, compression creep methods also produce valuable data since structural materials are often maintained in compression.

Most of the present data on irradiated refractory metals and alloys have been obtained from tensile creep tests, while little data have been published regarding compressive creep studies. In the normal situation, one would expect similar data from tensile and compressive creep studies on the same materials; however, there is some evidence that this is not necessarily so in unirradiated materials. When materials are irradiated then, there exists the distinct possibility that they may behave differently in tension and compression since now there exists internal damage that might contribute significantly to making both modes of creep different.

This investigation analyzed the experimental data from compressive creep studies performed on irradiated and unirradiated molybdenum at elevated temperatures and attempted to correlate these data with the prior history of the sample and the influence of radiation effects. In addition to this, some metallographic studies were performed in an attempt to identify the effects of the radiation damage and compressive creep on the structure of the specimens.

Material Selection

Molybdenum was chosen as the material of interest for this study because it possesses several special advantages among the refractory metals. It has a high melting point (2610°C), high temperature strength, very good thermal conductivity ($0.34 \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ } ^\circ\text{C}^{-1}$), and a low thermal neutron capture cross section (2.7 barns). None of the other refractory metals combine all of these properties to the same high degree that molybdenum does.

Another advantage that molybdenum possesses is the absence of long-lived highly radioactive isotopes. This can be extremely important for control units and loading mechanisms which may operate outside the reactor.

When molybdenum is irradiated, no very long-lived gamma-active isotopes are detected. Ten artificial isotopes of molybdenum have been identified. The lower isomer of molybdenum-93 is the longest lived with a half-life of approximately 10^4 years. It decays by K-capture. The radioactive isotope species of molybdenum are listed in Table 1. Molybdenum-99 has a strong β -active decay. However, it is formed from molybdenum-98 which has a very low capture cross-section and, therefore, the production of molybdenum-99 is very low.

Table 1
RADIOACTIVE ISOTOPE SPECIES
OF MOLYBDENUM[1]

Isotope	Half-Life	Mode of Decay
88	27 min	β^+ , γ
89	7 min	β^+
90	5.7 hr	β^+ , γ
91 ^a	.65 sec	β^+ , γ
91 ^a	15.5 min	β^+
93 ^a	6.9 hr	γ
93	10^4 yr	K-capture
99	67 hr	β^- , γ
101	14.6 min	β^- , γ
102	11 min	β^-
104	1.6 min	β^- , γ
105	40 sec	β^-

^aDenotes nuclear isomers.

Literature Review

In recent years, the interest in radiation damage has produced an overwhelming accumulation of literature in this and its related fields. No attempt will be made to give a complete historical review of the literature, for to do so would result in volumes of information. Rather, an attempt will be made to set the background for the present study.

This survey will be devoted to the following main topics:

1. Radiation Damage particularly as it relates to molybdenum;
2. Neutron Irradiation Effects on Mechanical Properties confined primarily to molybdenum;
3. Creep of Molybdenum as it relates to the present study; and
4. The Effect of Prior Cold-Working on Neutron Irradiated Material.

1. RADIATION DAMAGE

All metals are adversely affected to some degree by neutron irradiation. Metals that have been irradiated with neutrons are damaged in two basic ways. These include the displacement of atoms from their normal position in the crystal lattice and the transmutation of atoms of the irradiated metal as the result of neutron capture.

The displacement of atoms results in vacant lattice sites (vacancies) and moves the displaced atoms to interstitial positions (interstitials). These reactions that occur as a result of neutron capture are the (n,p) and (n, α) type which produce protons (hydrogen nuclei) or alpha particles (helium nuclei). The rate at which defects are produced and the nature and distribution of these defects throughout the lattice affect the microstructure, physical and mechanical properties of the metal subjected to neutron irradiation.

Displacement of Atoms

If an atom is to be displaced from its normal lattice site into an interstitial position, a certain amount of energy must be supplied to that atom. This energy called the displacement energy (E_d) was estimated by Seitz [2] to be approximately 25 eV.

The basis of his value was that twice as many bonds would have to be broken in order

to remove an interior atom from its lattice site as compared to the removal of a surface atom, thus the binding energy of an interior atom must be twice the sublimation energy. Displacement is not a reversible process and once it occurs the atom cannot return to its original lattice site. Following the logic of his argument then, he estimated that the displacement energy (E_d) would be four to five times the sublimation energy. For most solids, the displacement energy would be approximately 25 eV. Kelly [3] later determined experimental values that are in good agreement with Seitz's value. The value for molybdenum being 37 eV.

When a material is irradiated by neutrons, several mechanisms can produce atom displacements. One mechanism is the result of nuclear reactions of the type $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$ or $^{27}\text{Al}(n,\alpha)^{24}\text{Na}$. The recoil nucleus if it leaves its lattice site with sufficient energy can cause other displacements. The reaction products (such as the α particle) can interact with other lattice atoms. Another mechanism would be the transfer of kinetic energy as a result of the elastic collision of a neutron with an atom. If the kinetic energy transferred is sufficient enough, the atom will be displaced from its normal lattice site. It is also possible that enough kinetic energy is transferred to the atom to produce additional displacement.

Reactions such as (n, α), (n,p), (n, γ), (n, 2n) account for a minute percentage of the total displacements and as such can be ignored from all except the most exacting analyses. The elastic scattering, however, is a significant contributor to the atomic displacements that occur as a result of the collision of fast neutrons with lattice atoms. The maximum amount of energy, E_{Max} , which may be transferred from a neutron of energy E_n to a nucleus of atomic weight A in an elastic collision is given by:

$$E_{\text{Max}} = \frac{4A}{(A+1)^2} E_n \quad \text{or} \quad (1)$$

$$E_{\text{Max}} = C_1 E_n, \quad \text{where } C_1 = \frac{4A}{(A+1)^2}$$

For isotropic scattering, there exists an equal probability for the struck nucleus to receive any energy between 0 and E_{Max} . It is possible then to say that the average energy transferred by isotropic scattering is $E_{\text{Max}}/2$. If, however, the neutron energy is greater than 1 MeV, the energy transfer process becomes less efficient because forward scattering is dominant. The number

of displaced atoms is reduced as a result of this type of anisotropic elastic scattering.

When an atom is struck by a neutron and kinetic energy in excess of the displacement energy is transferred a collision cascade results. The original displaced atom which is called the Primary Knock-on Atom (PKA) travels through the lattice, it can strike other atoms and transfer energy to these atoms. If this energy is greater than the displacement energy, these atoms are knocked out of their lattice sites. These atoms are called secondary knocked-out atoms (SKA) and can produce TKA's and so on.

Kinchin and Pease [4] developed a model to determine the number of additional displacements made by the Primary Knock-on Atom as it slows down from energy E to the position in the lattice where it is in thermal equilibrium with its surroundings. This value is expressed as $\bar{\nu}(E)$ and is given as:

$$\bar{\nu}(E) = \begin{cases} 0 & \text{for } 0 \leq E < E_d \\ 1 & \text{for } E_d \leq E < 2E_d \\ E/2E_d & \text{for } 2E_d \leq E \leq E_{IC} \\ E_{IC}/2E_d & \text{for } E \geq E_{IC} \end{cases} \quad (2)$$

E_{IC} is the ionization cut-off energy which is simply the energy of an atom moving through a solid above which energy is lost only by ionization or electronic excitation and below which energy losses occur only by elastic collisions.

Dienes and Vineyard [5] estimate that:

$$E_{IC} = A \times 10^3 \text{ eV}. \quad (3)$$

For isotropic scattering where neutrons of energy E_n produce PKA's with an average energy $E_{Max}/2$, the average number of displacements produced by PKA's is:

$$\bar{\nu}(E_n) = \begin{cases} 0 & \text{for } E_n < E_d/C_1 \\ 1 & \text{for } E_d/C_1 \leq E_n \leq 2E_d/C_1 \end{cases} \quad (4)$$

$$\bar{\nu}(E_n) = \begin{cases} [A/(A+1)^2] E_n/E_d & \text{for } 2E_d/C_1 \leq E_n < E_{IC}/C_1 \\ \frac{E_{IC}}{4E_d} \left[2 - \frac{E_{IC}}{C_1 E_n} \right] & \text{for } \frac{E_{IC}}{C_1} \leq E_n \end{cases} \quad (4)$$

Figure 1 shows a plot of $\bar{\nu}(E_n)$ as a function of E_n for molybdenum ($A = 95.94$). As can be seen from the figure, the number of displacements per PKA increases linearly with neutron energy between approximately 10^3 and 10^6 eV then saturates rapidly for energies above approximately 2 MeV. The number of displacements per unit volume and unit time is expressed as:

$$\frac{d_n}{dt} = N_0 \int_{E_d/C_1}^{\infty} \phi(E_n) \sigma(E_n) \bar{\nu}(E_n) dE_n, \quad (5)$$

where: N_0 = the number of atoms per unit volume,

$\sigma(E_n)$ = the atomic cross-section for elastic scattering, and

FIGURE 1 - Average number of displacements produced by a collision with a neutron of energy E_n for molybdenum.

$\phi(E_n)dE_n$ = neutron flux having energies between E_n and $E_n + dE_n$.

The spatial distribution of displacement damage produced by fast neutrons is not uniform and is important to note. Initially the PKA's have a uniform distribution throughout the bulk of the material because neutron-atom collisions have a mean free path in the centimeter range. On the atomic scale, however, the defects produced by the individual PKA's are not homogeneously produced. According to Seitz and Koehler [6], an atom moving with less energy than E_a will undergo hard-sphere collisions. They calculate E_a by:

$$E_a \approx 4 Z^{7/3} R_h, \quad (6)$$

where: Z = the atomic number, and

R_h = the Rydberg energy for hydrogen (~ 13.605 eV).

In the case of molybdenum ($Z = 42$), the PKA's having less than approximately 3.34×10^5 eV of energy undergo hard-sphere collisions. If we use appropriate neutron energies in Equation (1), it becomes obvious that most of the PKA's have less energy than E_a . The effective radius of an atom for hard-sphere collisions is a function of the PKA energy and is expressed as:

$$R_{eff.} \sim \frac{a_0}{(Z)^{1/3}} \left[\ln \frac{Z^2 e^2}{R_h E_{ma}} \right], \quad (7)$$

where:

a_0 = the Bohr radius of the hydrogen atom (5.29×10^{-9} cm)

e = the electron charge (1 eV), and

E_{ma} = the energy of the moving atom.

For molybdenum, then:

$$R_{eff.} \sim 1.52 \times 10^{-9} \text{ cm} \left[\ln \left(\frac{129.66}{E_{ma}} \right) \right] \quad (7a)$$

The mean free path between hard-sphere collisions is expressed as:

$$D_{HS} = \frac{1}{\pi (R_{eff.})^2 N_0} \quad (8)$$

From the above then, it is obvious that $R_{eff.}$ will increase and D_{HS} decrease as the energy of the moving atom decreases. The moving atom with its kinetic energy dissipated will begin to collide with essentially every atom in its path. Most

of the atom displacement will occur in a very small volume region called the displacement spike.

Kinchin and Pease [4] assume that this displacement spike will consist of a volume region having a high vacancy concentration surrounded by a shell which contains a high concentration of interstitials. Seeger [7] suggests that after the displacement spike, there is an immediate rearrangement after which the spike will be a region of high vacancy concentration. Brinkman [8] postulates that small clusters of vacancies and interstitials will be left in the spike since a large amount of energy is dissipated in a small volume region and the atoms will recrystallize in correct order with the surroundings. Beeler [9, 10] has performed computer modeling calculations which show that the primary damage state is similar to that assumed by Kinchin and Pease.

Transmutation Reactions

When a material is being irradiated with neutrons, reactions such as (n, α) , (n, p) , and (n, γ) are initiated by the nuclei of the atoms which capture neutrons. The reactions of the type (n, α) and (n, p) result in chemically different species, while the (n, γ) reaction produces new isotopes.

For the most part, the chemically different species produced by transmutation reactions are of no consequence since the concentration of these impurities increases slowly and usually does not exceed the concentration of the impurities originally present in the material or the solubility limits for the product species. Helium and hydrogen are perhaps the only exceptions to this observation.

The (n, p) reactions produce hydrogen, while the (n, α) reactions give rise to an α -particle (helium atom). Such reactions are possible not only with the molybdenum atoms but also the atoms of the impurities present in the molybdenum.

Since it has a chemically inert electronic structure, helium is highly insoluble in a metal lattice.

Since a helium atom in an interstitial position would have a large amount of strain energy associated with it, Cottrell [11] suggested that each atom would by vacancy capture enter substitutional solution. Using a statistical thermodynamic approach (Appendix A), the solubility of helium in molybdenum is estimated as 2.63×10^8 atoms cm^{-3} at

1000 K and unit gas pressure and is shown to be primarily vacancy in nature.

When the helium atoms are in substitutional solution, annealing the material to higher temperatures results in the precipitation of helium gas bubbles [12]. The material lattice initially contracts as the helium atoms capture vacancies and move into solid solution; the lattice then expands and approaches the unirradiated value as the helium precipitates in bubbles.

When irradiation occurs in a fast reactor neutron spectrum, the (n, α) reactions with high energy neutrons account for most of the helium production. Alter and Weber [13] have presented cross sections for (n, α) and also (n, p) reactions for a large number of metals in a fission neutron spectrum. Freeman, et al [14] recently reported on the (n, α) cross sections for molybdenum irradiated in a fission neutron spectrum, using the absolute determination of helium produced.

The number of impurity atoms produced per cm^3 for a particular reaction is given by:

$$C = N_0 \sigma \phi \quad (9)$$

where: σ = the cross section for the particular reaction

ϕ = the time integrated neutron flux density (fluence).

The calculated amount of hydrogen and helium produced using Equation (9) for a fast neutron fluence of $1 \times 10^{19} \text{ n cm}^{-2}$ is presented in Table 2.

The data presented in Table 2 indicate that only approximately 3.2 ppb of hydrogen and helium are produced from molybdenum and its impurity elements. The total amount of hydrogen present initially in the molybdenum is much greater than the total impurities produced and, therefore, transmutation products will not produce an excessive amount of gas atoms in molybdenum.

Calculations of this type are not extremely accurate since cross sections for (n, α) and (n, p) reactions are in general not well known; however, they do show the relatively minor effect that the impurity elements have on total helium and hydrogen production. The (n, α) cross section for molybdenum, however, was determined by experimental procedures by Freeman [14] and should be more accurate than the values of Alter and Weber. [13]

Radiation Damage State

The primary damage state produced by the PKA consists of a volume of a high concentration of vacancies surrounded by a shell of a high concentration of interstitials. Since the irradiation temperature is in most situations high enough to result in at least one of the irradiation-produced defects being mobile, the primary damage state is very unstable and dynamic recovery occurs. Interstitials for the most part move at lower temperatures than vacancies. In fact, the temperature of vacancy mobility is still not known exactly. If one of the defects is mobile, many of the original irradiation-produced point defects will be annihilated by recombination, trapped at impurities or absorbed by dislocations and grain boundaries. Since the surviving defects will be thermodynamically unstable, defects of the same type may be recombined to produce cluster defects and lower the free energy of the system.

The final damage state of the material depends upon such parameters as the energy of formation of interstitials and vacancies, stacking fault and surface energies, migration energy of interstitials and vacancies and the binding energy of interstitials and vacancies to the defect clusters. The irradiation parameters such as fast neutron flux and fluence as well as the irradiation temperature can also effect the final damage state.

Irradiation Damage in Molybdenum

Most analyses of the refractory metals often consider the group Va metals, niobium and tantalum, and the VIa metals, molybdenum and tungsten, simultaneously. However, there are some characteristic differences in electronic properties between both groups of metals. These differences are reflected in the physical properties [15, 16]. The heat of solution of interstitial impurities, Young's modulus, the electronic specific heat and the superconductivity transition temperature are significantly different for each group. In fact, Young's modulus for the group Va metals is approximately a third of the value for the VIa metals.

As a result of the differences in the physical properties, the migration energies of point defects, that are theoretically calculated using an elastic model, differ significantly for both groups. The activation energy for mono-vacancy migration in tungsten was estimated to be 2.26 eV, while the calculated value for tantalum was 0.66 eV [17].

This difference also in part accounts for the different recovery behavior between the group Va and VIa metals.

Molybdenum and tungsten in contrast to niobium and tantalum have a very low solubility of interstitial impurities in equilibrium at room temperature [15]. This means that the mobility of defects at room temperature is relatively low; however, impurity atoms still affect the nature and degree of irradiation damage in these metals.

On the basis of the above information, then, it is not realistic to expect tantalum and niobium to exhibit the same radiation damage as molybdenum and tungsten. One would, however, expect molybdenum and tungsten to behave the same when exposed to neutron radiation at the same conditions. This, however, is not true. Rau, et al [18] in examining voids in irradiated tungsten and molybdenum discovered that while the general nature of the irradiation damage was approximately the same and the damage behaved essentially the same, the specific characteristics and concentrations of the damage population (voids) were different. Specifically, they irradiated tungsten and molybdenum at the same homologous temperatures (approximately $0.34 T_M$ and approximately $0.43 T_M$) and observed that the void populations were different for the two metals. Tungsten contained smaller voids and a lower percentage of void volume than molybdenum. They attributed these differences to the fact that for comparable neutron fluences about twice as many voids are created in molybdenum as in tungsten, while only insignificant amounts of impurities are generated in molybdenum as a result of thermal neutron reactions; the reactions, however, produce significant numbers of rhenium and osmium impurity atoms in tungsten. These impurity atoms can act as individual trapping sites for many of the vacancies, thus reducing the tendency for them to agglomerate into resolvable voids.

Therefore, rather than consider the nature of irradiation damage in all bcc metals, this review will be confined to only the irradiation damage in molybdenum.

Maher, et al [19] examined arc cast, vacuum annealed and triple pass zone-refined, vacuum annealed molybdenum. The material they examined was irradiated at ~ 77 K in the HERALD reactor. The integrated fission neutron dose was 4.65×10^{17} n cm⁻². The arc cast molybdenum was observed to contain black spot clusters with an estimated density greater than

5×10^{16} cm⁻³. The zone-refined material also contained black spot clusters with a density of approximately 6×10^{15} cm⁻³. Calculations showed that 75-80% of the images observed in the zone-refined material were interstitial loops, while the balance were vacancy loops. The majority of the defects in the arc cast molybdenum were also interstitial in nature. The average size range of the defects was 40 to 50 Å.

Meakin [20] irradiated a molybdenum single crystal to a fast neutron dose of 1×10^{18} n cm⁻² at 600°C. His material contained 15 ppm carbon impurity. His analysis showed that the effects were primarily interstitial type loops with a density of approximately 2×10^{13} cm⁻³ and an average size of 1100 Å.

Mastel, et al [21] earlier had irradiated molybdenum to a higher fast neutron dose (1×10^{19} n cm⁻²). Their samples contained three different carbon impurity levels: 10, 150, and 450 ppm. The samples irradiated at 40°C possessed a uniform distribution of black spots (75 to 100 Å). The black spots were resolved into loops in the molybdenum samples containing more than 150 ppm carbon.

Mastel and Brimhall [22] irradiated molybdenum samples containing different carbon levels (less than 10, 100 to 200, 400 to 500 ppm) at 40°C to fast neutron doses in the range of 4×10^{18} to 1×10^{20} n cm⁻². Black spot defects were observed in all the specimens after exposure to doses of 4×10^{18} n cm⁻². As the dose was increased to 1×10^{19} n cm⁻², the spot density in the high purity material (<10 ppm carbon) increased rapidly as compared to the other material. The spot size was approximately the same for all the materials at a fluence of 4×10^{18} n cm⁻², but it increased at higher fluences. The concentration, however, was different. The concentration was two orders of magnitude higher in the high carbon impurity samples (>100 ppm). The cluster density reached saturation in all the materials at a fluence of 1×10^{19} n cm⁻². Resolved loops were observed in the high carbon impurity samples. Their diameters were twice those observed for the spot defects. At fluences of approximately 1×10^{20} n cm⁻², a highly complex structure was observed in all samples with spot densities of approximately 1×10^{16} cm⁻³. The spot defects were thought to be small interstitial clusters.

They concluded that carbon acts as nucleating sites for cluster formation. They suggested the theory that interstitials

Table 2

IMPURITIES PRODUCED IN A TYPICAL MOLYBDENUM ROD FROM TRANSMUTATION REACTION

Element	Wt. %	ppm by Atoms	$\sigma(n,p)^a$ (mb)	$\sigma(n,\alpha)^a$ (mb)	Hydrogen Produced			Helium Produced			Total H + He	
					Atoms	ppm	Atom cm ⁻³	Atoms	ppm	Atom cm ⁻³	ppm	Atom cm ⁻³
Mo	99.9	$\sim 10^6$	0.19 ^b	0.13 ^c	1.9×10^{-3}	---	1.22×10^{14}	1.3×10^{-3}	---	8.35×10^{13}	3.2×10^{-3}	2.05×10^{14}
C	.0037	296	<0.001 ^b	0.45 ^b	2.96×10^{-10}	---	1.90×10^7	1.33×10^{-6}	---	8.55×10^{10}	1.33×10^{-6}	8.55×10^{10}
N	.001	68.8	---	11 ^b	---	---	---	2.82×10^{-5}	---	1.81×10^{12}	2.82×10^{-5}	1.81×10^{12}
O	.0015	90	0.017 ^b	6.0 ^b	1.53×10^{-8}	---	9.80×10^8	5.4×10^{-6}	---	3.46×10^{11}	5.42×10^{-6}	3.46×10^{11}
Fe	.006	103.0	0.87 ^b	0.18 ^c	8.95×10^{-7}	---	5.73×10^{10}	1.85×10^{-7}	---	1.15×10^{10}	1.08×10^{-6}	6.9×10^{13}
Si	.0035	120.0	4.0 ^b	0.74 ^b	4.8×10^{-6}	---	3.08×10^{11}	8.88×10^{-7}	---	5.7×10^{10}	5.69×10^{-6}	3.65×10^{11}
Ni	.0020	33.0	111 ^b	4.7 ^c	3.66×10^{-5}	---	2.35×10^{12}	1.55×10^{-6}	---	9.95×10^{10}	3.82×10^{-5}	2.45×10^{12}
H	.0004	384.0	---	---	---	---	---	---	---	---	---	---
TOTAL												2.79×10^{14}

^aCross-section values are in millibarns (10^{-27} cm²).^bReference 13.^cReference 14.

become mobile at irradiation temperatures and are bound to the carbon atoms which act as nucleating sites for the growth of clusters. A high carbon impurity material would have heterogeneous cluster nucleation, while nucleation would be homogeneous for low carbon (<10 ppm) material.

They explained the dilemma of the cluster defect saturation at a fluence of 1×10^{19} n cm⁻² and decrease at 1×10^{20} n cm⁻² by proposing that each nucleated cluster was surrounded by a zone of defects and the defects within the zone would enlarge the cluster and those outside the zone would have no effect on the cluster. Saturation in this condition occurs when the zones surrounding the nucleated clusters start interacting with each other, thereby inhibiting cluster growth. At a fluence of 1×10^{20} n cm⁻² defect clusters and vacancies interact and cluster density is decreased.

Downey and Eyre [23] irradiated molybdenum at 60°C to a fast neutron dose of 2.5×10^{20} n cm⁻². The irradiated material showed black spots. The cluster density was 2.85×10^{16} cm⁻³ with an average diameter of 60 Å. The number of point defects associated with the cluster defects was calculated as 1.4×10^{19} cm⁻³; this value was three orders of magnitude less than the value calculated using the Kinchin-Pease model. Based upon this information, they proposed the theory that less than 10% of the interstitials surviving recombination are present as observable clusters, the balance are present as single defects trapped by interstitial impurity atoms.

Maher and Eyre [24] examined molybdenum irradiated to a fluence of 5×10^{19} n cm⁻² at 60°C and then annealed for one hour at 900°C. They found that the loops present in the samples were mixed vacancy and interstitial types. This was true for the as-irradiated as well as the irradiated and annealed specimens.

They suggested that the mixed nature of the loops was due to sample impurities, anneal heating profiles or the fact that since the vacancy loops were so small they might have gone undetected previously.

Brimhall, et al [25] irradiated molybdenum foil to a neutron dose of 3.5×10^{19} n cm⁻² at 600°C. The damage consisted of large loops (~1000 Å-diameter) with a density of 3.5×10^{14} cm⁻³. Upon analysis of the loops, it was determined that only 50% were interstitial with the rest being vacancy. Another new observation was that there were loop-denuded zones at the grain

boundaries. Some of these zones were one micron wide and all the zones contained 20 to 40 Å diameter spot clusters.

The denuded zones were suggested as being the result of the fact that grain boundaries act as sinks for interstitial atoms. The small spots in the zones were vacancy clusters which were due to the short range mobility of vacancies at the 600°C irradiation temperature. This work showed that elevated temperature irradiation did not affect the microstructure the same as ambient temperature irradiations followed by annealing at elevated temperatures.

Moteff, et al [26] examined molybdenum samples that were irradiated to a fast neutron dose of 1.4×10^{20} n cm⁻² at 70, 700, and 1000°C. Black spot clusters with an average size of 50 Å and a density greater than 1×10^{16} cm⁻³ were observed in the 70°C sample. The clusters were homogeneously distributed and no grain boundary denuding was observed. The 700°C specimens had a high density (5×10^{14} cm⁻³) of loops with the average size being approximately 1000 Å. Grain boundary denuding was observed in these specimens and for the first reported time voids were observed. The 1000°C samples also contained voids but very few loops and dislocations in the grains.

They also observed another previously unreported feature. Dislocation debris was observed as being arranged in series of bands which were parallel to the grain boundaries. These bands were comprised of loops varying in diameter from 200 to 5000 Å.

Brimhall and Mastel [27] systematically studied the effects of carbon impurities and irradiation temperatures on the irradiation damage in molybdenum. They studied molybdenum that contained 3 and 200 ppm carbon impurity. The neutron fluence was 5.2×10^{19} n cm⁻² and the test temperatures were 50, 400, 500, 575, 650, and 750°C.

The microstructure observed in both the 3 and 200 ppm carbon impurity samples irradiated at 50°C was the same. It consisted of a very uniform and high-density distribution of black spot clusters.

In the 400°C samples, the black spots formed agglomerates called rafts. These were aligned along the <110> directions and were parallel to the {111} planes. Since these rafts had the same character as loops, they were considered to be made of prismatic loops. At this temperature,

the rafts found in the molybdenum containing 200 ppm carbon were larger than those found in the molybdenum containing 3 ppm carbon. Grain boundary denuding of rafts was also observed. Rafts were observed in the 500 and 575°C samples also. The 650 and 750°C samples had dislocation loops as the significant microstructure; these loops were interstitial in nature. Voids of 30 to 40 Å in diameter were also observed in the 650°C samples. The existence of voids as vacancy clusters indicated that the rafts observed in the samples were agglomerates of interstitial clusters and loops.

The samples of 200 ppm carbon impurity molybdenum irradiated at 575, 650, and 750°C showed an anomalous structure which developed near the grain boundaries. This anomalous structure consisted of small rafts and small loops in a band approximately one micron wide from the boundary to the dislocation segments and large rafts. The bands were only observed near the high angle boundaries, not the low angle boundaries. This structure did not develop in the molybdenum containing 3 ppm carbon.

Annealing of Irradiated Molybdenum

The samples of Downey and Eyre [23] mentioned earlier were subjected to various annealing temperatures to observe any changes in the damage structure. No change in the damage structure was observed until an annealing temperature of 600°C was reached. Between 600 and 800°C, slight coarsening occurred; above 800°C, loops grew rapidly and the cluster density decreased somewhat. As the loops grew, dislocation lines resulted; above 1000°C, these lines began to form a hexagonal dislocation network. This network was well developed at 1200°C and all the loops had annealed out.

On the basis of their examination, Downey and Eyre [23] concluded that the distribution of irradiation damage in bcc metals and its behavior on post-irradiation annealing is controlled by the presence of interstitial impurities and their mobility at the irradiation temperature.

Mastel and Brimhall [22] also annealed some of their samples which were discussed earlier. They annealed molybdenum containing less than 10 and greater than 100 ppm carbon impurity. This molybdenum was irradiated to a fluence of 1×10^{19} n cm⁻² at 40°C prior to two-hour anneals up to a maximum of 900°C.

As the annealing temperature was increased to 750°C, the spot density decreased while the size remained constant. This was true for both the high and low carbon impurity material. In the high carbon impurity (>100 ppm), molybdenum loop densities increased up to 750°C and then decreased. The spots and also the loops were eliminated at 900°C in both the 10 and >100 ppm carbon impurity material.

Similar annealing studies were also performed on the same type of samples which were irradiated to a dose of 1×10^{20} n cm⁻². Annealing at 750°C for two hours resulted in the appearance of large interstitial loops. The loops and spots that were present were completely removed at 900°C. This was true for both the high and low carbon impurity molybdenum and none of the mechanistic models that they proposed would account for this complete removal.

Brimhall, et al [25] also studied the effects of post-irradiation annealing on molybdenum. They examined samples which were irradiated to a dose of 3.5×10^{19} n cm⁻² at 600°C. One series of tests consisted of isothermal anneals at 800°C for 2, 25, and 250 hours. The other series involved isochronal anneals at 100°C intervals in the range of 700 to 1000°C.

They found that small clusters (<70 Å) annealed rapidly compared to loops (>70 Å). Below 1000°C, all the loops were interstitial in nature; above 1000°C, approximately 5% of the loops were vacancy. The small clusters present in the denuded zone grew into large loops on annealing, and they all were vacancy in nature. The isothermal annealing studies showed that the vacancy loops formed from the small defects increased in size with a corresponding decrease in number density.

They explained the rapid annealing of the small visible clusters by saying that the isolated vacancies and vacancies formed from the break-up of the very small clusters migrated to the interstitial type loops which then decreased in size. As the annealing continued, larger vacancy clusters broke up and the vacancies could either annihilate interstitial loops or add on to the larger vacancy loops which would grow. After long annealing times at high temperatures, recovery was controlled by the emission of vacancies from the loops or clusters; these vacancies then migrated through the lattice and were absorbed at the interstitial loops so that the activation energy approached

the self-diffusion value. Since the defects were of a mixed nature, little or no change in the size of the loops in the matrix occurred. The loops near the grain boundary grew because only one type of defect was present.

Brimhall and Mastel [27] took the molybdenum samples which they had irradiated to a dose of 5.2×10^{19} n cm⁻² at 400°C and studied the thermal stability of rafts between 600 and 1000°C. The annealing samples were maintained at each of the test temperatures for two hours prior to examination. This study showed that rafts transformed to loops. The largest loops present after the 900 to 1000°C anneals were interstitial in nature in the molybdenum that contained 3 ppm carbon impurity. They were vacancy type in the molybdenum that contained 200 ppm carbon. No explanation was offered for this difference.

Voids in Neutron-Irradiated Molybdenum

A void is often defined in general terms [28] as a gas bubble with zero gas pressure inside. More specifically, bubbles nucleate preferentially on precipitates, dislocations, and grain boundaries; while voids do not exhibit this tendency [29]. Voids are either gas-free or contain gases at low pressures; bubbles, however, contain gases, primarily helium, from the (n,α) reaction. These gases are at pressures in equilibrium with surface tension. This internal pressure aids in further distinguishing the gas bubbles and voids during post-irradiation annealing. Gas bubbles grow and voids shrink during the high temperature annealing.

The behavior and properties of helium bubbles in molybdenum due to neutron irradiation have not been studied. However, some recent studies [30,31,32,33] have been performed on helium gas bubbles in molybdenum and other bcc metals using helium-ion injection. This treatment results in surface deformation in the target area and bulk defects within an implanted layer and as such differs from neutron-irradiation damage and, therefore, will not be considered in this work.

Voids in irradiated metals have and are being studied rather extensively. Norris [34,35] has recently reviewed the subject of voids in metals.

Voids in irradiated molybdenum were first reported by Moteff, et al [26] and Rau, et al [36,37]. They observed voids in

molybdenum irradiated at 700 and 1000°C to a fast neutron fluence of 1.3×10^{20} to 1.4×10^{20} n cm⁻² ($E > 1$ MeV).

Brimhall and Mastel [38] reported the presence of voids in molybdenum irradiated to a dose of 3×10^{19} n cm⁻² at 800°C. Kulcinski, et al [39] observed voids in molybdenum irradiated to a dose of 1×10^{21} n cm⁻² at 1050 and 1150°C. Brimhall and Mastel [27] also observed voids in molybdenum irradiated at only 650°C to a fast neutron fluence of 5.2×10^{19} n cm⁻². The lowest irradiation temperature at which voids have been observed was reported by Elen, et al [40]. They observed voids in samples irradiated at 440°C to a neutron fluence of 3.5×10^{20} n cm⁻².

Wiffen [29] subjected molybdenum to a neutron dose of 2.5×10^{22} n cm⁻² ($E > 1$ MeV) at 425°C and observed no voids. Brimhall, et al [41] subjected molybdenum to a fast neutron fluence of 3×10^{21} n cm⁻² at 450°C and did not observe any voids. In a later study, Brimhall, et al [42] irradiated two different grades of molybdenum at 720°C to a fast neutron fluence of 5×10^{22} n cm⁻². These molybdenum samples were commercial high purity and triple pass zone-refined. On the basis of this work, it is suggested that voids were preferred vacancy defects in molybdenum at temperatures above 0.3 T_M. The low temperature limit of void formation is due to a low vacancy mobility and increased recombination of vacancies and interstitials.

Void density, size, and distribution are sensitive functions of impurities. Brimhall, et al [42] showed that commercial high purity molybdenum and triple pass zone-refined molybdenum affected the void parameters mentioned above in slightly different ways. The somewhat higher purity triple pass zone-refined molybdenum showed larger size voids which were fewer in number which indicated that impurities might be serving as nucleating sites.

Elen [43] studied the annealing of voids in molybdenum irradiated to a fluence of 3.5×10^{20} n cm⁻² at 440°C. He showed that the void volume fraction remained unchanged for a period of the anneal and then suddenly dropped to zero. The complete removal of the voids occurred at 1300°C (0.55 T_M). He suggested that the annealing occurred at the grain boundaries and no gas bubbles remained.

Evans [44] demonstrated the high efficiency of vacancy retention that occurs when voids are formed in molybdenum annealed at 900°C

after being neutron irradiated at 60°C. He indicated that the efficiency is a factor of 50 greater than the theoretical maximum expected during void formation in molybdenum which is irradiated with neutrons at high temperatures. His samples were irradiated to a fast neutron dose of 5×10^{19} n cm⁻² at 60°C and subsequently annealed in vacuum at 900°C for periods up to one hour.

He suggested that the high temperature irradiation void formation depends on a slight preference of dislocations for interstitials to result in the creation of a vacancy-interstitial imbalance, while in his samples a massive imbalance was obtained because the vacancy and interstitial defects which survive the irradiation are spatially separated into frozen displacement spikes and interstitial clusters, respectively.

In addition to the above condition, the interstitial clusters form very stable loops. As a result of these occurrences, the interstitials are effectively removed from the system leaving the vacancies and di-vacancies in the spikes situated so that when they become mobile they can collapse into loops or voids. During further annealing, the interstitial and vacancy components of the damage develop somewhat independently with the annealing of the interstitial component occurring by means of a glide and climb mechanism while the development of the vacancy component occurs primarily through bulk diffusion [45].

Evans also made the observation that the apparent 0.3 T_M threshold for void formation in metals during high temperature irradiations corresponds to the upper limit of the thermal stability of vacancy loops in molybdenum. He suggested that this is true because vacancies are trapped as loops below 0.3 T_M and, therefore, have only a small probability of reaching voids during irradiation; while above 0.3 T_M, although loops still form [46], vacancies are quickly released from them back into the system (to voids or dislocations). The temperature dependence of void growth is then a function of both the temperature dependence of vacancy emission from loops and of vacancy migration.

Voids in irradiated materials are important to consider because if they are relatively stable, they can affect the high temperature mechanical properties of the materials since they can be strong barriers to dislocation motion [47]. This would result in the retention of

radiation-induced strengthening at temperatures higher than might otherwise be considered as maximum.

Swelling of Molybdenum

Swelling in molybdenum as the result of radiation can occur at all irradiation temperatures, but it is only significant in the intermediate temperature region. Kissinger, et al [48] measured the length change produced in molybdenum irradiated to a fluence of 5×10^{19} n cm⁻² at 40°C. The length increase saturated at a value of approximately 0.5%. Brimhall, et al [41] showed that this type of volume increase was typical in molybdenum for irradiation temperatures below 0.27 T_M. The amount of swelling at a constant fluence decreases, however, as the irradiation temperature is increased from 40 to 500°C (0.27 T_M). This type of swelling is a measure of the different amount of lattice relaxation around interstitial loops and vacancy defects. The degree of swelling is insignificant in the operation of reactor components.

In the intermediate temperature range, swelling occurs as the result of the precipitation of vacancies to form voids. This is accompanied by the precipitation of interstitials in dislocation loops. The degree of swelling is dependent on the fluence. To illustrate this, we can compare Brimhall and Mastel's [38] study in which they irradiated molybdenum at 800°C to a fluence of 5.7×10^{19} n cm⁻² and observed a volume increase of 0.12% with Wiffen's [49] work in which he irradiated molybdenum at 790°C to a fluence of 2.5×10^{22} n cm⁻² and observed a volume increase of 1.2%.

The effect of temperature on swelling seems to reach a maximum and then decrease with increasing temperature. Adda [50] indicated that, for molybdenum, maximum swelling occurs in the 800 to 900°C range.

Swelling in the intermediate temperature range can affect reactor coolant channels, fuel rods, and clearance of various reactor components. Brimhall, et al [51] analyzed the volume changes in molybdenum irradiated to various fluences over the temperature range 50 to 1300°C. This work presents a rather extensive review of the swelling of molybdenum and presents a three-dimensional plot of swelling versus temperature versus fluence.

Irradiated-Strained Molybdenum

Molybdenum that has been plastically deformed after irradiation has channels

cleared in defect clusters in a parent matrix that retains its as-irradiated appearance [21,41]. These channels coincide with the planes upon which slip is expected. These channels are called "dislocation channels" and are bounded by the surface of the sample and the two extreme parallel planes of the set of planes upon which slip has occurred.

Mastel, et al [21] observed dislocation channeling in neutron irradiated [$\sim 1 \times 10^{19}$ n cm⁻² (E > 1 MeV)] molybdenum exposed to an irradiation temperature of 40°C. They strained the molybdenum uniaxially until they observed that 1.5% of the channels were free of radiation damage. In samples containing approximately 10 ppm carbon impurity, the channels originated at irregularities which were in the grain boundaries. In samples containing 150 ppm carbon impurity, the channels originated at either irregularities in the grain boundaries or at carbide particles located at the grain boundaries.

Smidt [52] summarized the many different mechanisms of channeling in irradiated metals; however, no one mechanism can fully explain all the observed features. Channeling is, however, a general feature of the deformation of metals in which defect aggregates have formed as a result of irradiation. Qualitatively, channeling can be shown to influence the ductility, work-hardening coefficient and impact energy absorption of metals, but as Smidt points out little quantitative evidence of this exists.

Physical Property Alterations

Damage introduced into a sample during irradiation can alter the physical properties of that material. Properties such as lattice parameter, length, electrical resistivity, bulk density, and hardness are affected by radiation damage.

Moteff [53], Schultz [15], and a 1971 conference [54] have reviewed physical changes in bcc metals. Some of the more important aspects of the effect of radiation damage on molybdenum are presented below.

Gray and Cummings [55] performed X-ray and microhardness measurements on as-irradiated molybdenum. The material they studied was irradiated at approximately 30 to 40°C to fast neutron fluences in the range of 6.5×10^{16} to 1.2×10^{20} n cm⁻². They determined that the hardness increased significantly as the fast neutron fluence increased to 6×10^{19} n cm⁻².

Above that fluence, the hardness value appeared to level off as though a saturation condition existed. The lattice parameter, exhibiting similar behavior, increased with increasing fluence to a maximum fluence of 5×10^{19} n cm⁻²; however, it decreased with higher fluences.

The saturation effect in the hardness curve indicated that additional cluster formation due to higher fluences has no effect on the hardening of molybdenum once the breakover point has been reached.

Kissinger, Brimhall, and Mastel [56] studied the effects of fluence on the length and lattice parameter of molybdenum which they had irradiated to fluences in the range of 7×10^{18} to 1×10^{20} n cm⁻². Keys and Moteff [57] plotted the sum of the length change and the lattice parameter changes observed by Kissinger, et al [56]. The sum of the length change increased to a maximum at a fluence of 4×10^{19} n cm⁻²; it then decreased as the fluence was increased to 1×10^{20} n cm⁻². In addition to the above, Keys and Moteff [57] also plotted the radiation-induced resistivity increment of molybdenum as a function of the fast neutron fluence. The resistivity increment increased to a maximum value at a fluence in the range of 5×10^{19} to 1×10^{20} n cm⁻² (E > 1 MeV); it then decreased as the fluence was increased to 1.5×10^{21} n cm⁻².

Sikka [28] has summarized the various physical property changes that occur in molybdenum as a function of fast neutron fluence. This summary is presented in Figure 2. The saturation effect is obvious in all studies including the latest performed by Sikka and Moteff [58].

Annealing Recovery in Irradiated Molybdenum

Recovery of defects in irradiated molybdenum as a result of isochronal annealing is a much disputed research area. Six prominent recovery stages are discussed. These stages are categorized by temperature bounds and are listed below with their corresponding homologous temperature regions:

Stage I	$T < 0.03 T_M$
Stage II	$0.03 T_M \leq T \leq 0.1 T_M$
Stage III	$T \approx 0.17 T_M$
Stage IV	$T \approx 0.22 T_M$
Stage V	$T \approx 0.30 T_M$
Stage VI	$T \approx 0.35 T_M$

FIGURE 2 - Changes in various properties as a function of neutron fluence showing the saturation effect in neutron irradiated molybdenum (from Sikka [28]).

The recovery of defects has been discussed in great detail by Mott [53,57], Schultz [15], Nihoul [16,59], Eyre [60], and Stals, et al [61] and many other investigators [54]. Sikka [28] recently summarized the various theories and this summary is presented in Table 3.

Keys and Mott [57] have correlated defect recovery with the change in electrical resistivity, while Sikka [28] has recently studied the change in cluster density, microhardness, and tensile elongation. The data of both investigations are shown in Figure 3. The data indicate that electrical resistivity recovers in a manner different from the other three properties which have a similar trend.

Radiation Hardening

Neutron irradiation produces a hardening in metals. This hardening effect corresponds to an increase in the yield strength. This effect in molybdenum was reported by Bruch, et al [62] in 1955. In their study, molybdenum samples were tensile tested after exposure to a thermal neutron flux of 1.9×10^{20} to 5.9×10^{20} nvt at ambient temperature. These samples embrittled and the transition temperature for this material had shifted from -30 to +70°C.

Radiation hardening is the term used to describe the hardening that occurs as a result of neutron irradiation. The models used to describe this effect assume that defect clusters are introduced during irradiation and these impede the motion of slip dislocations during plastic deformation. The number of clusters or more appropriately the density of the defect clusters is proportionate to the radiation dose and these clusters have a random distribution on the slip plane.

Seeger [63, 7] proposed a theory of radiation hardening in which vacancy-rich zones called depleted zones act as obstacles to the motion of slip dislocations. Seeger assumes that the defect clusters produced during irradiation are potential energy "hills". Dislocations on the slip plane overcome these hills with the aid of both applied stress and thermal vibrations. The strain rate in a crystal is determined by the thermally activated process which advances a dislocation past the obstacles.

Seeger [63] postulated that N dislocations per unit volume which were held up at N_0 uniform obstacles per unit volume of strength, U , and would give a strain rate, $\dot{\epsilon}$, were related to the frequency, ν_0 , with which a dislocation of strength, b , attempts to overcome the obstacles in the following way:

Table 3

SUMMARY OF DEFECT RECOVERY THEORIES

Investigators ¹	Stage Classification (From Sikka [28])					
	I $T < 0.03 T_M$	II $0.03 > T > 0.1 T_M$	III $T \sim 0.17 T_M$	IV $T \sim 0.22 T_M$	V $T \sim 0.30 T_M$	VI $T \sim 0.35 T_M$
Eyre	Long-range migration of single interstitials.	Release of interstitials from traps (impurities, small aggregates) of various depths.	Not simple. Migration of a vacancy-type defect. Possible additional contributions due to release of self-interstitials from traps and migration of interstitial point defects.	Migration of a vacancy-type defect.	Recovery of dislocation structures controlled by short-circuit.	Recovery of dislocation structures controlled by bulk self-diffusion.
Grimes Decarlo	Close-pair annihilation. Long-range migration of single interstitials.	Break-up of interstitial impurity complexes and migration of interstitial impurity complexes.	Break-up of stage I interstitial complexes.	Migration of vacancies.	Break-up of vacancy-vacancy complexes and of vacancy-impurity complexes.	-----
Kothe	-----	-----	Migration of single vacancies.	Unclear. Possible release of impurity-trapped vacancies.	Migration of dislocations and possibly annealing of small vacancy clusters.	-----
Kulcinski Brimhall Kissinger	Close-pair annihilation. Long-range migration of single interstitials.	Release of interstitials from a variety of traps.	Not simple. Migration of dislocations to strongly-trapped interstitials, interstitial clusters, vacancy loops.	Migration of single vacancies.	Submicroscopic vacancy complexes become unstable, vacancies released from traps.	Interstitial loops dissolution due to thermal vacancy generation. Vacancies emitted from vacancy loops.

Table 3 (Continued)

Investigators ¹	Stage Classification (From Sikka [28])					
	<u>I</u> $T < 0.03 T_M$	<u>II</u> $0.03 > T > 0.1 T_M$	<u>III</u> $T \sim 0.17 T_M$	<u>IV</u> $T \sim 0.22 T_M$	<u>V</u> $T \sim 0.30 T_M$	<u>VI</u> $T \sim 0.35 T_M$
Moser	Close-pair annihilation. Long-range migration of single interstitials necessary for new defect.	-----	Not simple (substages).	-----	-----	-----
Stals Dihoul DeBatist	Close-pair annihilation. Long-range migration of single interstitials.	-----	Migration of intrinsic point defects primarily of interstitial type.	Migration of a vacancy-type defect.	Recovery of dislocation structures and defect clusters and recrystallization, dependent on mode of creation of defects.	
Shultz	Close-pair annihilation. Long-range migration of single interstitials.	-----	Migration of intrinsic point defects. Vacancy-type defects or complex. Both interstitial and vacancy-type defects.	-----	-----	-----
Moteff ² Smith	-----	-----	Self-interstitial migration.	Di-vacancy migration.	Vacancy migration.	Polygenization.
Keys ³ Moteff	-----	-----	Self-interstitial migration to immobile traps, predominantly vacancies.	Primarily di-vacancy migration. Other complex defects or impurity atoms may also contribute.	Vacancy migration.	Cluster or defect loop recovery. Polygenization.

Table 3 (Continued)

Investigators ¹	Stage Classification (From Sikka [28])					
	I $T < 0.03 T_M$	II $0.03 < T < 0.1 T_M$	III $T \sim 0.17 T_M$	IV $T \sim 0.22 T_M$	V $T \sim 0.30 T_M$	VI $T \sim 0.35 T_M$
MotEFF ²	-----	-----	Self-interstitial migration to immobile traps. Migration of interstitial impurity atoms (C, B, and N).	Primarily di-vacancy migration. Other complex defects or impurity atoms may also contribute.	Vacancy migration. Migration of oxygen impurity atoms.	Small cluster or loop defect recovery. Polygnization.

¹The reference for the mechanisms suggested by the first seven investigators is Session VI of the Proceedings of the International Discussion Meeting on Defects in Refractory Metals held at Mol, Belgium (1971).

²J. MotEFF and J. P. Smith, "Recovery of Defects in Neutron Irradiated Tungsten," ASTM STP-380, Flow and Fracture of Metals and Alloys in Nuclear Environments (1965).

³L. K. Keys and J. MotEFF, "Isochronal Resistivity Study of Defect Recovery in High-Neutron Fluence Irradiated Molybdenum," Journal of Applied Physics, 41, 2618 (1970) and L. K. Keys and J. MotEFF, "Neutron Irradiation and Defect Recovery of Tungsten," Journal of Nuclear Materials, 34, 260 (1970).

⁴J. MotEFF, review paper on "Radiation Damage in Body-Centered-Cubic Metals and Alloys" in AIME Symposium on Radiation Effects, Ashville, North Carolina (1965).

FIGURE 3 - Recovery of cluster defects, electrical resistivity, micro-hardness and % elongation for molybdenum irradiated at $\sim 70^\circ\text{C}$ to a fast neutron fluence of $1.1 \times 10^{20} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$). (from Sikka [28]).

$$\dot{\epsilon} = \frac{N}{N_0} b v_0 \exp\left(-\frac{U(\tau)}{kT}\right) \quad (10)$$

Solving Equation (10) for τ should yield the shear stress dependence on dose, through N_0 , and the test temperature, T . He obtained an expression for the critical shear stress; however, the expression did not seem accurate as published. Schwink [64] discovered that a factor was missing from the expression and the corrected analytical expression for the critical shear stress is:

$$\tau_c = \left(\frac{N_0}{Gb}\right)^{1/2} \left(\frac{U_0}{4x_0b}\right) \left\{ 1 - \left[(kT/\alpha U_0) \ln(Nb v_0 / N_0 \dot{\epsilon}) \right]^{2/3} \right\}^{3/2} \quad (11)$$

where: G = the shear modulus,
 b = the Burgess Vector,
 k = Boltzmann's constant,
 x_0 = the dislocation position,
 T = the test temperature in $^\circ\text{K}$,

N_0 = the number of obstacles per unit area of the slip plane,

N = the number of active slip dislocations per unit volume,

v_0 = the frequency with which a dislocation attempts to surmount the obstacles,

$\dot{\epsilon}$ = the strain rate,

U_0 = the potential energy height of the barrier, and

α = 2/3. This was the factor missing from the original expression.

The effect of the neutron irradiation on the critical shear stress is expressed in Equation (11) by a change in N_0 , which is directly proportional to the neutron dose. A close examination of Equation (11) shows that for all practical purposes Seeger's theory predicts that τ_c is proportional to $(N_0)^{1/2}$; however, since N_0 is directly proportional to ϕ , the neutron dose, τ_c is also proportional to $(\phi)^{1/2}$.

In the derivation of Equation (11), it was necessary to assume that τ was sufficiently large following irradiation in comparison to the other contributions to the critical shear stress so that the effect of irradiation could be considered the dominant factor. In general, however, this is not true for all cases in body-centered cubic metals. In bcc metals, there is a strong temperature dependence even before neutron irradiation.

Foreman [65] has also examined the motion of dislocations through a planar, random array of obstacles. He assumed that the line tension of the dislocation was not constant but varied in a logarithmic manner with its length. The critical shear stress is expressed as:

$$\tau_c = A \frac{Gb}{2\pi} \frac{1}{L} \left[\ell_n \left(\frac{L}{r_0} \right) + B \right], \quad (12)$$

where A is approximately 1 for edge segments and 1.5 for screw segments, and r_0 is the core radius of the dislocations. This expression has been used to explain less rapid hardening than the square root dependence of the neutron dose.

The neutron dose dependence of the yield stress is an important point that has to be considered if the basic hardening mechanism of irradiation is to be identified. The two basic mechanisms are source hardening and lattice friction hardening. Lattice friction hardening is the result of radiation induced defect clusters obstructing the movement of dislocations. Source hardening occurs when radiation-produced point defects pin dislocation sources and prevent their operation as dislocation sources. Arguments [66,67,68,69,70,71] in support of both mechanisms can be found for almost any metal. In fact for molybdenum, Bruch, et al [62] explained their results reported above as a consequence of lattice friction hardening. Johnson [70] later performed a study similar to the one reported by Bruch, et al [62] and explained his similar results using the source hardening mechanism.

Makin and Sharp [72] have suggested a model for radiation hardening which is a lattice hardening type that uses the deformation characteristics formerly used to support source hardening mechanisms. In this model, the critical shear stress is controlled by the initial operation of the source in a matrix of obstacles that have been produced by irradiation. The average spacing of the obstacles is more than the source length and, therefore, the source cannot operate without the

bowed out dislocation meeting another. In this model, then, both types of hardening are evident. They further state that once a loop is generated, the stress needed to expand it becomes less as the radius of the loop increases. This theory explains the yield drop in terms of lattice hardening even though previously it was explained as being characteristic of source hardening. Even though the critical shear stress appears to be a function of the operation of the source, they do not believe that radiation causes ideal source hardening by making the effective source length shorter. Radiation may, however, make it more difficult for the source to operate as it encounters obstacles adjacent to it.

Wronski, et al [73] found that for molybdenum irradiated in the dose range of 0 to 8.0×10^{18} epithermal neutrons cm^{-2} the increase in the lower yield stress showed a square root dependence on the dose rate. Epithermal neutrons are neutrons with a range of energies from thermal (0.025 eV) to approximately 0.1 MeV.

Downey and Eyre [23] observed black dots in irradiated molybdenum samples using the transmission electron microscope. They attributed these dots to point defect clusters. The diameter of the clusters ranged up to 200 Å. This was similar to the damage observed by Silcox and Hirsch [74] in neutron irradiated copper and Eyre [75] in neutron irradiated iron.

Downey and Eyre [23] reported that the observable damage remained unchanged upon annealing up to 600°C; and between 600 and 800°C, the only change observed was a coarsening of the clusters resulting in a higher proportion of them becoming resolvable as interstitial loops. After an 800°C anneal, there was evidence that rapid loop growth in some grains had commenced. This resulted in localized decreases in the cluster density. Above 1000°C, dislocation lines which were sections of large loops began to form hexagonal networks, which became well developed at 1200°C.

They also determined the defect density and size as a function of annealing temperature. Their data indicated that the number of clusters was reduced by two orders of magnitude as the post irradiation annealing temperature was increased to 1035°C. The cluster diameter grew from 60 to 435 Å and the number of point defects decreased by 50%.

Microhardness measurements taken by Downey and Eyre [23] on the same specimens

discussed above indicate that microhardness recovers significantly below 600°C, while the observable defects do not appear to change. This would tend to indicate that as in fcc metals [76] the small, submicroscope (<30 Å) defects are primarily responsible for radiation hardening in molybdenum.

Ibragimov, et al [77,78] and Sikka [28] have studied the recovery of irradiation induced room temperature hardness values in molybdenum by isochronal annealing. Ibragimov, et al showed hardness recovery in the temperature region of approximately 0.35 T_M , while Sikka observed recovery being initiated at approximately 0.34 T_M . The slight difference in the data of both investigations could easily be due to the range of experimental error. The significance of these data is that they indicate that molybdenum tends to show hardness recovery in the same temperature region as the other bcc metals [77], while fcc metals show recovery at 0.5 T_M [79]. This would imply that differences in recovery mechanics are primarily due to crystallographic structure.

Radiation Anneal Hardening

Radiation Anneal Hardening is the term used to describe the hardening (additional increase in yield and flow stresses) that occurs upon post-irradiation anneal. This phenomena occurs as a result of annealing at lower temperatures, before the significant recovery to pre-irradiation values occurs. This phenomenon has been observed for the yield stress and microhardness in molybdenum by a number of investigators.

Makin and Gillies [80] observed that the yield stress of neutron irradiated molybdenum, which was post-irradiation annealed for one hour at 200°C, increased. Wronski and Johnson [81] subjected irradiated molybdenum to one-hour anneals in the temperature range of approximately 150 to 260°C. The yield stress increased after each anneal and reached a plateau at the highest temperature. The total increase in yield strength as a result of the anneals was approximately 7100 psi above the pre-anneal value. The authors of both these studies proposed the migration of vacancies to dislocations as the mechanism of radiation anneal hardening.

Downey and Eyre [23] and Moteff [53] observed radiation anneal hardening in their microhardness studies on post-irradiation annealed molybdenum. The hardening was observed in samples annealed between 150 and 200°C.

Kamphouse, et al [82] have also performed hot hardness studies on irradiated and unirradiated molybdenum. They observed that the room temperature hardness values showed a further hardening above the as-irradiated condition following anneals at temperatures greater than 100°C. A peak in hardness value was observed at approximately 0.15 T_M , with another peak occurring over the temperature region from 200 to 700°C. This second peak was described as a broad, non-exponential peak. They observed complete hardness recovery occurring at an annealing temperature between 950 and 1070°C. This study indicated that room temperature hardness values and hot hardness values recover in about the same manner and at similar temperatures.

In all the cases reported above, it seems that the radiation anneal hardening plateaus at about 200 to 260°C. This temperature is significant because it is approximately the temperature ($0.16 \pm 0.004 T_M$) at which Stage III annealing occurs in electrical resistivity samples of molybdenum. The mechanisms that account for the Stage III annealing of electrical resistivity can, therefore, be assumed to be the same for radiation anneal hardening. This is where the problem begins, since as was discussed earlier many theories have been put forth to explain the recovery stages of electrical resistivity. Specifically, Stage III has been attributed to interstitial impurity migration [83,84,85,86, 87,88] or the migration of intrinsic defects [23,89,90,91,92,93] (interstitial, di-interstitials, vacancies, or di-vacancies). No attempt will be made to explain or promote any of the theories.

Temperature Dependence of the Yield Stress

Neutron irradiation has an effect on the temperature dependence of the yield stress in metals. This dependence is rather significant for irradiated fcc metals [69, 94,95,96,97]; however, in bcc metals, the yield stress shown a significant sensitivity to temperature in the unirradiated condition [98,99,100] and a less significant change following neutron irradiation [101,102,103].

The significant temperature dependence of the yield stress in bcc metals has been attributed to impurity effects [104,105, 106], mainly interstitial impurities or precipitates, or intrinsic lattice properties [98,99,100,107,108]. The intrinsic lattice properties explanation seems to be the most accepted; however, Frank and Seeger [109] are convinced that the impurity effects are the dominant

rate-controlling mechanisms for plastic deformation. Recently, studies performed on both irradiated [110] and unirradiated [111] iron indicated that the interaction of dislocations with centers of tetragonal symmetry (viz., interstitial impurities) was the controlling factor of the temperature dependence of the yield stress.

2. NEUTRON IRRADIATION EFFECTS ON MECHANICAL PROPERTIES

The properties which will be reviewed in this section will be hardness, ductile-brittle transition temperature, tensile, and creep rupture of molybdenum. In the previous section on Radiation Damage, these properties were briefly discussed from the point of view of how the nature of the radiation damage affected them. This section will review the more practical test data available on the mechanical properties and how they are affected by neutron irradiation.

Most of the mechanical properties of irradiated molybdenum [62,70,81,112] have been determined at ambient room temperature on test specimens which were irradiated at reactor ambient temperatures. Some higher temperature ($T > 0.22 T_M$) studies have been performed on specimens irradiated at reactor ambient temperatures [26,82,113] and at elevated temperatures [25].

Hardness

Irradiation induced room temperature hardness increases were reviewed quite extensively in Part 1 of the literature review and will not be presented again.

Ductile-Brittle Transition Temperature

The ductile-brittle transition temperature is that temperature for bcc metals at which a transition from ductile to brittle behavior occurs. At temperatures above the transition temperature, material deforms plastically; at temperatures less than the transition temperature, brittle fracture occurs without significant plastic deformation. Molybdenum exhibits a ductile-brittle transition temperature.

Neutron irradiation increases the transition temperature for molybdenum. This decrease in fracture ductility with decreasing temperature is accompanied by a sharp increase in the yield strength of molybdenum [114]. The irradiation induced transition temperature shift has been measured by several investigators [62,80,115], and found to vary from 0 [115] to 100°C [62]. These conflicting

results indicate that variables other than irradiation effects may be the overriding factors in determining the ductile to brittle transition temperature of molybdenum after irradiation.

These variables can be interstitial impurities, grain size, or environmental factors that increase the surface energy of the molybdenum.

Tensile Tests

Tensile tests have been performed on molybdenum which has been irradiated at low temperatures to fast neutron doses up to $\sim 1 \times 10^{20}$ nvt [70,80,81,112,116]. Wiffen [117] completed a study in which he tensile-tested molybdenum specimens at temperatures between 20 and 800°C. Wiffen's specimens were irradiated to fluences in the range of 1.5×10^{22} to 6.1×10^{22} neutrons cm^{-2} ($E > 0.1$ MeV) at temperatures in the range of 390 to 1140°C.

Tensile tests performed at temperatures near the irradiation temperature in general show that the strength properties are increased and ductility is severely reduced [70,80,81,112,116]. Tensile tests [29] performed on samples irradiated to 425°C and tested at temperatures up to 650°C show that irradiation increased the ultimate strength by a factor of 2.5 to 3; however, the uniform elongation was reduced to zero and the total elongation reduced to less than 10%. Fracture of these specimens even at test temperature as high as 550°C were brittle. The irradiation effectively shifted the tensile ductile-to-brittle transition temperature from below room temperature to a strain-rate sensitive value in the range of 400 to 600°C. The data presented by Wiffen [117] would indicate that irradiated molybdenum does not work harden and fails at temperatures above the ductile to brittle transition temperature by local deformation and the tensile fracture elongation is severely reduced.

Tensile tests [117] performed on molybdenum irradiated near 450°C and tested at a strain rate of $0.002 \text{ in-min}^{-1}$ showed a ductile-to-brittle transition temperature between 550 and 600°C. Below 550°C, the specimens fractured in a brittle manner; at 650°C the maximum load occurred after less than 0.2% deviation from the modulus line, and the specimen reached and showed appreciable elongation and reduction in areas before failure at a load much below the maximum. When the strain was reduced by a factor of 100, brittle failure occurred at 200°C, and

the same type of unstable curve as was observed in the previous sample at 650°C was now observed at 550°C.

Samples of molybdenum that were irradiated at a variable temperature between 857 and 1136°C were also tensile tested at 0.02 in-min⁻¹ [117]. These samples were brittle at 20°C but ductile at 400°C and the stress strain curve at 400°C was not unstable as those previously reported. This indicated the ability of the material to work harden while straining approximately 6% before the onset of plastic instability.

Another sample irradiated at 455°C was annealed for one hour at 1050°C prior to tensile testing [117]. This sample was tested at 400°C and 0.02 in-min⁻¹. The results of this test indicated that the sample's yield strength was significantly below that of a sample that had been irradiated and not annealed. After yield, the annealed sample work hardened and strained uniformly to 6.3%; the sample failed abruptly at the ultimate load without any necking.

Creep Rupture

Creep-rupture data for irradiated molybdenum are in short supply. Post-irradiation creep studies of molybdenum have been performed by Moteff and Kingsbury [113] and Moteff, Rau and Kingsbury [26]. In these studies, it was shown that molybdenum irradiated to a dose of 6.9×10^{18} nvt and tested at 870 and 980°C was not affected by the irradiation.

Specimens irradiated to fast neutron doses of 1×10^{19} and 3.8×10^{19} nvt were also tested in the temperature range of 560 to 650°C. In all cases, the time to rupture for the specimens decreased slightly and the linear creep rate correspondingly increased. This increase was 25 times for samples irradiated to a dose of 1×10^{19} nvt and 60 to 270% for those irradiated to 3.7×10^{19} nvt. Data obtained on the samples of the material irradiated to 1×10^{19} nvt showed that there was very little instantaneous plastic strain on loading for both the as-irradiated and as-irradiated plus annealed (~ 1 hr at $\sim 0.31 T_M$) even though the pre-irradiation creep rates were restored in the annealed specimens. These results were in opposition to the results obtained for the control specimen. It appears that annealing does not remove the defect causing the loss in plastic properties in the as-irradiated material.

In another study [26,118], they showed that an increase in irradiation temperature resulted in an increase in rupture life. Samples of molybdenum were irradiated to 1.6×10^{20} nvt at 70, 700, and 1000°C. These samples were subsequently creep tested at 750°C with a stress of 25,600 psi. The results of these studies showed that the time to rupture increased as a function of irradiation temperature and the time to reach a certain strain value also increased. In particular, the time to reach 20% strain in the control sample was less than 10 hr, while it took in excess of 325 hr to reach 20% strain in the sample irradiated at 1000°C. The ductilities of all specimens were comparable to the value for the control specimen, decreasing slightly at the higher temperatures.

Post-irradiation [26] annealing at 1000°C in vacuum was also performed on some of the specimens irradiated at 70 and 700°C. After the anneal, the specimens were creep rupture tested under the same conditions as the irradiated specimens. Annealing a sample irradiated at 70°C changed the creep-rupture properties. The period of delayed creep was shortened, the creep rate was reduced and time of rupture became similar to that of the control specimen. The post-irradiation anneal had little effect on the sample irradiated at 700°C. The minimum creep rate did not change significantly; however, the rupture life increased 25%. These studies showed that while irradiation temperature has little effect on the rupture ductility of irradiated molybdenum, it does affect the mode of deformation, (i.e., strain-rate vs time, etc.).

Recent studies performed at Oak Ridge National Laboratory [119] have evaluated the creep rupture properties of molybdenum samples that had been irradiated to a fluence of 6.1×10^{22} n cm⁻² ($E > 0.1$ MeV). The irradiation temperature rose from 860 to 1140°C during the course of the irradiation. The samples were tested at 750 and 1200°C and at stresses varying from 6,000 to 33,000 psi. A sample tested at 1200°C with a stress of 8,000 psi gave a strain-time curve that was of the same general shape as one obtained by testing a control specimen under the same conditions. The elongation to fracture for the irradiated specimen was only 80% of the value obtained for the control specimen. The rupture life of the irradiated specimen was 428 hr, while that of the control specimen was 13.7 hr. These results indicated that there was a significant irradiation strengthening in the test but a relatively minor effect on the ductility.

A sample tested at 750°C under a stress that had been step-wise increased from 25,600 to 33,000 psi was tested for 5,000 hr (400 hr at 33,000 psi) and showed approximately 1% elongation. This is in contrast to the data of Moteff [26] and the proposed explanation for this difference was that the higher fluence of this recent specimen resulted in much greater strengthening.

3. CREEP OF UNIRRADIATED MOLYBDENUM

Creep of Molybdenum in the Temperature Range of 600 to 1000°C

Pugh [120] performed one of the earliest studies on the creep of molybdenum. In this investigation, recrystallized molybdenum containing a total nonmetallic impurity of 0.0543% was tested. The tests were conducted in the temperature range of 1600°F (~870°C) to 2000°F (~1095°C) with nominal applied stresses of 9 to 36 Ksi in an argon atmosphere. In this study rupture life, minimum creep rate, true stress, and total strain were reported for each sample. The Zener-Holloman Parameter and the Larson-Miller Parameter were used to analyze the test data. The data obtained using the Zener-Holloman Parameter ($\log \dot{\epsilon}_s + 43,200/T$) ranged from a low of 22.7441 for 9 Ksi at 2000°F to a high of 36.8134 for 34 Ksi at 1600°F. Analysis of the rupture data in terms of the Larson-Miller Parameter was performed using a Larson-Miller Constant of 15. This value provided the least amount of scatter in the Larson-Miller Plot. The activation energy of creep determined by analyzing the test data using the equation [121]

$$Q = R \ln(\dot{\epsilon}_1/\dot{\epsilon}_2) \left[(1/T_2 - 1/T_1) \right]^{-1}, \quad (13)$$

averages out to approximately 62 Kcal/mole.

Carreker and Guard [122] studied the tensile deformation of molybdenum as a function of temperature and strain rate. The temperature range of interest was -196° to 1540°C. Their data are in general agreement with Pugh's [120] and their general conclusions were that the yield strength and tensile strength are insensitive to temperature between 400 to 800°C and that molybdenum of differing processing histories showed only minor differences in tensile properties when annealed similarly prior to testing.

Semchyshen and Barr [123] performed a detailed study on the creep rupture behavior of arc-cast molybdenum. This material contained 0.015% carbon and was tested in vacuum in the temperature range of 1600 to 2000°F (~870 to ~1095°C). The applied stress ranged from 12 to 45 Ksi and both recrystallized [1 hr at 2150°F (1177°C)] and stress-relieved [1 hr at 1800°F (982°C)] material was tested. Their investigation showed that the strength of the recrystallized material differed significantly from that of the stress-relieved material. Strain hardening tends to increase the strength of a material. They also observed that as the recrystallization temperature was exceeded, a decrease in material strength was also noted; this is the result of the crystal structure change which occurs.

Green, Smith, and Olson [124] studied the creep rupture of powder-metallurgy prepared molybdenum rod at higher temperatures [$>2912^\circ\text{F}$ ($>1600^\circ\text{C}$)] in helium. As part of their investigation, however, they performed a least squares analysis to represent the rupture data in terms of the Larson-Miller Parameter. They applied this analysis to Pugh's data [120] and obtained a value of $C = 13.9$. Combining their data and Pugh's they obtained a value of C of 14.3.

Bowers, et al [125] have also studied the creep behavior of arc-cast molybdenum and sintered molybdenum at 650 and 750°C in argon. Their data show that the sintered material exhibits more creep resistance than the arc-cast material. The results that they obtained for the arc-cast material at 650°C were lower than those obtained by Semchyshen and Barr [123] on the same type of material. Conway and Flagella [126] studied this difference and also noticed a similar observation in the results of Semchyshen and Barr [123] and Pugh [120] for recrystallized molybdenum at a test temperature of 870°C. They concluded that the carbon content might be the cause of these differences and have shown on a plot of 100 hr-rupture stress vs. carbon content that the rupture stress of molybdenum increases with carbon content.

Carvalhinhos and Argent [127] have studied the compressive creep of molybdenum in the temperature range of 946 to 1385°C. Their samples were recrystallized for 1 hr at 1500°C prior to testing. The samples were tested in vacuum at stresses that varied from 3.5 to 12 Ksi. They determined that the activation energy for creep was stress dependent and varied from 61 Kcal mole⁻¹

at 3.5 Ksi to 88 Kcal mole⁻¹ at 10 Ksi. They explained this behavior by saying that the structural terms in the steady state creep equations were stress dependent.

They determined activation energies by conducting their tests at the same stress but different temperatures. The data obtained from such a test correlated well with the data obtained using the temperature change technique [127].

A majority of the other data available on the creep of molybdenum has been obtained at temperatures much higher than those of interest in the present study and the reader is directed to Conway and Flagella [126] for a detailed review of these studies.

Creep Structure

Sherby and Burke [128] have performed a general review of the effects of subgrain size on the steady state creep rate for pure metals. Their results indicate that subgrains are developed during transient creep. The size of these subgrains is dependent of the initial grain size, previous thermal and mechanical history of the material, impurity content, and test temperature. The subgrain size, they report, is strongly independent of the applied stress. Increasing the creep strain once an equilibrium is established has no effect on the altering of that size. Mathematically, they used a power relation:

$$\sigma_a = Ad^{-b}, \quad (14)$$

where

σ_a = the applied stress,

A = a material constant,

d = the subgrain diameter, and

b $\approx$ 1,

to explain the equilibrium subgrain diameter.

Since the mobile dislocation density is a function of applied stress, it increases with increasing stress. Since the steady state creep rate is proportional to $\gamma^{3.5}$ for the metals, where γ is the stacking fault energy, subgrain size is also a function of the stacking fault energy [129] for fcc metals.

Holt [130] associates subgrain size and the density of mobile dislocations in the following manner:

$$d \approx K_C(\rho_O)^{-1/2} \quad (15)$$

where

d = the subgrain size,

K_C = a constant, and

ρ_O = the density of mobile dislocations.

Specific studies concerning the substructure changes in molybdenum during creep are rather limited [127,131,132,133,134,135,136]. Prekel and Lawley [131] using the etch pit technique studied the dislocations in deformed molybdenum. They reported that the shape and orientation of the etch pits were independent of the Burgers vector and the angle of inclination of the dislocation to the free surface of the crystal.

They also reported that a one-to-one correspondence of etch pits to dislocations was observed only on the {421} plane.

Clauer, et al [132,133,134] have studied the creep substructure of molybdenum single crystals. They reported that the subgrains which were produced consisted of bands of narrow subgrains alternating with bands of coarser ones. Subboundaries were identified as [111] tilt boundaries composed of dislocations from two slip directions. As the creep strain increased, the mobile dislocation density was observed to decrease. Tilt walls were reported to move by glide and as a result of this movement contributed to the creep strain.

They determined an activation energy for creep by studying the [011] direction. The value which they determined (107 Kcal mole⁻¹ [132]) suggests that the creep rate is diffusion controlled.

They also reported that the substructure primarily consisted of edge dislocations and eliminated the movement of jogged screw dislocations as a rate controlling mechanism of creep.

Clauer, et al [132,133,134] also reported that an observed decrease in the creep rate that occurred during primary creep was the result of the recovery of the substructure and not of work hardening.

Carvalhinhos and Argent [127] also examined the substructure of their tested samples and observed two and three dimensional networks showing that climb takes place in the range of 0.41 to 0.55 T_M . They also determined a subgrain size of approximately 20 μm . Zielinski [135] in some recent work on the creep of molybdenum in tension and compression at approximately the same stress levels used by Carvalhinhos and Argent has determined subgrain sizes that are significantly smaller than those determined previously. Zielinski used the transmission electron microscope instead of the X-ray techniques employed by Carvalhinhos and Argent, and his data indicate that the subgrain size for compressive creep samples is approximately a factor of 5 less than that determined by Carvalhinhos and Argent. The subgrain size determined for his tensile creep specimens is approximately a factor of 10 less than that determined by Carvalhinhos and Argent. These differences in subgrain size of tensile versus compressive creep specimens have to be the result of differences in primary creep.

Ericksen and Jones [136] studied the substructure of polycrystalline molybdenum. Their samples were the result of primary creep studies at elevated temperatures, and they showed that subboundaries are formed at an early stage in the transient creep region. They also showed that subgrain diameter decreased with applied stress.

4. COLD WORKING AND IRRADIATION

Since some of the samples which will be examined during this investigation were worked and stressed relieved prior to neutron irradiation, a survey of literature concerning worked and irradiated material was made. The most relevant information available concerning neutron irradiation after working is that concerning stainless steels [137,138,139] and the one study on molybdenum [140]. This information is reviewed below.

Laidler and Mastel [137] found that cold working prior to neutron irradiation reduced the tendency for void formation in austenitic stainless steels irradiated to fast neutron fluences at elevated temperatures. They assumed that this occurred because the increased dislocation density in cold worked stainless steel provided an increased concentration of sinks for point defects.

After irradiation, their specimens contained voids and Frank dislocation loops. The mean void size decreased with

increasing cold work from a value of 125 Å at 0.5% strain to 75 Å at 15% strain. At the lower strains, the void and Frank loop distributions were reasonably uniform. At 15% strain, the void concentration was greatly reduced and the void distribution was markedly non-uniform. The loops tended to cluster in bands. They suggested that increasing cold work prior to irradiation may increase the threshold fluence for defect nucleation.

Fish, et al [138] studied the creep behavior of 316 stainless steel that had been cold worked approximately 20% prior to neutron irradiation ($1 \times 10^{22} \text{ n cm}^{-2}$ [$E > 0.1 \text{ MeV}$]) at temperatures between 450 and 840°C. Little effect of the irradiation was noted in the tensile properties of samples tested at or below 540°C. At test temperatures in excess of 650°C, helium embrittlement caused a significant decrease in tensile ductility. They concluded that irradiation increased creep rates and either decreased or did not affect creep ductility depending upon specific sample and conditions. In all tests, reduced rupture times were observed.

Their examination of the post irradiation, pre-test microstructure of the samples showed three specific categories. The samples irradiated at 450°C had their pre-irradiation fine substructure of free dislocations and tangles replaced by Frank loops, perfect loops, and free dislocations probably formed as a result to perfect loop interaction. No voids were evident in the microstructure. The samples irradiated at 580°C possessed a loosely defined cell structure in place of the free dislocations and tangles. No evidence of displacement damage was observed at 580°C. Irradiation at 850°C resulted in complete recrystallization and removal of all substructure components.

Brager and Straalsund [139] showed that the effect of irradiation temperature on void formation in neutron-irradiated cold worked 316 stainless steel is markedly different from that in solution-treated steel. They attributed this difference to the thermal instability of the cold-worked microstructure. For low temperature irradiation, voids and Frank faulted loops are produced in 316 stainless steel which has been cold-worked 20 to 27%. Voids are produced in a manner similar to that in solution-treated steels, but at a lower rate. At intermediate temperatures, the defect supersaturation decreases because of the increased thermal equilibrium vacancy concentration and defect mobility; at the same time, the sink density remains high.

However, since the void nucleation rate is critically dependent upon defect supersaturation, the void nucleation rate in cold-worked stainless steels decreased rapidly with increasing temperature and resulted in the suppression of void formation at intermediate irradiation temperatures. At high irradiation temperatures, the cold-worked microstructure becomes thermally unstable and the dislocation density decreases as a result of the mutual annihilation of mobile dislocations. In this temperature regime, voids are formed preferentially in localized regions where substantial dislocation recovery has taken place. At the highest irradiation temperature ($> 725^{\circ}\text{C}$) void formation is suppressed regardless of microstructure. This is true even for solution-treated steel.

Brimhall and Mastel [140] in their study prestrained molybdenum samples to their yield point, 2, 5, and 20% at 20°C prior to irradiating the specimens at 40°C to a fluence of 7×10^{18} nvt ($E > 1$ MeV). These samples were 75 μm thick and contained <10 ppm carbon. Using the electron microscope to examine their samples, they found black spot clusters present in all samples and no significant change in the distribution or configuration of dislocations. They observed no denuding of clusters adjacent to grain boundaries and cell boundaries. They summarized their study by saying that dislocations do not alter the damage structure in neutron-irradiated molybdenum and that old dislocations apparently play no part in the subsequent mechanical deformation of irradiated molybdenum.

Experimental Procedures

1. MATERIAL

Molybdenum used in the present investigation was in rod form. The specimens were approximately 0.4-in. in length with a nominal diameter of 1/8 in.

The chemical analysis of the material is listed in Table 4. This analysis represents the impurities present in the control specimens and the irradiated specimens prior to irradiation. Neutron irradiation produces transmutation products, which increase the pre-irradiation impurity levels. The impurities produced by transmutation reactions are discussed in an earlier section of this investigation and are presented in Table 2 (Page 11)

Table 4

CHEMICAL COMPOSITION OF MOLYBDENUM USED IN THE PRESENT INVESTIGATION

Element	Quantity (ppm) by Weight
C	37
O	15
N	10
H	4
Fe	60
Si	35
Ni	20

The specimens used in the present investigation were divided into four major categories: annealed, stress-relieved, annealed-irradiated, and stress-relieved irradiated. The annealed specimens (AM) were annealed for approximately 1 hr at 1350°C in vacuum prior to testing. The annealed-irradiated specimens (ARET) were annealed in the same manner as the AM specimens. After annealing they were inserted in the reactor environment and were irradiated to a fast neutron fluence of approximately 5×10^{19} n cm^{-2} ($E > 1$ MeV) at 480°C . The irradiation temperature was measured using thermocouples. The stress-relieved specimens (SRM) were reduced approximately 75% and then relieved for 1 hr at 900°C . The resulting microstructure was completely fibrous. The stress-relieved irradiated specimens (SRAT) were placed in the reactor environment following fabrication and were irradiated to a fast neutron fluence of approximately 1×10^{19} n cm^{-2} ($E > 1$ MeV) at reactor ambient temperature (approximately 70°C). Again, thermocouples were used to measure the irradiation temperature.

2. CREEP TEST PROCEDURES

The specimen used for the creep test is shown in Figures 4 and 5. A Satec Model D creep-rupture tester modified for high temperature and high vacuum applications was used in this study. This machine provides lever loading of either a 20:1 or 3:1 ratio for constant load tests. For this particular study, the load ratio of 3:1 was employed. The machine was calibrated before use by means of a load cell mounted in series with the load train

and the actual lever ratio was found to be 3:1.002 for an approximate deviation of -0.20%. Heating of the specimen was performed by a tungsten mesh resistance furnace operated in a vacuum atmosphere. The temperature was monitored by two contact thermocouples - one attached to the mid-region of the sample and one attached to the bottom of the sample. Chromel-Alumel thermocouples calibrated against a secondary standard were used for all tests. The load train was modified to incorporate the tungsten compression fixture shown in Figure 6. During standardization and control runs, the outer fixture tube developed cracks and finally fractured in a brittle manner. Since the availability of centerless ground tungsten tubing was very limited, T-222 was used as a substitute material. Problems developed during the Electron Discharge Machining (EDM) of the T-222 and the material had to be repeatedly cleaned or it would not machine. A passivation layer appeared to develop on the surface during machining. Thus, what seemed to be a routine machine process turned out to be rather involved. The tube was completed and used with the remaining tungsten portions of the fixture. The fixture permitted the use of a tensile creep tester for compression tests. The specimens were placed in the

FIGURE 4 - Illustration of the compressive creep specimens.

FIGURE 5 - High magnification photograph of the surface of a compressive creep specimen prior to test.

FIGURE 6 - Compressive creep test fixture.

load train, positioned in the furnace, and heated to test temperature in a vacuum atmosphere. The samples were maintained at test temperature for a minimum of 0.50 hr before loading. This was done to allow the system to equilibrate and the vacuum atmosphere to stabilize to about 10^{-6} Torr. The strain was measured by an optical extensometer sighted on a knife-edge located on the compression fixture.

The higher temperature tests were stopped after a change in slope was noted on the true strain vs time curve. This signified that the sample area had changed so significantly that the applied stress was effectively reduced. The tests conducted at the lower temperatures were stopped after 500 hr unless some unusual effect was observed.

At the conclusion of a test, the furnace power was shut off and the sample was cooled in vacuum under load prior to removal from the test fixture. The creep strains observed during the tests are believed accurate to ± 0.0005 in.

3. TRANSMISSION ELECTRON MICROSCOPY

Two types of samples were examined using the transmission electron microscope.

These represented the pre-test condition and creep-tested condition.

Transverse slices, to 0.008 ± 0.002 in. thick, were cut from the mid-point of the specimens using a Buehler Isomet thin sectioning machine. The specimens were electro-chemically thinned in a Fischione [141] electropolishing apparatus shown in Figure 7. The electrolyte used was 12.5% H_2SO_4 and 87.5% CH_3OH by volume. The polisher was operated at 50 volts and 90 mA. Thinning was performed with the electrolyte maintained at $-40^\circ C$. Thinning was stopped once perforation occurred. The foils were then washed with ethanol, dried with filter paper, and examined.

The foils were examined in both a JEOL 200A electron microscope operated at 200 keV and equipped with a 30° tilting stage with 360° azimuth rotation and a Norelco Philips 300 electron microscope operated at 100 keV and equipped with a goniometer stage capable of 60° tilt and 360° rotation. The quantitative electron microscopy techniques which were employed during the course of this study are described in Appendix B. Four or more foils were examined from each specimen.

FIGURE 7 - Electropolishing apparatus used to prepare thin electron microscopy samples.

4. SCANNING ELECTRON MICROSCOPY

When cracks were observed on the surfaces of some of the tested samples, it was a logical extension of the study to examine the surfaces using scanning electron microscopy. Pre- and post-test specimens were examined using an ETEC Scanning Electron Microscope operated at 20 kV.

The specimens were mounted on sample stubs by using conductive silver paint. The sidewall surfaces of the specimens were examined for the appearance of any unique features. Comparison of the sidewall features was also made with samples of molybdenum that were tensile-creep tested for another purpose.

5. OPTICAL MICROSCOPY

Samples corresponding to those examined in the electron microscope were also examined using optical microscopy. These specimens were taken from the same area as the electron microscopy specimens. They were polished on the vibratory polisher using 1 μ m diamond compound, and were etched using Murakami's Reagent (10g - $K_3Fe(CN)_6$, 10g - KOH, 100 ml - H_2O). The quantitative optical

microscopy techniques used during this study are also described in Appendix B.

6. MICROHARDNESS DETERMINATION

The samples prepared for optical microscopy were also used for microhardness determination. These determinations were made using a Vickers Hardness Tester and all values are reported in DPH.

Observations and Results

1. CREEP TESTS

While the specimens were tested at various temperatures, the limited number of available samples precluded variation in applied stress. Slight variations in sample cross-sectional area were taken into account for each test and load modifications were made so that each sample was exposed to the same initial applied stress.

The lubricant used on the ends of the test specimens minimized macroscopic frictional effects but did not completely eliminate them. This is shown in Figure 8, which is a drawing of typical shadow graph

FIGURE 8 - Shadowgraph appearance of the pre- and post-test compressive creep specimens.

results showing the initial sample profile and the as-tested profile. From the drawing, it is obvious that some "barreling" occurred, but since it was not extreme, its effects were ignored in the analysis of the test data.

The results of all tests are listed in Table 5. Typical creep test curves obtained at the 800° and 900°C test temperatures are shown in Figures 9 and 10. These curves differ from tensile creep curves, in that a limiting creep rate value is approached as the increasing cross-sectional area of the sample effectively reduces the applied stress. In tensile creep, the cross-sectional area of the sample is constantly reduced until a critical value is reached where the creep rate accelerates rapidly and the sample fractures at a severely necked-down region. This is not meant to imply that fracture does not occur in compressive creep tests for as will be shown in a later section, a fracture effect occurred in some of the compression samples - in the side wall region.

The creep curves obtained on the stress-relieved and stress-relieved irradiated samples at 700, 750, and 800°C differed from the typical creep curves and in particular from the compressive creep

FIGURE 9 - Test results of sample AM-2 at 800°C.

FIGURE 10 - Test results of sample SRAT-4 at 900°C.

Table 5

CREEP-TEST RESULTS FOR MOLYBDENUM TESTED IN VACUUM WITH AN
INITIAL APPLIED STRESS OF 176.5 MPa [(18 kg mm⁻²), (25,602 psi)]

Specimen No.	Test Temp. °C	Strain on Loading (%)	Final Strain (%)	Linear Creep Rate (in.-Min ⁻¹)
ARET-1	600	0.05	5.86	1.839×10^{-6}
ARET-2	700	0.30	25.50	3.794×10^{-5}
ARET-3	800	1.32	50.00	2.617×10^{-4}
AM-1	750	1.92	36.50	1.770×10^{-4}
AM-2	800	4.41	53.25	1.410×10^{-3}
AM-3	900	9.84	74.25	7.898×10^{-3}
SRAT-1	700	0.02	2.46	2.002×10^{-6}
SRAT-2	750	1.77	21.50	2.351×10^{-5}
SRAT-3	800	4.54	48.60	6.486×10^{-4}
SRAT-4	900	19.70	70.00	2.791×10^{-3}
SRM-1	750	0.54	17.25	1.164×10^{-4}
SRM-2	800	16.04	54.50	1.752×10^{-3}
SRM-3	900	21.29	89.00	5.809×10^{-2}

ARET: Annealed, Irradiated at 480°C, 5×10^{19} n cm⁻²

AM: Annealed

SRAT: Stress-Relieved, Irradiated at Reactor Ambient, 1×10^{19} n cm⁻²

SRM: Stress Relieved

curves obtained on the annealed material. The difference is clear in Figure 11 which shows a dimensionless curve comparing typical creep-test results on stress-relieved and annealed molybdenum. This curve has been exaggerated somewhat to show the effect that occurred early in the test. This effect can best be described as incubation or delayed creep phenomena during which the creep rate of the stress-relieved material is significantly reduced; then a normal creep curve is obtained with the creep rate and final strain being less than that obtained for the annealed material. This effect was also observed for the stress-relieved irradiated material. A possible cause, which will be elaborated on later, might be a microstructural change due to recovery and recrystallization.

Figures 12 through 15 show point-to-point plots of the linear creep rate vs reciprocal absolute test temperature for all the samples. Figure 16 shows a plot of the loading strain vs test temperature for all the samples. Several observations can be made when the test data are compared.

Working and stress-relieving the material seem to produce the greatest effect on the compressive creep behavior of

FIGURE 11 - Typical creep curves.

FIGURE 12 - Linear creep rate vs reciprocal test temperatures for ARET specimens.

FIGURE 13 - Linear creep rate vs reciprocal test temperatures for AM specimens.

FIGURE 14 - Linear creep rate vs reciprocal test temperatures for SRAT specimens.

FIGURE 15 - Linear creep rate vs reciprocal test temperatures for SRM specimens.

FIGURE 16 - Loading strain vs test temperature.

molybdenum in the temperature range and at the particular stress level examined in this study. Neutron irradiation does have an effect on the mechanical behavior of both the annealed and stress-relieved molybdenum. In the case of the annealed molybdenum, the neutron irradiation resulted in a lower initial strain and lower linear creep rate over the entire temperature region. For the stress-relieved molybdenum, however, a cross-over point is observed at approximately 760°C. At lower temperatures, the neutron-irradiated samples had a greater strain on loading; above 760°C, a reversal occurred and the samples that were only stress relieved had a greater initial strain. The linear creep rate of the stress-relieved material is greater than that of the stress-relieved irradiated material at all test temperatures.

Figure 17 shows a plot of the final strain as a function of test temperature for the annealed and annealed-irradiated specimens. Below approximately 750°C, the final strain for the annealed-irradiated samples is greater than that for the annealed specimens. Above 750°C, the annealed samples exhibit the greater final strain.

FIGURE 17 - Final strain as a function of test temperatures for annealed samples.

Figure 18 shows a plot of the final strain as a function of test temperature for the stress-relieved and stress-relieved irradiated specimens. Again, a cross-over is observed at approximately 750°C. Below that temperature, the stress-relieved irradiated material exhibits a greater final strain. Above that temperature, the stress-relieved material exhibits the greater final strain.

Figure 19 is a composite plot of the data presented in Figures 17 and 18. The plot indicates that the annealed and annealed-irradiated materials initially exhibit the greater final strains but eventually the stress-relieved and stress-relieved irradiated materials cross over with the stress-relieved materials exhibiting a significantly larger final strain than the other samples at comparative temperatures.

These brief observations of the actual test data show that the strongest factors affecting the compressive creep behavior of molybdenum at the test temperatures and stress level of the present study were the working and subsequent stress-relieving of the material prior to testing.

FIGURE 18 - Final strain as a function of test temperatures for stress-relieved samples.

2. METALLOGRAPHIC EXAMINATION

As pointed out previously, different analytical techniques were employed to collect the microstructural data from the creep tested specimens. Optical microscopy was used to examine the specimens, and the micrographs which are presented in Figures 20 through 27 provide a fairly representative study of the microstructure. All samples of the tested specimens which were examined were taken from the middle of the specimens.

Figure 20 shows a comparison of the starting microstructures of all the samples. The most obvious difference that was observed was that the stress-relieved-irradiated material etched more extensively than the stress-relieved material; otherwise no significant differences were observed when the irradiated material was compared to its unirradiated counterpart. The fact that the stress-relieved material is completely fibrous is illustrated effectively in Figure 21, which shows a cross-section taken parallel to the length direction of a control specimen of the stress-relieved irradiated material.

FIGURE 19 - Final strain as a function of test temperatures for all samples.

FIGURE 20 - Pre-test microstructure.

FIGURE 21 - Pre-test microstructure of the stress-relieved irradiated material (cross section taken parallel to the length direction).

FIGURE 22 - Post-test microstructure of the annealed material.

FIGURE 23 - Post-test microstructure of the annealed-irradiated material.

Figure 22 shows cross sections of as-tested annealed material. No significant differences were observed in these samples. Figure 23 shows cross sections of as-tested annealed-irradiated material. There were no significant differences between these samples, but when they are compared to the annealed samples, two visible differences are apparent. The grain boundaries of the annealed-irradiated material etched more rapidly and some of the grains in the annealed-irradiated samples show a texturing effect.

The as-tested material cross sections of the stress relieved-irradiated material are shown in Figure 24. The specimen tested at 700°C, while it retains a great deal of fibrous structure, shows some refinement of the microstructure and what appears to be the nucleation of primary grains. This would indicate the onset of recrystallization. The specimen tested at 750°C shows a rather complicated microstructure. The center of the sample exhibited complete recrystallization and some grain growth, while the edge exhibited a worked structure with some hint of recovery and recrystallization being initiated. Between the two areas, there seems to be a band of primary

grains. The sample from the 800°C specimen shows complete recovery and recrystallization with just a narrow edge of small primary grains. The sample of the 900°C specimen shows complete recrystallization with a higher density of larger grains. Some of the larger grains seem to be engulfing smaller grains.

The as-tested microstructures of the stress-relieved material are shown in Figure 25. Again, the sample tested at 750°C shows a complicated microstructure. This is very similar to that reported for the stress-relieved irradiated microstructure. The sample tested at 800°C appears similar to that of the stress-relieved irradiated material except it possesses a much wider band of primary grains at the edge as shown in Figure 26. This would suggest that recrystallization kinetics of the stress-relieved material lag behind those of the stress-relieved irradiated material. Because of the amount of final strain on the 900°C specimen, it was not possible to obtain a representative microstructure of that sample.

The complicated microstructure obtained in both the stress-relieved and stress-relieved irradiated specimens at 750°C

FIGURE 24 - Post-test microstructure of the stress-relieved irradiated material.

FIGURE 25 - Post-test microstructure of the stress-relieved material.

FIGURE 26 - Edge effect observed in the stress-relieved specimen tested at 800°C.

is shown at a lower magnification in Figure 27. The microstructure can be divided into three concentric rings, which are uniform around the samples. The cause of this feature can only be speculated on in this study, since the lack of additional samples prevented a detailed investigation.

It appears that the strain distribution in the sample might not be uniform throughout the sample. The sidewalls, since they are not restrained and barrel slightly, are at a lower strain state than the center of the sample. Recovery and recrystallization would follow the strain pattern with the area of highest strain being the first to recrystallize. In this case, the area of greatest strain is the center of the specimen. The resulting strain distribution, consequently, resulted in a difference in recrystallization kinetics, thus producing a banded structure.

Another possible explanation for this effect that could be postulated would be reaction of the surface with gaseous impurities, which would inhibit recovery and recrystallization. This has been discounted, however, since the test atmosphere was periodically monitored during all tests using a quadrupole mass

FIGURE 27 - Non-uniform microstructure of specimens tested at 750°C.

spectrometer. The results of this monitoring showed that the atmosphere was essentially the same during all test runs. If the atmosphere was reactive, the annealed samples tested at the same test temperature and all the samples tested at higher temperatures would show reaction zones. This condition, however, was not observed.

The fact that localized strain fields have an important effect on the recovery and recrystallization behavior of a metal during creep can best be illustrated by Figure 28. This figure shows a series of cross sections taken from a molybdenum tensile creep specimen tested at 1000°C with an applied stress of 103.42 MPa. Cross section A represents the area just behind the fracture zone. In this area, the resulting test strain is very high and recrystallization and grain growth have occurred. Cross section B represents the mid-point of the tapered down cross section of the sample. In this area, recrystallization and grain growth were again evident with the greatest amount of grain growth occurring in the zone illustrated by the arrows. Cross section C represents a sample taken from the interface of the tapered/untapered region. Recrystallization and

grain growth is again apparent in this sample. The arrows indicate the same orientation as was shown in cross section B and again they also point out the zone where the greatest amount of grain growth occurred.

This figure seems to point out that in tensile creep tests of rod specimens, the strain fields are not uniform and oriented fields of higher strain develop and result in a non-uniform microstructure. The effect of variable strain fields should also be present in compressive creep tests; however, in contrast to tensile creep, the strain fields in compression seem to be ordered in the form of concentric cylinders as has been evidenced by the data presented above.

3. TRANSMISSION ELECTRON MICROSCOPY

Transmission Electron Microscopy was employed to examine a majority of the specimens. Post-test geometry prevented the examination of some of the higher strain specimens.

The typical substructure of the annealed material is shown in Figure 29. The structure consists of grain boundaries

FIGURE 28 - Post-test microstructure of a tensile creep specimen tested at 1000°C.

FIGURE 29 - Pre-test specimen of annealed material.

with some isolated, free dislocations located in the matrix. The structure of the annealed-irradiated specimens consists of grain boundaries, some isolated dislocation lines and the features shown in Figures 30 and 31. In Figure 30, the presence of black spot clusters, small loops and planar dark regions, which are agglomerations of individual black spots, is readily apparent. Brimhall and Mastel [27] referred to these regions as rafts of loops. Figure 31 shows a grain boundary denuded zone which develops in molybdenum irradiated at elevated temperature. The grain boundary acts as a sink for the interstitial defects of the rafts. The width of the zone is used as a measure of the mobility of the defects. The average width of the zone shown in Figure 31 is 3704 Å. Brimhall and Mastel [27] worked with material very similar to that used in the present study and plotted the width of the denuded zone versus the reciprocal irradiation temperature to measure the activation energy for interstitial migration. The data obtained in the current study fits very accurately on that plot and agrees well with the data of Sikka [28] who performed a similar study.

The appearance of the stress-relieved material is shown in Figure 32. This sample exhibits a substructure consisting of well-developed subgrains with some isolated dislocation structure present within some of the subgrains. This structure should be typical of stress-relieved material. The stress-relieved irradiated material exhibited a similar substructure at low magnifications as is shown in Figure 33. The subgrain boundaries in the stress-relieved irradiated material appeared coarsened when compared to the stress-relieved samples. Subgrain size determinations were made for both control specimens. The average subgrain size for both was essentially the same, approximately 0.776 μm.

As the stress-relieved irradiated material was examined at higher magnifications, it was expected that a high density of black spot clusters and loops would be apparent since these were the features found in annealed material irradiated at the same temperature to similar fluences. Eyre, et al [142] reported a high density of black spots and dislocation loops; they identified the black spots as being a predominant distribution of interstitial

FIGURE 30 - Substructure observed in the pre-test specimen of annealed-irradiated material.

FIGURE 31 - Grain boundary denuded zone observed in the pre-test specimen of annealed-irradiated material.

FIGURE 32 - Well developed substructure observed in the pre-test stress-relieved material.

FIGURE 33 - Substructure observed in the pre-test stress-relieved irradiated material.

type loops. Sikka [28] reported a high density of black spot clusters and isolated loops as being the basic constituents of the as-irradiated microstructures. Figure 34 shows a comparison study of the substructure observed by Sikka [28] and the substructure observed in the current study. The difference is rather dramatic. In the annealed material, which had essentially the same carbon content as the present samples and had no dislocation substructure, a high density of radiation damage is observed. Defect clusters marked by the letter 'a' and loops marked by the letter 'b' are readily resolvable. In the stress-relieved material, the radiation damage is not readily resolvable.

Earlier, the work performed by Brimhall and Mastel [140] concerning the effect of pre-strain and subsequent neutron irradiation on molybdenum was reviewed. They pre-strained foils ($\sim 75 \mu\text{m}$ thick) approximately 2%, 5%, 20%, and 50% prior to irradiating them to a fluence of 7×10^{18} nvt ($E > 1$ MeV) at 40°C . The pre-irradiation examination of the strained foils showed only the presence of dislocations. Post-irradiation examination showed that the dislocations per se did not play a significant role

in the alteration of microstructure. This is the only prior work reported on deformed molybdenum and suggests that what has been observed in the present study is unique to stress-relieved material.

To explain this apparent anomaly, a comparison of the material used in the present study with that used by Sikka [28] was made. The only significant difference was the grain size. The material studied by Sikka was annealed and had an average grain size of $29 \mu\text{m}$ in the as-irradiated condition, while the material used in the present study had a well-defined subgrain structure with an average subgrain size of $0.776 \mu\text{m}$. Since this difference is quite large, it is quite possible that the mobile point defects (i.e., interstitials with low migration energy) migrated to the subgrain boundaries, which should be sinks for interstitials, during the time that the material was in the reactor.

The distance (X) that an interstitial would have to travel to reach a boundary in a bulk sample can be approximated as:

FIGURE 34 - Molybdenum Irradiated at Reactor Ambient.

$$X = \sqrt{6Dt} \quad (16) \quad \text{where:}$$

where X = half the grain size

D = diffusivity of interstitials,
and

t = time, sec.

The time that the present samples were in the reactor was approximately 430 hr at a sample temperature of 70°C. Equation 16 can be modified into the form:

$$X^2 = 6Dt \quad (17)$$

and D can be expressed as:

$$D = D_0 \exp^{-\frac{E_i^m}{RT}}, \quad (18)$$

D_0 = the diffusion constant assumed to be 0.1,

E_i^m = the interstitial migration energy assumed to be 1 eV, 96.3 (kJ) (g-mole)⁻¹ or 23 Kcal-mole⁻¹,

T = the temperature in °K (343 K).

The above expression for D can be used to modify Equation 17 into

$$X^2 = 6t\{D_0 \exp^{-\frac{E_i^m}{RT}}\}, \quad (19)$$

and when the appropriate values are substituted into this equation, the value of X is determined to be 0.505 μm.

Since the calculated value of X is greater than $0.388 \mu\text{m}$ which represents half the subgrain size in the material being examined in the present study, it is obvious that a large number of point defects have migrated to the subgrain boundaries. In fact, all the point defects generated in the first 176 hr of irradiation should have migrated to the subgrain boundaries, and it is safe to assume that a great deal of other interstitials could have migrated to the boundaries during the time in the reactor.

The above explanation was based solely upon the migration of the interstitials to the subgrain boundaries as a result of the thermal environment of the reactor. It is also possible that the phenomenon that was observed was enhanced by the reactor environment. The migration of the interstitials could have been enhanced during the continuous process of irradiation.

It is well established [143] that a metal which is mechanically tested during irradiation can show a greatly increased deformation and creep rate compared with either unirradiated or post-irradiated properties. This phenomenon is radiation-enhanced creep and it is significant under conditions of high fast neutron flux ($\sim 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$), low temperatures ($\lesssim 0.5 T_m$) and low stresses ($< \text{post-irradiation yield stress}$). In fact, Ashby [144] has developed a model which shows that the creep rate may be almost independent of temperature and depends solely on the generation of point defects during the irradiation.

Chang [145] has shown that temperature spikes which are the states of local temperature distributions from the heat generated in the neighborhood of primary knock-ons can cause irreversible changes even in metals irradiated at low temperatures.

Sikka and Moteff [146] in their work on the characterization of neutron-irradiation damage in molybdenum suggest that the damage state present in the reactor is different from that observed during post-irradiation examination. They point out that rafts were observed in molybdenum irradiated to a fast neutron fluence of approximately $1 \times 10^{22} \text{ n cm}^{-2}$ at 430°C , but they were not observed at an irradiation temperature of 580°C . The samples irradiated at 430°C were given post-irradiation anneals at various temperatures. There were no observable changes in the rafts

at an anneal temperature of 550°C , but they were completely annealed at 700°C . They also observed changes in loop density and size as a function of irradiation temperature. These changes occurred at irradiation temperatures in the range of 580 to 700°C . Similar changes in loop parameters were observed by Downey and Eyre [23] and Mastel and Brimhall [22] in molybdenum specimens irradiated at low temperatures and followed by thermal anneals where the threshold temperature occurred between 700 and 800°C .

Both of the above observations concerning the rafts and loops suggest a radiation-enhanced recovery process equivalent to a 100°C shift in temperature as a result of in-reactor defect migration kinetics.

The observed phenomena which are summarized above seem to point out that the in-reactor environment enhances many processes and suggest that an effective shift in process temperature occurs in the reactor environment. If the 100°C shift in temperature suggested by Sikka and Moteff [146] is incorporated into the present analysis, it would mean that all the point defects generated in the 430 hr irradiation migrated to the subgrain boundaries. This phenomenon would result in a vacancy-rich substructure, and this would account for the microstructural differences observed in the present samples.

Examination of the substructure of the as-tested specimens showed that the primary difference between the unirradiated and irradiated specimens in both the annealed and stress-relieved condition was the presence of loops in the irradiated specimens. This was somewhat expected in the case of the annealed material. Since the test temperatures were higher than the irradiation temperature, the radiation damage was expected to transform into loops. This transformation was well illustrated by Brimhall and Mastel [27] and effectively confirmed by the samples examined in the present study. Since it has been shown that for the stress-relieved irradiated material, the remaining predominant damage components were vacancies, no appearance of defect clusters was expected or observed in the tested samples.

Some of the features observed in the tested specimens are shown in the following series of micrographs. Figure 35 shows the appearance of cross-slip observed in the annealed-irradiated specimen tested at 600°C . Jogged dislocations, dislocation tangles, and small loops were also observed

in this specimen. The slip lines observed in this specimen are rather distinct and this observation is in line with an earlier one made by Brimhall [147]. He previously reported that slip lines in irradiated and deformed molybdenum are coarser and more distinct than in unirradiated material.

The post-test appearance of the annealed-irradiated specimen tested at 700°C is shown in Figure 36. The concentration of loops has increased significantly in this specimen. Dislocation tangles, jogged dislocations, and elongated dislocation loops were also observed in this specimen. The elongated dislocation loops were probably produced by the pinching off of jogs on screw dislocations. Figure 37 shows the appearance of the annealed-irradiated specimen tested at 800°C. Loops and jogged dislocations were observed in this specimen. Additional features which were observed in this specimen were subgrain boundaries, dislocation networks, and helical dislocations.

The appearance of the stress-relieved irradiated specimen at 700°C is shown in Figure 38. The subgrain matrices appear rather devoid of dislocation structure. Loops are readily apparent. The intersection of tilt boundaries and grains devoid of any substructure are also

FIGURE 35 - Cross-slip observed in the annealed-irradiated specimen tested at 600°C.

FIGURE 36 - Post-test specimen of the annealed-irradiated material test at 700°C.

FIGURE 37 - Substructure of the post-test specimen of the annealed-irradiated material tested at 800°C.

FIGURE 38 - Substructure found in the post-test stress-relieved irradiated specimen tested at 700°C.

present. Figures 39 and 40 show the appearance of the stress-relieved irradiated specimen tested at 800°C. In Figure 39, the presence of loops is readily apparent. Figure 40 shows the pile-up of dislocations at a grain boundary. The appearance of the stress-relieved irradiated specimen tested at 900°C is shown in Figure 41. Some dislocation tangles and the start of dislocation networks are observed.

4. SCANNING ELECTRON MICROSCOPY

The surfaces of various samples were examined using the scanning electron microscope. The purpose of this examination was to determine the effects of the mechanical test on the sidewall of the test pieces.

Figures 42 and 43 show the sidewall of the annealed sample, tested at 750°C, prior to test. Figures 44 and 45 show the sidewall of the same sample after testing. It appears that the surface grains after test are pushed away from the matrix but otherwise appear undistorted. This is in contrast to the effects of a tensile creep test. A sample tested in tension at approximately the same temperature and initial stress is shown in Figures 46 and 47. The

grains in the tensile specimen remain close to the matrix and are elongated in the tension direction.

These contrasting effects can be explained somewhat by an examination of Figure 48. In this figure of a compressive creep specimen, the surface tension and the internal tension lines for the unrestrained sidewall are shown. At the test temperature of 750°C, the surface tension effects are apparently at a minimum and the surface grains are bulged out away from the sample and do not get distorted. In the tensile creep specimen, the surface grains are under a compressive force field and the grains are bonded to the matrix so well that they distort (elongate) in a manner similar to all other grains in the affected region of the test specimen.

At higher temperatures, the surface tension is sufficient to confine the surface grains to the matrix and they elongate in tension as shown in Figure 49. This is the stress-relieved specimen tested at 900°C. The elongation of the sidewall grains as well as the tensile failure of the sidewall are readily apparent. Figures 50 and 51 show the appearance of the material inside one of the cracks. The failure is obviously intergranular in nature and some rounding of the grains due to thermal effects seems to have occurred. The stress-

FIGURE 39 - Substructure observed in the stress-relieved irradiated specimen tested at 800°C.

FIGURE 40 - Dislocation pile-up observed in the stress-relieved irradiated specimen tested at 800°C.

FIGURE 41 - Substructure found in the post-test specimen of the stress-relieved irradiated material tested at 900°C.

FIGURE 42 - Pre-test appearance of the annealed specimen tested at 750°C.

FIGURE 43 - Pre-test appearance of the annealed material tested at 750°C and shown at high magnification.

FIGURE 44 - Post-test appearance of the annealed specimen tested at 750°C.

FIGURE 45 - Post-test appearance of the annealed specimen tested at 750°C and shown at high magnification.

FIGURE 46 - Post-test appearance of tensile creep specimen tested at 750°C.

FIGURE 47 - Sidewall of a tensile creep specimen tested at 750°C.

FIGURE 49 - Post-test appearance of the stress-relieved specimen tested at 900°C.

FIGURE 48 - Deformation of a cylinder under uniform axial compression. (Surface tension is shown by the solid lines, internal tension by the dotted lines.)

FIGURE 50 - Interior surface of a crack observed in the stress-relieved specimen tested at 900°C.

FIGURE 51 - Appearance of the grains observed in a crack located in the stress-relieved specimen tested at 900°C.

relieved irradiated specimen tested at 900°C suffered the same fate, and it appeared similar in nature to the stress-relieved sample.

5. MICROHARDNESS MEASUREMENT

Microhardness measurements were routinely taken for each specimen. The samples used for microhardness determination were the same samples used for optical microscopy. Five indents were made on each sample and a numerical average taken. The most meaningful data obtained from this study are the microhardness values determined for the control samples since a common basis of comparison exists. It was originally planned to compare the microhardness of the tested specimens with that of specimens subjected only to thermal anneals at the test temperatures to determine the effects of the thermal anneal versus the applied stress. This comparison was not possible since additional samples were not available for the thermal anneal study. Therefore, the data presented here will primarily be that for the control specimens.

Microhardness change will be defined as:

$$\Delta H = H_2 - H_1 \quad (20)$$

where H_1 represents the hardness of the annealed control specimen for that specific series of samples and H_2 represents the conditioned sample, whether it be stress relieved or irradiated or both. Modern convention expresses hardness values in dimensionless units, however, the correct expression of kg mm^{-2} will be used here.

Figure 52 shows a comparison of the microhardness values for the annealed and annealed-irradiated control specimens. The ΔH value determined from the figure is 14 kg mm^{-2} . The increase in hardness for the irradiated material is the result of the irradiation damage acting as barriers to dislocation movement. This causes an increase in the frictional stress which impedes the plastic flow of the metal.

Sikka [28] has shown in his post-irradiation anneal study that hardness changes in irradiated samples can be related to loop size and density changes. He associates hardness changes with loop

FIGURE 52 - Microhardness values determined for the annealed and annealed-irradiated control specimens.

separation in the following equation:

$$\Delta H = \alpha \mu b / \ell \quad (21)$$

where α is the hardening coefficient (a dimensionless constant determined to be 5.1), μ is the shear stress modulus ($12.2 \times 10^3 \text{ kg mm}^{-2}$), b is the dislocation Burgers Vector (2.725 Å), and ℓ is the average separation between the loops expressed in centimeters.

If the value of ΔH , 14 kg mm^{-2} , is substituted into Equation 21, the average separation between the loops is determined to be $1.21 \times 10^{-4} \text{ cm}$. Using this value and the estimated loop density determined for the annealed-irradiated sample, the size of the loops can be determined. The separation between loops is related to the loop size in the following manner.

$$1/\ell = (Nd)^{1/2} \quad (22)$$

In Equation 22, N represents the dislocation loop density which for the sample under discussion was estimated to be $1.1 \times 10^{14} \text{ cm}^{-2}$, and d represents the average loop size. Solving Equation 22 for d , a value of 61.98 Å is obtained. This value compares favorably with data reported by Sikka [28] for samples irradiated at the same temperature but to a slightly higher fluence ($6 \times 10^{19} \text{ n cm}^{-2}$) than that used for the present samples — $5 \times 10^{19} \text{ n cm}^{-2}$. He reported a dislocation loop density of $2.1 \times 10^{15} \text{ cm}^{-2}$ and an average loop size of 92 Å.

The microhardness values of the stress-relieved and stress-relieved irradiated control specimens are shown in Figure 53. Also shown in Figure 53 are the microhardness values of an annealed and an annealed-irradiated control specimen. The annealed-irradiated specimen was irradiated at reactor ambient to approximately the same fluence as the stress-relieved material and provides a good comparison point. The data presented in Figure 53 give a good idea of the sink power of the stress-relieved material which, when irradiated, yields a lower hardness value than the annealed-irradiated material. This results because the density of point defects is less since a large number of the point defects have migrated to the subgrain boundaries which acted as sinks. On the other hand, the increase in hardness of the stress-relieved material

FIGURE 53 - Comparison of the microhardness values determined for the stress relieved and stress relieved-irradiated control specimens with annealed and annealed-irradiated specimens representing the same material.

when compared to the annealed material is the result of the substructure hindering by elastic interaction the development of loops from active sources.

If it is assumed that the subgrain size is similar to the separation between loops, Equation 21 can be used to express the hardness change as a function of subgrain size. Since the value of ΔH is known to be 88 kg mm^{-2} , and the subgrain size was determined to be $7.76 \times 10^{-5} \text{ cm}$, these values can be substituted into Equation 21 and a hardening coefficient determined. The value of α would be 20.5 for this case. This value is in contrast to the value of 5.1 determined by Sikka [28] for loop hardening and the value of 6 used in the barrier hardening expressions.

Since it was not possible to perform thermal anneal studies on the material presently under investigation, a comparison with some of the data in the literature was made. Moteff and Kamphouse [148] performed a hardness study on low carbon molybdenum that was irradiated at reactor ambient temperature to a fluence of $2.6 \times 10^{19} \text{ n cm}^{-2}$. A plot of their results is shown in Figure 54. These data are the results of 1-hr anneals at the temperatures indicated and show a gradual increase in hardness change up to

FIGURE 54 - Microhardness recovery as a function of annealing temperatures for molybdenum neutron irradiated at reactor ambient to a fluence of $2.6 \times 10^{19} \text{ n cm}^{-2}$.

about 400°C, then a gradual decrease to approximately 700°C. A drastic decrease in hardness change occurs between 700 and 1200°C. This would imply that very little change occurs in the radiation damage structure between ambient and 700°C but above 700°C, the defect cluster density decreases and their size increases. This process has a very significant effect on the hardness change.

Superimposed on Figure 54 are the results of the hardness change measurements performed on the stress relieved and stress relieved-irradiated creep test specimens used in the current study. While these results cannot be accurately compared with the data of Moteff and Kamphouse [148], they suggest similar results. An increase in hardness occurs between ambient and some higher, undetermined temperature and a significant decrease in hardening is observed in the temperature range of the study (750 - 900°C).

Discussion of Results

Many empirical relations have been developed to define creep in terms of stress level and test temperature. Many hypotheses [121] have been proposed and expounded upon to interpret the empirical parameters in terms of the physical changes that take place in the material. There exist, however, no physical laws of creep at the present time.

Starting from first principles then, it is known that creep strain is a function of several variables and can be expressed as:

$$\epsilon = f(St, \sigma, T, t), \quad (23)$$

where St represents material structure, σ is stress, T is the test temperature, and t is the time of the test. In more common terms:

$$\epsilon = \frac{\sigma}{E} + \epsilon_p + \epsilon_{tr} + \dot{\epsilon}_{ss}t, \quad (24)$$

where σ/E is the elastic strain; ϵ_p is the plastic strain that is observed immediately after the application of the stress; ϵ_{tr} is the transient strain; $\dot{\epsilon}_{ss}$ is the strain rate during steady state or secondary creep.

The current series of tests were designed to study the steady state creep rate, $\dot{\epsilon}_{ss}$ and the discussion of the data will be confined to secondary creep.

The dependence of the steady state creep rate, $\dot{\epsilon}_{ss}$, on St , σ , and T has been well established and the steady state creep rate is usually expressed as:

$$\dot{\epsilon}_{ss} = f(St, \sigma, T) e^{-Q/RT} \quad (25)$$

where Q is the activation energy of creep. The structure factor takes into account such effects as grain size, number and identification of dislocations, and the other microstructure variables. Although it has not been confirmed experimentally, it is common practice to assume the structure factor to be constant for

specific series of test samples with essentially the same thermomechanical history. This assumption leads to a modified version of Equation 25:

$$\dot{\epsilon}_{ss} = A_{St} f(\sigma) e^{-Q/RT}. \quad (26)$$

To correlate steady state creep behavior, it is obvious that the structure terms, the pre-exponential term, and Q must be identified.

For a constant temperature, one of the most common methods of expressing creep rate is the power stress law, where:

$$\dot{\epsilon}_{ss} = A_{St} (\sigma)^n e^{-Q/RT}. \quad (27)$$

In Equation 27, σ is the applied stress and n is the stress dependency constant. Current studies [149,150] show that the creep rate is related not to the applied stress but to an effective stress, σ^* . This effective stress is expressed as:

$$\sigma^* = (\sigma_a - \sigma_i) \quad (28)$$

where σ_i is the internal stress that develops due to the thermomechanical history. The internal stress is affected by the subgrain diameter, dislocation density and applied stress. The value of σ^* can be determined experimentally. This method involves prestraining a series of test samples and then determining the value of the applied stress necessary to maintain a given strain rate. The value of the applied stress necessary to maintain the given strain rate after prestraining is plotted against the prestraining stress. Extrapolating the value of the prestrain stress to zero, where σ_i also equals zero, $\sigma_a = \sigma^*$ and a unique value of σ^* is obtained. When the effective stress is determined the steady state creep rate can be determined by:

$$\dot{\epsilon}_{ss} = A_{St} (\sigma^*)^n e^{-Q/RT}. \quad (29)$$

Creep is normally divided into two areas; high temperature creep and low temperature creep. The transition from one stage to the other occurs at approximately one-half the melt temperature ($0.5 T_M$). High temperature creep is thought to be controlled by diffusion; low temperature creep, however, appears to be controlled

by non-diffusion mechanisms which cannot be accurately specified. The activation energy Q for creep progressively increases up to approximately $0.5 T_M$. Above that point, it essentially remains constant as the temperature is increased.

Typically, creep data have appreciable scatter. This scatter is due in fact to the many unpredictable factors which are difficult to analyze and yet significantly affect the results. These factors would include variations in chemical composition, prior working history, different heat treatments, and radiation damage. When the amount of data is limited, as in the case of the present study, it becomes extremely difficult to accurately specify these effects on creep properties. However, if differences in chemical composition, internal structure, and thermomechanical history of a group of test specimens are assumed to be random and representative of that particular material, the creep data are amenable to statistical analysis.

In this particular study, an exponential curve fit program was used to treat the steady state creep data. The program computed the least squares fit of n pairs of data points for an exponential function of the form:

$$\dot{\epsilon} = A e^{-(Q/RT)} \quad (30)$$

where: $\dot{\epsilon}$ = the linear creep rate,

$$A = A_{St} \cdot f(\sigma)$$

$$R = \text{Gas Constant}$$

$$T = \text{Test Temperature in } ^\circ K, \text{ and}$$

$$Q = \text{The activation energy of creep.}$$

The results of this program are listed in Table 6. Figure 55 shows the data plots of $\dot{\epsilon}$ versus $1/T$ for all the sample sets based upon the least squares fit of the exponential equation.

Some general observations regarding the data presented in Table 6 can be made. The pre-exponential constants and the activation energies determined for the annealed and annealed-irradiated material are very similar. This fact strengthens the observation, made from the actual test data, that the influence of the elevated temperature irradiation on the creep behavior of the molybdenum specimens

Table 6

EXPONENTIAL CURVE FIT OF COMPRESSION CREEP TEST
DATA TO THE EQUATION $\dot{\epsilon} = Ae^{-(Q/RT)}$

1. Data Set: ARET (Annealed, Irradiated at 480°C, 5×10^{19} n cm⁻²)

Specimen No.	$1/T$ Reciprocal Test Temperature (°K ⁻¹)	$1/RT$	$\dot{\epsilon}$ Linear Creep Rate, in.-min ⁻¹
ARET-1	1.1455×10^{-3}	5.7853×10^{-4}	1.839×10^{-6}
ARET-2	1.0277×10^{-3}	5.1906×10^{-4}	3.794×10^{-5}
ARET-3	9.3200×10^{-4}	4.7070×10^{-4}	2.617×10^{-4}

Determined Values:

A: 7.96227×10^5 (psi-min⁻¹) - 5.4898×10^9 (Pa-min⁻¹)
 Q: 4.6162×10^4 (cal/g-mole) - 1.9327×10^2 (kJ/g-mole)
 r^2 Correlation: 0.9954

2. Data Set: AM (Annealed)

Specimen No.	$1/T$ Reciprocal Test Temperature (°K ⁻¹)	$1/RT$	$\dot{\epsilon}$ Linear Creep Rate, in.-min ⁻¹
AM-1	9.7752×10^{-4}	5.1906×10^{-4}	1.770×10^{-4}
AM-2	9.3200×10^{-4}	4.7070×10^{-4}	1.410×10^{-4}
AM-3	8.5251×10^{-4}	4.3056×10^{-4}	7.898×10^{-3}

Determined Values:

A: 8.36757×10^5 (psi-min⁻¹) - 5.7692×10^9 (Pa-min⁻¹)
 Q: 4.2914×10^4 (cal/g-mole) - 1.7968×10^2 (kJ/g-mole)
 r^2 : 0.9999

3. Data Set: SRAT (Stress Relieved, Irradiated at Reactor Ambient, 1×10^{19} n cm⁻²)

Specimen No.	$1/T$ Reciprocal Test Temperature (°K ⁻¹)	$1/RT$	$\dot{\epsilon}$ Linear Creep Rate, in.-min ⁻¹
SRAT-1	1.0277×10^{-3}	5.1906×10^{-4}	2.002×10^{-6}
SRAT-2	9.7752×10^{-4}	4.9369×10^{-4}	2.351×10^{-5}
SRAT-3	9.3200×10^{-4}	4.7070×10^{-4}	6.486×10^{-4}
SRAT-4	8.5251×10^{-4}	4.3056×10^{-4}	2.791×10^{-3}

Determined Values:

A: 2.4701×10^{13} (psi-min⁻¹) - 1.7031×10^{17} (Pa-min⁻¹)
 Q: 8.3778×10^4 (cal/g-mole) - 3.5076×10^2 (kJ/g-mole)
 r^2 : 0.9299

FIGURE 55 - Steady state creep rate data obtained from the computer analysis of the test data plotted as a function of reciprocal temperature.

Table 6 (Continued)

4. Data Set: SRM (Stress Relieved)

Specimen No.	1/T Reciprocal Test Temperature (°K ⁻¹)	1/RT	Linear Creep Rate, in.-min ⁻¹
SRM-1	9.7752×10^{-4}	4.9369×10^{-4}	1.164×10^{-4}
SRM-2	9.3200×10^{-4}	4.7070×10^{-4}	1.752×10^{-3}
SRM-3	8.5251×10^{-4}	4.3056×10^{-4}	5.809×10^{-2}

Determined Values:

A: 9.4879×10^{16} (psi-min⁻¹) - 6.5417×10^{20} (Pa-min⁻¹)
 Q: 9.7154×10^4 (cal/g-mole) - 4.0676×10^2 (kJ/g-mole)
 r^2 : 0.9932

is very minimal. The data obtained on the stress-relieved and stress-relieved irradiated samples are very much different from that obtained on the annealed specimens. The data obtained on the stress-relieved material showed the greatest deviation, while the data obtained on the stress-relieved irradiated material imply a recovery effect due to the ambient temperature irradiation. This recovery effect results in a lowering of the values of both the pre-exponential form and the activation energy.

The wide range of results obtained in this study were somewhat expected because of the significantly different pre-test conditions to which each set of test specimens was exposed. The discussion of the results of this study, therefore, will center around the data obtained for the annealed material since it essentially represents the control material.

Earlier it was mentioned that the structure term, the pre-exponential term, and the activation energy must be considered in any correlation of steady state creep behavior. This discussion will, therefore, address itself to a consideration of the three terms.

The apparent activation energy for creep determined for the annealed material is lower than the values summarized by Begley, et al [151]. Robinson and Sherby [152] also show lower activation energies for lower test temperatures for molybdenum, however, as indicated in Figure 56. Begley, et al [151] and Robinson and Sherby [152] also show this trend for the other refractory metals. This is not surprising, since the

activation energy for creep of a polycrystalline metal, when it is evaluated as a function of temperature over a wide range of temperatures, shows a distinct relationship with temperature.

Sherby and Burke [128] have presented a comprehensive explanation of this phenomenon. They indicate a variation of the activation energy for creep of pure polycrystalline aluminum as a

FIGURE 56 - Activation energies of creep for molybdenum.

function of temperature. This variation is the result of the mechanism of creep which predominates over a certain temperature range. The activation energy increases as the temperature is increased up to approximately $0.5 T_M$. At that point, the activation energy remains fairly constant and the slight changes that occur are attributed to a modulus effect. As the elastic modulus decreases with increasing temperature, the activation energy for creep increases slightly. This type of effect should be typical for most metals.

Sherby and Burke [128] define three temperature ranges: In Range I ($0-0.27 T_M$) dislocation intersection processes control creep. In Range II ($0.27 T_M-0.43 T_M$) cross-slip is the controlling creep process. In Range III ($0.5 T_M-1.0 T_M$) creep is controlled primarily by dislocation climb. The temperature ranges for the different creep controlling processes are more than likely dependent on the strain rate. This fact is also illustrated well by Sherby and Burke. As the strain rate is increased, the temperature ranges shift to higher temperature boundaries and dislocation climb is not the dominant creep process at $0.5 T_M$. They conclude that this is true because high strain rates allow insufficient time for diffusion-controlled processes to contribute to deformation and other mechanisms are dominant. When the temperature is sufficiently high ($> 0.75 T_M$), however, the increased atomic mobility will again permit dislocation climb to be the rate controlling process and $Q_c \approx Q_{s.d.}$.

Since the present study was conducted in the $0.3 T_M$ to $0.4 T_M$ region, the activation energy for creep observed for the annealed material is in line with the data summarized by Begley, et al [151] and in fact correlates well. It agrees with the explanation put forth by Sherby and Burke [128]. The creep controlling mechanism suggested by Sherby and Burke would be cross-slip. Conrad [153], however, suggests that the interaction of dislocations should be the controlling mechanism for the creep of molybdenum in the $0.3 T_M-0.4 T_M$ temperature range. The electron microscopy data presented previously show that both mechanisms are operational with cross-slip being observed in the annealed-irradiated specimen tested at 600°C and dislocation interaction being observed in all the test specimens.

It has been pointed out by Sherby and Burke [128] that the controlling processes of creep are dependent on

strain rate. Higher strain rates shift the temperature ranges for the creep controlling processes to higher temperature boundaries. If this occurs, then it is quite possible that dislocation interaction can be the controlling creep mechanism. For aluminum, they list the activation energy of creep controlled by dislocation interaction as varying between $0.20 Q_{s.d.}$ to $0.68 Q_{s.d.}$, depending upon test temperature. Also, if one were to assume that the data presented by Robinson and Sherby [152] on the activation energies for the creep of tungsten were to follow the same general trend as aluminum and copper for which they have a partial comparison, the value of the activation energy of the creep of tungsten controlled by dislocation interaction would vary from $0.20 Q_{s.d.}$ to $0.74 Q_{s.d.}$, depending upon the test temperature. Since the activation energies for the creep of the annealed and annealed-irradiated molybdenum specimens used in the present study were determined to be $0.46 Q_{s.d.}$ and $0.49 Q_{s.d.}$, respectively, it appears that dislocation interaction was the primary controlling mechanism of creep. Cross-slip was also operational as has already been shown.

The fact that the activation energy for the annealed-irradiated material is not much different from that obtained for the annealed material suggests that the elevated temperature irradiation had just a minor effect on the creep behavior of the material. The neutron irradiation hardened the material somewhat as evidenced by the lower steady state creep rates observed for the irradiated specimens and confirmed by the microhardness data presented in the previous section. The creep test temperatures, however, were higher than the irradiation temperature and each sample was annealed at test temperature for approximately 0.5 hr while the test system equilibrated. The elevated temperature annealed and creep test permitted the radiation damage to transform into loops which should have little effect on creep properties. This transformation was well illustrated by Brimhall and Mastel [27] and discussed in detail in a previous section on transmission electron microscopy.

Since the activation energy of creep was higher for the annealed-irradiated material than for the annealed material, and cross-slip was observed in the annealed-irradiated material only; this might suggest that cross-slip plays a more predominant role in the creep of the annealed-irradiated material. This could be the direct result of the radiation damage; however, this can only be confirmed by a more detailed study specifically designed to make that determination.

The data obtained for the stress-relieved and the stress-relieved irradiated material show results that are very different from those obtained for the annealed material. These differences were somewhat expected since several different processes were occurring in the stress-relieved material. Recrystallization and creep occurred in the stress-relieved material, while the additional phenomenon of recovery of radiation-induced defects occurred in the stress-relieved material. All of these processes were expected to affect the mechanical behavior of the metal and the data obtained in the present study confirmed this.

The value of the activation energy obtained for the stress-relieved material was $406.7 \text{ kJ mole}^{-1}$. This value compares closely with the activation energy of lattice diffusion ($405.5 \text{ kJ mole}^{-1}$) and that reported by Bechtold [154] for the recrystallization of molybdenum ($355.67 - 384.96 \text{ kJ mole}^{-1}$).

If the state of the pre-test material is reviewed, a most logical relationship develops that clearly rationalizes the high activation energy of the stress-relieved material.

The pre-test microstructure had been effectively stress-relieved as was evidenced in the transmission electron microscopy study which showed well-defined subgrains free of any major dislocation structure. This subgrain structure set a limit to the rate at which further plastic flow could develop in the material. This limit effectively resulted in a slow, steady state creep. The limit applied as long as no other structural changes occurred in the material. However, as Tweeddale [155] pointed out, the limiting effect may be superseded by that of a structural change or increasing ease of grain boundary movement. This did occur. As was mentioned earlier and was shown in Figure 11, the creep curves of the stress-relieved material showed a change in creep rate. This effect was referred to as an incubation or delayed creep phenomenon during which the creep rate was lower than that which occurs in a normal creep curve. This effect was observed for all of the stress-relieved and stress-relieved irradiated specimens tested between 700 and 800°C. It was more pronounced at 700°C and became progressively less as the test temperature was increased. It was not observed in the 900°C tests. As the optical micrographs confirmed, the limited effect was superseded by recrystallization.

The phenomenon of recrystallization involves the migration of high-angle grain boundaries which sweep out the deformed structure. Cahn [156] points out that in recrystallization, the crystal orientation of any region in the deformed material is altered, perhaps several times. This is the result of the high-angle grain boundaries sweeping through the material.

For the initiation of primary recrystallization, a population of new grains must be nucleated. These nuclei are formed in regions where the dislocation concentration and strain hardening are at a maximum. Hu [157] postulates that for heavily deformed material, subgrains rotate bodily through substantial angles and then become viable nuclei.

A threshold strain is required to bring about a nucleus; and for longer annealing times and higher temperatures, the value of the required threshold strain is reduced. Recrystallization requires thermal activation. This explains the incubation periods of the creep curves; when the creep rate changes, recrystallization has been initiated. At 900°C, the temperature is sufficiently high and the strain which occurs on loading is sufficient to initiate recrystallization and, therefore, no incubation period is observed.

The activation energy observed in this study then represents the dominant phenomenon which is occurring in the tests and that is recrystallization.

The reason why the activation energy of the stress-relieved irradiated material is somewhat less than that obtained for the stress-relieved material becomes obvious as the discussion regarding recrystallization continues.

The nucleated new grains' high-angle boundaries are sufficiently imperfect to be considered as sources of lattice vacancies. The effective vacancy concentration in the boundaries is limited and this in turn limits the rate of recrystallization which depends on grain boundary diffusion.

A boundary in addition to being a vacancy source is also a vacancy sink; and it has been tacitly assumed [156] that the boundary structure is not altered when vacancies are absorbed. There is indirect evidence, however, from grain boundary migration measurements, that vacancy absorption can so alter a boundary as to increase its migration rate drastically.

Christ, et al [158] have observed a substantial acceleration of recrystallization in heavily rolled copper which is neutron irradiated before rolling. This acceleration is attributed to the cutting of vacancy clusters by the moving boundary and the redistribution of the vacancies. This transfer of vacancies from the clusters to the boundary presumably enhances the mobility of the boundaries.

In the present study, it has already been demonstrated that the stress-relieved irradiated material possessed a vacancy-rich structure which should accelerate recrystallization. This is reflected by the lower activation energy and substantiated by the optical micrographs of the tested specimens which show a higher degree of recrystallization for the stress-relieved irradiated material than for the stress-relieved material.

The activation energies obtained in the present study are indicative of two distinctly different modes of deformation. The deformation of the annealed and annealed-irradiated material occurs as a result of cross-slip and dislocation interaction. The resulting activation energies of creep are low because of these mechanisms and the creep test temperature. The deformation of the stress-relieved and stress-relieved irradiated material is controlled by a diffusion mechanism. These samples are recrystallized during test and the activation energy obtained from the tests approximates the recrystallization energy.

To complete the correlation of steady state creep behavior using the power stress law, the structure term and the pre-exponential term must be identified. In the least squares analysis of the test data, these terms were combined into the factor A. In reality, though, $A = A_{St}f(\sigma)$, where $f(\sigma) = (\sigma_A - \sigma_i)^n = (\sigma^*)^n$.

The term σ^* was defined as the effective stress and σ_i was identified as the internal stress. Changes in the internal stress reflect variations in the structural parameters which control the creep process.

Experimental methods to determine the internal stress have been developed [149] and if a series of controlled tests are performed the value of the internal stress can be accurately identified. From the data obtained in the current study, however, the internal stress cannot be identified and, consequently, the stress exponent, n , cannot be determined. Because of these limitations, no further

reduction of the constant A can be made; but it should be remembered that $A = A_{St}(\sigma^*)^n$.

An examination of the values obtained for A show that for the annealed and annealed-irradiated material, the A term is approximately the same, again indicating that the elevated temperature irradiation had little effect on the annealed material. The values of A obtained for the stress-relieved and stress-relieved irradiated material, however, are quite different from those obtained for the annealed material. This was expected because of the structural differences. The value of A for the stress-relieved irradiated material is a factor of 10^3 lower than the value obtained for the stress-relieved material. This difference has to be the direct result of the radiation damage and its effects on both the structure of the material and the internal stresses in the material. Unfortunately, this difference cannot be rationalized any further with the presently available data.

An attempt was made to compare the data obtained in the current study with previous work. There exists, however, no published data on the compressive creep of neutron-irradiated molybdenum. In fact, the only compressive creep testing of molybdenum found in the literature was the work reported by Carvalhinhos and Argent [127]. They investigated the compressive creep of arc-cast molybdenum over the temperature range of $0.41-0.55 T_M$ at stresses of 24.1 - 82.7 MPa. The grain size of their starting material was approximately 2 to 4 times larger than in the annealed material used in the present study. The results obtained in their study yielded activation energies that varied from 255.4 to 368.4 kJ mole⁻¹. They concluded, however, that the activation energy for creep was stress dependent. Therefore, while they indicated activation energies less than self-diffusion at temperatures below $0.5 T_M$, which is the trend observed in the present study, there can be no direct comparison of their work and the present study since the current work was performed at one stress level.

Since it was not possible to accurately compare the present study against the compressive creep studies on molybdenum, a comparison of tensile creep data was attempted. A companion study to the present one, testing the same material in tension at the same applied stress and test temperatures has been outlined but has not been completed. Therefore, an attempt was made to survey the literature for comparative data.

The most comprehensive study performed on the tensile creep of irradiated molybdenum was that carried out by the Nuclear Materials and Propulsion Operation (NMPO) of General Electric during the 1960's. The data were published in a series of GEMP reports. The creep rupture data presented in those reports were reviewed and Table 7 presents a summary of that data.

A quick survey of Table 7 showed that only one set of specimens was tested at an applied stress of 176.5 MPa (18 Kg-mm⁻²). These samples were tested at 750°C. Specific details regarding these specimens were reported by Moteff, et al [26]. The material contained 220 ppm C with traces of fine Mo₂C carbides within the grains. It also had a hardness of 165 DPH. The annealed material used in the present study had 37 ppm C, no observed carbides, and a hardness of 203 DPH. The material tested by Moteff, et al [26] was irradiated at 70°C to a fluence of 1.4×10^{20} n cm⁻² ($E > 1$ MeV) while the molybdenum used in the current study was irradiated at 480°C to a fluence of 5×10^{19} n cm⁻². In addition to the pre-irradiation material variables, it has also been shown above that irradiation temperatures significantly affect the damage state of the material; therefore no valid 1:1 comparison of tension vs compression creep of irradiated molybdenum can presently be made. Once the comparison study to the present one is performed; however, a good correlation will be possible.

Moteff, et al [26] did report on a series of unirradiated molybdenum samples which they tested in tension at 750°C with applied stresses that varied from 137.3 to 196.1 MPa. When their data are taken and fitted to a log-log plot of Linear Creep Rate vs Applied Stress, a straight line should be the result as shown in Figure 57. If the data from the present study are superimposed on the curve, the linear creep rate observed for the annealed material used in the present investigation is approximately four times greater than that observed by Moteff, et al [26]. The material differences mentioned in the previous paragraph would account for some of this difference. The basic nature of the test accounts for the rest.

For the sake of clarity, the compressive strain has been expressed, throughout this study, as an absolute value without sign convention, however in all calculations the negative sign which designates compression was used. Sherby [159] deems

FIGURE 57 - Plot of linear creep rate vs applied stress (data from Moteff, et al [26].)

the use of the negative sign to designate compressive strain as being proper and correct; it does, however, result in higher creep rates and strain values for compressive creep experiments. The equation used to designate true strain is:

$$\epsilon = \ln(1 + e) \quad (31)$$

where e is the engineering strain. When e is negative as it is in compression, a larger true strain results. Therefore, all the creep rates and true strain values reported in this study will be somewhat higher than values obtained in comparable tensile creep tests.

For small plastic strains ($\sim 1.2\%$) the engineering tensile and compressive strains are nearly equal. This can be shown simply by use of the series expansion of Equation 31. This would be:

$$\epsilon = \ln(1 + e) = e - \frac{e^2}{2} + \frac{e^3}{3} - \frac{e^4}{4} + \frac{e^5}{5} \dots (32)$$

Table 7

CREEP RUPTURE TEST RESULTS SUMMARIZED
FROM GE NMPO PROGRAM

Specimen No.	Condition	Material	Post Irradiation Annealing Temperature (°C)	Test Temperature (°C)	Applied Stress (kg/mm ²)	Linear Creep Rate (in.-min ⁻¹)	Elongation (%)	Rupture Life (Hours)
850	Control ⁽¹⁾	Sheet		560	21.09	6.06×10^{-6}	56.9	487.90
692	3.7 x 10 ¹⁹ nvt ⁽²⁾ R.A.	Sheet		560	21.09	1.28×10^{-5}	51.9	237.90
851	(1)	Sheet		580	21.09	2.15×10^{-5}	52.3	115.60
690	(2)	Sheet		580	21.09	6.78×10^{-5}	53.1	41.30
699	(1)	Sheet		600	21.09	6.18×10^{-5}	49.8	40.30
693	(2)	Sheet		600	21.09	9.72×10^{-5}	49.7	27.30
698	(1)	Sheet		650	21.09	4.62×10^{-4}	51.8	5.74
853	(2)	Sheet		650	21.09	9.48×10^{-4}	55.8	3.01
1037	Control ⁽¹⁾	Sheet	None	580	21.09	3.47×10^{-5}	53.4	68.20
1042	1 x 10 ¹⁹ nvt R.A. ⁽²⁾	Sheet	None	580	21.09	$\sim 1.30 \times 10^{-3}$	50.9	2.25
1038	(2)	Sheet	None	580	21.09	8.82×10^{-4}	51.4	3.62
1040	(2)	Sheet	757-1 hr	580	21.09	2.53×10^{-5}	42.2	110.48
1043	(2)	Sheet	779-8 hr	580	21.09	2.50×10^{-5}	-	75 ^a
*Sample 1043 - Temperature controller malfunction at 75 hours.								
2103	Control ⁽¹⁾	Sheet	None	700	20.0	3.65×10^{-5}	49.2	118.9
2122	1.1 x 10 ²⁰ nvt R.A. ⁽²⁾	Sheet	None	700	20.0	2.47×10^{-5}	46.8	180.5
2126	(2)	Sheet	1200°C-1 hr-H ₂	700	20.0	1.56×10^{-5}	41.3	229.8
2127	(2)	Sheet	900°C-1 hr-H ₂	700	20.0	1.35×10^{-5}	43.1	271.4
1610	Control	Rod		750	18.0	1.28×10^{-4}	39.5	20.38
1594	1.4 x 10 ²⁰ nvt - 70°C	Rod		750	18.0	7.2×10^{-5}	40.4	56.06
1622	1.4 x 10 ²⁰ nvt - 700°C	Rod		750	18.0	1.38×10^{-6}	37.6	244.06
1612	1.3 x 10 ²⁰ nvt - 1000°C	Rod		750	18.0	4.32×10^{-6}	31.1	355.09
1597	1.4 x 10 ²⁰ nvt - 70°C	Rod	1000°C-1 hr-Vac.	750	18.0	4.98×10^{-5}	41.7	87.5 ^b
1623	1.4 x 10 ²⁰ nvt - 700°C	Rod	1000°C-1 hr-Vac.	750	18.0	1.26×10^{-6}	34.0	306.7
^a Lever Arm Problem.								
2120	Control	Sheet		980	10.55	4.31×10^{-4}	>56.8 ^b	>10.6 ^b
2115	1.1 x 10 ²⁰ nvt R.A.	Sheet		980	10.55	4.46×10^{-4}	77.0	13.54
^b Level Arm Problem.								
2123	Control	Sheet		850	14.00	9.36×10^{-5}	73.0	57.52
2116	1.1 x 10 ²⁰ nvt R.A.	Sheet		850	13.82	7.02×10^{-5}	68.8	80.12
2118	1.1 x 10 ²⁰ nvt R.A.	Sheet		850	13.30	5.96×10^{-5}	63.5	107.44
2664	Control	Sheet		600	19.40	3.73×10^{-5}	44.3	59.1
2685	3.0 x 10 ¹⁹ nvt R.A.	Sheet		600	19.40	4.29×10^{-7}	32.7	206.98

Table 7 - Continued

Specimen No.	Condition	Material	Post Irradiation Annealing Temperature (°C)	Test Temperature (°C)	Applied Stress (kg/mm ²)	Linear Creep Rate (in.-min ⁻¹)	Elongation (%)	Rupture Life (Hours)
2670	Control	Sheet		580	20.00	2.25×10^{-5}	40.1	81.4
2696	4.8×10^{18} nvt R.A.	Sheet		580	20.00	2.42×10^{-5}	51.4	132.35
2656	Control	Sheet		580	19.40	1.12×10^{-5}	45.2	221.15
2684	3.0×10^{19} nvt R.A.	Sheet		580	19.40	$< 6 \times 10^{-8}$	-	259 ^c
2679	4.8×10^{18} nvt R.A.	Sheet		580	19.40	3.26×10^{-5}	50.1	98.45
^c Test Stopped at This Time.								
588	Control	Sheet		870	14.77	7.5×10^{-4}	60.6	6.63
586	6.9×10^{18} nvt R.A.	Sheet		870	14.77	1.02×10^{-3}	-	-
589	Control	Sheet		870	15.47	1.32×10^{-3}	53.1	3.55
585	6.9×10^{18} nvt R.A.	Sheet		870	15.47	1.53×10^{-3}	55.5	3.38
892	Control	Sheet		980	10.55	1.04×10^{-3}	69.7	4.53
587	6.9×10^{18} nvt R.A.	Sheet		980	10.55	1.03×10^{-3}	77.2	4.85
2713	Control	Low Carbon C - 26 ppm O ₂ - 18 ppm		700	17.50	1.1×10^{-4}	58.3	37.5
2728	Control	Low Carbon	1200°C-1 hr-H ₂	700	17.50	1.15×10^{-4}	50.3	31.0
2731	Control	Low Carbon	1450°C-1 hr-Vac.	700	14.50	4.8×10^{-5}	58.0	75.7
2716	Control	Low Carbon	1600°C-1 hr-H ₂	700	13.00	6.9×10^{-5}	44.1	47.6
2700	3.1×10^{20} nvt R.A. (1)	Low Carbon		700	17.50	3.47×10^{-4}	41.6	39.7
2702	(1)	Low Carbon	700°C-18 hr-H ₂	700	17.50	3.03×10^{-4}	40.4	37.6
2704	(1)	Low Carbon	800°C-1 hr-H ₂	700	17.50	2.72×10^{-4}	43.4	46.3
2705	(1)	Low Carbon	900°C-1 hr-H ₂	700	17.50	1.5×10^{-4}	45.0	69.8
2706	(1)	Low Carbon	1200°C-1 hr-H ₂	700	17.50	2.25×10^{-5}	43.8	199.7
2718	1.2×10^{20} nvt R.A. (2)	Low Carbon		700	17.50	3.88×10^{-4}	40.1	35.4
2723	(2)	Low Carbon	850°C-1 hr-H ₂	700	17.50	3.82×10^{-4}	-	30.6
2722	(2)	Low Carbon	900°C-1 hr-H ₂	700	17.50	1.94×10^{-4}	44.6	50.3
2721	(2)	Low Carbon	950°C-1 hr-H ₂	700	17.50	1.15×10^{-4}	40.5	74.1
2720	(2)	Low Carbon	1200°C-1 hr-H ₂	700	17.50	6.12×10^{-5}	46.5	68.3
2725	(2)	Low Carbon	1450°C-1 hr-Vac.	700	14.50	1.8×10^{-5}	54.6	176.3
2726	(2)	Low Carbon	1600°C-1 hr-H ₂	700	13.00	$\sim 1.86 \times 10^{-5}$	42.0	173.8

and for ϵ less than 2%:

$$\epsilon \approx \epsilon. \quad (33)$$

Earlier, it was pointed out in the section on Metallographic Examination that the strain distribution in the tested samples might not be uniform and this could result in the phenomenon observed in the microstructure of the stress-relieved and stress-relieved irradiated samples. Theoretically, in ideal compression, where there exists no friction effects on the sample ends, the sample does not barrel but deforms uniformly as a cylinder. In this case, the strain should be uniform throughout the sample. In the present study, however, minor barreling was observed and, therefore, the strain was not uniform. Kobayashi [160] in his work on deformation has discussed effective strain distributions in cylinders deformed in compression with frictional effects present at the ends of the cylinders. Figure 58 illustrates a typical distribution based upon his work. In this figure, 1.00 represents the measured strain; all the other numbers represent the strain factor present at that location, thus the value 1.99 means

that the strain in that location is approximately twice the measured sample strain. Since the sample in this figure suffered no deformation at the ends because of frictional effects, it is not truly representative of the samples tested in the present study. In the current study, frictional effects at the ends were reduced by the use of a lubricant. The use of the lubricant did not, however, eliminate the frictional effects and the strain distribution of the samples used in the present study should appear somewhat similar to those shown in Figure 58.

When Figure 58 is examined, it is obvious that the strain at the center of the midplane of the sample is much greater than at the edge. This supports the explanation that the critical strain for recrystallization was not present at the edges of some of the stress relieved and stress-relieved irradiated samples. The strain distribution in the midplane would also explain the banded structures which were observed. The strain distribution in locations other than the midplane shows that the strain fields are not in the form of concentric cylinders as was suggested earlier based upon the metallographic examination of just the midplane section.

FIGURE 58 - Strain distribution in a cylinder deformed in compression and subjected to barreling.

Conclusions

The value of the activation energy of compressive creep for annealed molybdenum in the 0.3 to 0.4 T_M range was determined to be 180 kJ mole⁻¹. This value, while it appears low compared to self-diffusion activation energies (~410 kJ mole⁻¹) normally observed for creep tests at temperatures above 0.5 T_M , seems to be in agreement with the data of other investigations for temperatures below 0.5 T_M .

The activation energy of compressive creep obtained for the annealed samples irradiated at 480°C to a fast neutron fluence of approximately 5×10^{19} n cm⁻² ($E > 1$ MeV) was 193 kJ mole⁻¹.

The values of the activation energy for the two conditions suggest that dislocation interaction with forest dislocations and perhaps cross-slip were the primary operational creep mechanisms in the specific test range of this study. Cross-slip was observed in the irradiated material.

Although the activation energy of creep obtained for the annealed-irradiated material was not much different from that obtained for the annealed unirradiated material, there was about a factor of 5 reduction in the creep rate for the irradiated material tested at the same temperature and stress level. It is concluded that the elevated temperature irradiation had very little effect on the activation energy of creep in the post-irradiation tests of the material at the specific test temperatures of the present study. However, since the test temperatures (600-800°C) were significantly higher than the irradiation temperature (480°C), the radiation-induced defects would migrate resulting in a state consisting of loops which apparently did have an effect on the creep properties. The loops would tend to harden the molybdenum through a dispersion barrier mechanism, thereby reducing the creep rate.

The activation energies of compressive creep obtained for the stress relieved samples (407 kJ mole⁻¹) and stress relieved-irradiated sample (351 kJ mole⁻¹) approximate that established for recrystallization. This suggests that recrystallization was the dominant structural change occurring in these samples.

The stress-relieved specimens were irradiated at reactor ambient to a fluence of 1×10^{19} n cm⁻² ($E > 1$ MeV).

They exhibited an unexpected microstructure in that the defect density was significantly lower than that observed in annealed specimens irradiated to the same conditions. It is concluded that for the small subgrain size of these specimens compared to the grain size of the annealed material, the interstitials created during neutron bombardment in the reactor migrated to the subgrain boundaries during irradiation and were eliminated because the subgrain boundaries acted as sinks; i.e., the migration length of the interstitials is slightly greater than the radius of the small subgrains in the stress relieved samples but about a factor of 35 times less than the grain size radius of the annealed material. This circumstance resulted in a vacancy-rich substructure in the stress-relieved samples which aided the recrystallization process.

Recommendations for Future Work

- A specific program should be established to determine if tensile creep and compressive creep tests yield the same results. At temperatures above 0.5 T_M , diffusion should be the controlling process in both tension and compression. At lower temperatures, however, several different mechanisms might be operational and the controlling one might be different for compression and tension.
- More compressive creep tests of molybdenum at different stress levels are required to confirm the present observations and to provide an engineering model of compressive creep.
- Studies should be initiated to determine the effects of different fluences and irradiation temperatures on the compressive creep properties of molybdenum.
- The observations made with regard to the effects of a well defined substructure on the neutron irradiation damage of molybdenum should be pursued further. The effectiveness of subgrain boundaries as sinks should be determined. The radiation damage of stress-relieved molybdenum irradiated to higher fluences should also be examined. A very important study will be to investigate the effects of a well-defined substructure on the ordered void structure formation to determine swelling.
- The effect of stress relief and stress-relief irradiation on the compressive creep properties of molybdenum should be studied at conditions where

recrystallization is suppressed or does not take place at all to establish if a minimum creep rate can be maintained. This would provide invaluable data to the design engineer.

- These studies should be expanded to alloys of molybdenum which quite possibly will make up the structural components of the second generation fast breeder reactors and fusion reactors. TZM is now being mentioned as a prime candidate for the first wall of the second generation fusion reactor. This wall is toroidal in shape and will be under compressive stresses.

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Appendix A

DETERMINATION OF THE SOLUBILITY OF HELIUM IN MOLYBDENUM AT 1000 K

The solubility of helium in molybdenum at the specific temperature of 1000 K was estimated using the statistical thermodynamics approach employed by Sung [A-1] for helium solubility in UO_2 and more recently by Kershner [A-2] for helium solubility in tantalum. The interstitial solubility of helium in molybdenum is based upon a model in which helium atoms will occupy the $\frac{1}{2} \frac{1}{2} 0$ and $\frac{1}{2} 00$ octahedral interstitial sites in the molybdenum lattice, these sites are more energetically favored than the tetrahedral sites in the bcc lattice for interstitial solutes other than hydrogen.

The basic assumptions for this model are that no bonding interaction exists between the solvent and solute and that the heat of solution is primarily the result of the elastic strain produced within the solvent lattice as a consequence of the hard sphere solute atoms. For helium which possesses high ionization and resonance potentials this does not appear to be unreasonable.

When the dissolved helium and gaseous helium are at equilibrium at constant temperature and pressure, the following expression is true:

$$\left(\frac{dF_g}{dn}\right)_{P,T} = \left(\frac{dF_s}{dN_i}\right)_{P,T} \quad (\text{A-1})$$

Where: F_g = Gibbs free energy of helium in the gas phase,

F_s = Gibbs free energy of helium in the crystal lattice,

n = number of helium atoms in the gas phase, and

N_i = number of helium atoms in the crystal lattice.

P = pressure, mm

T = temperature, K

To use basic atomic and physical parameters for expressing the above free energy changes, the statistical thermodynamic relationship for the Gibbs free energy is employed. This relationship is expressed as:

$$F = -kT \ln \Gamma + V kT \left(\frac{\partial \ln \Gamma}{\partial v} \right) \quad (\text{A-2})$$

where Γ is the complete partition function for either n or N_i helium atoms, V is the volume in liters, and v is the frequency of oscillations in sec^{-1} .

Since helium is a monatomic gas, the complete partition function in the gas phase can be attributed primarily to translational energy. The complete partition function of gaseous helium, therefore, becomes:

$$\Gamma_g = \frac{\gamma_t^n}{n!}, \quad (\text{A-3})$$

where γ_t is the translational partition function for helium. More specifically, γ_t can be expressed as:

$$\gamma_t = \frac{(2\pi m k T)^{3/2} n k T}{P h^3}, \quad (\text{A-4})$$

where m = mass of gaseous helium atom, g

k = Boltzmann's constant

P = pressure of helium, mm

h = Planck's constant.

The free energy expression in Equation A-2 can be differentiated with respect to n if Stirling's approximation is applied to the $\ln n!$ terms of the partition function, this differentiation yields the expression:

$$\frac{dF_g}{dn} = -kT \ln \frac{(2\pi m k T)^{3/2} k T}{P h^3} \quad (\text{A-5})$$

The expression for the free energy of helium in the crystal lattice is assumed to be described by the energy required for lattice dilation plus configurational and vibrational contributions. The complete partition function for a helium atom in the crystal lattice can, therefore, be expressed as:

$$r_s = \frac{N!}{N_i!(N - N_i)!} \gamma_v^{3N_i} \exp\left(-\frac{E_o}{kT}\right), \quad (A-6)$$

where $\frac{N!}{N_i!(N - N_i)!}$ represents the total number of ways in which N_i helium atoms can be distributed at infinite dilution in N interstitial sites, E_o represents the lattice dilation energy or enthalpy of solution at 0 K and γ_v is the vibrational partition function. When $h\nu/kT < 1$ at temperatures above 1800°C, γ_v is approximately the same as the classical oscillator partition function:

$$\gamma_v = \frac{kT}{h\nu}, \quad (A-7)$$

where ν is the vibrational frequency of the host lattice. Substituting again into Equation A-2 for F_s and differentiating with respect to N_i , the following expression is obtained:

$$\frac{dF_s}{dN_i} = E_o - 3kT \ln \frac{kT}{h\nu} - kT \ln \frac{N - N_i}{N_i}. \quad (A-8)$$

Equations A-5 and A-8 can be substituted into Equation A-1 and the expression relating the fraction of filled interstitial sites to the fundamental system parameters is obtained. When it is noted that $N \gg N_i$, this expression becomes:

$$\ln \frac{N_i}{N} = - \ln \frac{(2\pi m)^{3/2} k^{5/2} \theta^3}{Ph^3 T^{1/2}} - \frac{E_o}{kT}, \quad (A-9)$$

where θ is the Debye temperature, k , of molybdenum:

$$\theta = \frac{\nu h}{k}, \quad (A-10)$$

assuming that the vibrational frequency is the Debye frequency.

Since in a bcc unit cell with a volume of a^3 , there are $6N$ interstitial sites, equation A-9 can be expressed as:

$$S_i = \frac{6Ph^3 T^{1/2}}{(2\pi m)^{3/2} k^{5/2} \theta^3 a^3} \exp\left(-\frac{E_o}{kT}\right), \quad (A-11)$$

where S_i is the solubility in atoms of solute per unit volume of solvent at unit gas pressure.

Before the solubility can be determined a value of E_o is needed. Ferro [A-3] calculated the activation energy of interstitial diffusion in bcc metals using:

$$Q = 1.3NAGa(d - h)^2 \left(1 - \frac{\beta Q}{15 RT_M}\right), \quad (A-12)$$

where Q = activation energy in cal mole⁻¹,

N = Avogadros number,

A = thermal equivalent of work,

a = lattice constant of the metal

d = hard sphere diameter of the diffusing species (1.82 Å for helium),

h = height of the interstitial cavity, cm

β = temperature coefficient of the elastic modulus variation

T_M = melting temperature of the metal.

G in this expression is the shear modulus along the (110) plane in the [110] direction and can be expressed as:

$$G = \frac{1}{2}(C_{11} - C_{12}). \quad (A-13)$$

where C_{11} and C_{12} are the deformation coefficients along the cubic axes.

Equation A-12 is based upon the strain energy required to increase the height of a vacant interstitial cavity adjacent to one that was occupied. The major strain is assumed to involve the Z axis

of the cavity; because of this the overlapping of the strain energy of the new cavity and the adjacent occupied one was considered negligible due to the orthogonality of their strain distributions.

Reviewing Ferro's model, it becomes obvious that it describes the strain energy that results when an interstitial isolate is introduced into the lattice as well as the energy of migration. Since helium is a monatomic gas it can have no more than van der Waals interactions with the solid phase and, therefore, it can be assumed that the activation energy for diffusion and solution are equal. The value of Q calculated in Equation A-12 can be substituted for E_0 in Equation A-11 to yield:

$$S_i = \frac{6Ph^3T^{1/2}}{(2\pi m)^{3/2}k^{5/2}\theta^3a^3} \exp\left(-\frac{Q}{kT}\right), \quad (A-14)$$

which is the theoretical expression for the interstitial solubility of helium in molybdenum with S_i being expressed in units of atoms $\text{atm}^{-1} \text{cm}^{-3}$. This expression is believed more accurate than Kershner's [A-2] since in his equation he has eliminated the pressure term.

Equations A-13 and A-12 can be used to obtain the activation energy for interstitial diffusion in molybdenum. The following list of values was used in determining the activation energy:

C_{11} : $4.6 \times 10^{12} \text{ dyne cm}^{-2}$	Reference 4
C_{12} : $1.79 \times 10^{12} \text{ dyne cm}^{-2}$	Reference 4
a : $3.146 \times 10^{-8} \text{ cm}$	Reference 3
h : $0.42 \times 10^{-8} \text{ cm}$	Reference 3
β : 0.36	Reference 3
T_M : 2893 K	Reference 3

The value for the activation energy was determined to be 96,366 cal mole^{-1} . Using this value S_i was determined using Equation A-14 with the following appropriate values:

T : 1000 K	
m : $6.646 \times 10^{-24} \text{ g atom}^{-1}$	
θ : 375 K	Reference 5

The value for S_i was calculated as $4.11 \times 10^{-4} \text{ atoms atm}^{-1} \text{cm}^{-3}$. This value clearly indicates that there is no interstitial solubility of helium in molybdenum at 1000 K.

The vacancy solubility describing the entrapment of helium atoms at vacancy sites within the molybdenum lattice can also be determined using statistical thermodynamics. In this case, however, the fraction of solute-occupied vacancy sites N_i/N_v is primarily a function of the factors originating from entropy in Equation A-9. E_0 can, therefore, be assumed to be very small because the vacancy site in molybdenum can accommodate the helium lattice without any apparent lattice strain. No significant bonding reaction should occur between the helium atom and the lattice. Equation A-9 can now be modified and expressed as:

$$\ln \frac{N_i}{N_v} = - \ln \frac{(2\pi m)^{3/2}k^{5/2}\theta^3}{Ph^3T^{1/2}} \quad (A-15)$$

Since there are two lattice sites per unit cell volume, a^3 , in a bcc lattice and since the vacancy concentration can be expressed as:

$$N_v/N = \exp\left(-\frac{\Delta F_v}{kT}\right), \quad (A-16)$$

where ΔF_v = Gibb's free energy of vacancy formation, Equation A-15 can be expressed as:

$$S_v = \frac{2Ph^3T^{1/2}}{(2\pi m)^{3/2}k^{5/2}\theta^3a^3} \exp\left(-\frac{\Delta S_v}{k}\right) \exp\left(-\frac{\Delta H_v}{kT}\right), \quad (A-17)$$

where S_v is the solubility in atoms of solute per unit volume of solvent at unit pressure. The energy term in this expression is that energy which is required to produce a vacancy in the molybdenum lattice. This expression is also different than the one used by Kershner [A-2] who dropped the pressure term.

The vacancy solubility 1000 K was determined using Equation A-17 with the following appropriate values:

$\frac{\Delta S_v}{k}$: 5.70	Reference 6
ΔH_v : 2.24 eV	Reference 6

The vacancy solubility of helium in molybdenum at 1000 K was determined to be approximately 2.63×10^8 atoms $\text{atm}^{-1} \text{cm}^{-3}$.

This value shows that at 1000 K the solubility of helium in molybdenum is low and is primarily vacancy in nature.

References

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- A-2. C. J. Kershner, Helium Permeation Through Tantalum Metal, MLM-1846, (January 3, 1972), 26 pp.
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- A-5. W. D. Wilkinson, Properties of Refractory Metals, Gordon and Breach Science Publishers, New York, 1969.
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Appendix B

QUANTITATIVE MICROSCOPY TECHNIQUES

Subgrain Diameter

A grid overlay with random lines is placed on an electron micrograph plate and the number of grid line intersections with subgrain boundaries is obtained. The average subgrain diameter, $\bar{\lambda}$, in micrometers is now determined by:

$$\bar{\lambda} = \frac{L}{N} \times \frac{10^4}{M}, \quad (B-1)$$

where: L = the total line length of the grid in centimeters,

N = the total number of intersections of subgrain boundaries with grid lines,

M = the plate magnification.

A minimum of five random sample counts is made for each plate and the average subgrain diameter that is reported is the numerical average of these five determinations.

Foil Thickness

White thickness fringes occur at $t/t_0 = 0, 1, 2, 3$, etc., in bright field images on the transmission electron microscope. In the above expression t represents the real foil thickness and t_0 is the extinction distance which can be expressed as:

$$t_0 = \frac{\pi V \cos \theta}{\lambda F_g}, \quad (B-2)$$

where: V = the volume of the unit cell (31.167 Å³ for molybdenum),

θ = the Bragg angle,

λ = the electron wavelength (0.0251 Å at 200 KeV), and

F_g = the structure factor for the reflecting g .

F_g can be represented as:

$$F_g = f e^{2\pi i (h/2 + k/2 + l/2) (h + k + l)}, \quad (B-3)$$

where f is the scattering amplitude of the atoms in the cell. Taking $\bar{g}$ as (110) which occurs in the majority of molybdenum samples examined, F_g turns out to be even and can simply be expressed as:

$$F_g = 2f, \quad (B-4)$$

Now:

$$F_g = \frac{\sin \theta}{\lambda} = \frac{1}{2d} \quad (B-5)$$

and for molybdenum:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{3.147}{\sqrt{2}} = 2.225$$

Now:

$$\frac{\sin \theta}{\lambda} = \frac{1}{2d} = 0.225 \text{ Å}^{-1}$$

The scattering amplitude of molybdenum at this particular $(\sin \theta)/\lambda$ value is 4.765 Å. The value of F_g becomes 9.53 Å. The value of the Bragg angle can now be determined:

$$\sin \theta = \frac{\lambda}{2d} = (0.225 \text{ Å}^{-1}) (0.0251 \text{ Å}) = 0.0056$$

$$\theta = 19 \text{ minutes}$$

The cosine of this particular angle is 0.99998, which can be approximated as 1. solving for t_0 :

$$t_0 = \frac{(3.1416) (31.167 \text{ Å}^3) (1)}{(0.0251 \text{ Å}) (9.53 \text{ Å})} = 409 \text{ Å}$$

Since t_0 is now known, the number of bright fringes seen on the microscope viewing screen can be counted and usually approximate 7; therefore:

$$\frac{t}{t_0} = 7,$$

$$\text{or } t = (409\text{\AA}) (7) = 2865\text{\AA}$$

which approximates the average foil thickness of samples used in this study.

Mobile Dislocation Density

A circle overlay is randomly placed on an electron micrograph plate and the total number of intersections of free dislocations within the circumference of the circle is obtained. This number is then used in the following equation:

$$\rho = \frac{N}{C} \times \frac{10^8}{T} \times M, \quad (\text{B-6})$$

where: ρ = the free dislocation density, cm^{-2}

N = the number of intersections of free dislocations within the circumference of the overlay circle,

C = the circumference of the circle, cm,

T = the thickness of the metal foil, $\text{\AA}$,

M = the plate magnification.

Five determinations of mobile dislocation density are made for each micrograph plate and the values reported for each plate are the numerical averages of these five determinations.

The value of T for the foils used in this study is approximately 2800 $\text{\AA}$.

Grain Size Determination [B-1]

The polished and etched sample is placed on the viewing stage of an optical microscope. A circular pattern reticule is placed in the microscope and the number of grain boundary intercepts within the pattern are counted with the sample at 100X. Five random fields of the sample are counted and the average number of intercepts ($\bar{I}$) is the numerical average of these five counts.

The average is then converted to the equivalent Heyn grain size in micrometers using appropriate conversion tables.

Reference

- B-1. H. Abrams, "Practical Applications of Quantitative Metallography," in Stereology and Quantitative Metallography, ASTM STP 504, American Society for Testing Materials, Philadelphia, Pennsylvania, 1972, p. 138.

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