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RADIATION EFFECTS ON BCC METALS
AND ALLOYS*

PROGRESS REPORT

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SUMMARY

Rafting observed earlier in Mo, Mo-0.5Ti and W have also been observed in Nb. The raft formation at $\sim 70^{\circ}\text{C}$ occurs at a threshold fluence which lies between 4.2×10^{19} and $1.1 \times 10^{20} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$). Raft length decreased and density increased in Mo containing high carbon. High carbon Mo showed the formation of raft bands. The effect of increasing irradiation temperature was to produce cluster denuded zones at the grain boundaries. The difference in cluster denuded zone width at the grain boundaries yielded the values of binding energy between the carbon and Mo atoms to be 0.07 - 0.12 eV. The binding energy value agreed well with the formation energy of Mo_2C and thus, suggesting that carbon could play an important role in nucleation of clusters.

The black spot cluster density remained unchanged in Mo-0.5Ti. The difference between Mo and Mo-0.5Ti is believed to occur due to the significantly smaller grain size in Mo-0.5Ti. The smaller grain size in Mo-0.5Ti produces a relatively greater flux of interstitials to the grain boundaries and thus, yielding lower concentration of interstitials for cluster formation.

The void size and density for Mo irradiated in EBR-II

at six different temperatures have been expressed empirically as a function of irradiation temperature. The expressions for irradiation temperature range of (700-1000°C) were:

$$d_v = 1.5 \exp(9.44 T/T_m)$$

$$N_v = 3.6 \times 10^{20} \exp(-26.9 T/T_m)$$

where d_v and N_v are void size and density and T/T_m is the homologous irradiation temperature. The void volume fraction from empirical equations has been shown to be independent of the irradiation temperature.

The void density data of this investigation and that reported in the literature have been normalized to the displacement dose. The plot of voids $\text{cm}^{-3} \text{ dpa}^{-1}$ as a function of irradiation temperature yielded a separation of data for each reactor. The voids $\text{cm}^{-3} \text{ dpa}^{-1}$ was further corrected for the displacement rate per sec. The plot of voids $\text{cm}^{-3} \text{ sec}^{-1}$ as a function of irradiation temperature grouped the data of different investigators into a 30% band. Thus, voids density have been shown to be a very sensitive function of irradiation temperature, at a fixed dpa and a function of dpa sec^{-1} for the range of irradiation temperature. The void density has been shown to be

independent of dpa at fixed temperature.

The void volume swelling in neutron irradiated Mo has been fitted to the empirical expression,

$$(\Delta V/V) (\%) = \alpha(\text{dpa})^{1/2}$$

The ion data for void swelling has been fitted to,

$$(\Delta V/V) (\%) = \beta(\text{dpa})^{2/3}$$

Thus suggesting that the correlation of ion data to neutron data should take such a correction into account.

The void superlattice was observed in Mo at all six temperatures. The void lattice parameter was found to increase linearly with increases in irradiation temperature at a given fluence level. This behavior of superlattice dimensions can be used to monitor in-reactor temperature and may be a better technique than the use of melt wires.

The voids produced during EBR-II irradiation in Mo and Nb anneal out at relatively higher temperatures than those produced at a lower fluence level. The higher anneal temperature in EBR-II irradiated samples have been shown to exist due to the larger void size and the presence of the ordered void structure.

The void denuded zone near the grain boundaries were

observed in both Mo and Mo-0.5Ti. It is suggested that void denuded zones would be useful to prevent catastrophic failure of reactor parts in service.

The length change measurements on irradiated Mo showed the presence of various recovery stages (0.16 T_m Stage III, 0.22 T_m Stage IV, 0.31 T_m Stage V and 0.36 T_m Stage VI and 0.54 T_m Stage VII). The recovery stage at 0.54 T_m is shown to be consistent with the TEM observation of complete void removal at 0.60 T_m .

The suppression of void formation in Nb-1Zr has been explained on the basis of reduction of the vacancy supersaturation by vacancy trapping at the oversize solute atoms. The effectiveness of impurity atoms for void nucleation in Nb has been shown by computing our arrival rate ratio for impurity atoms and vacancies.

The addition of 25 percent Re in W is shown to completely suppress the void swelling. The as-irradiated structure of W-25Re is primarily made up of precipitates.

The hardening due to various types of defect clusters have been calculated for Mo, Mo-0.5Ti and Nb, Nb-1Zr and shown to be consistent with the experimental data. The equations used for hardening were:

$$\Delta H_{\text{loops}} \approx 3\mu b \sqrt{N_d d_d}$$

$$\Delta H_{\text{disl.}} = 3\mu b\sqrt{\rho}$$

$$\Delta H_{\text{voids}} = 6\mu b\sqrt{N_v d_v}$$

N_l and d_l are the loop density and size, ρ is the dislocation density and N_v and d_v are the void density and size. μ is the shear modulus and b the Burgers vectors.

It has been shown that diffusional processes are enhanced in a reactor environment by at least 100°C. Examples of radiation enhanced processes for the formation of annihilation of rafts, black spot clusters and voids are presented.

A preliminary study on irradiation fatigue interaction has been made and possible experiments are suggested.

OBJECTIVE

The objective of this program is to evaluate the influence of numerous variables on the substructure of BCC metals and alloys with the ultimate view that the substructure will influence the elevated temperature mechanical properties. The variables studied include the following:

1. Irradiation temperature.
2. Fast neutron fluence of displacement per atom (dpa).
3. Fast neutron flux or displacement per atom per sec (dpa sec^{-1}).
4. Neutron spectrum (ETR, ORR, EBR-II).
5. Interstitial impurity atoms (carbon).
6. Dilute concentration of substitutional atoms (0.5%Ti in Mo and 1%Zr in Nb).
7. High concentration of substitutional atoms (25% Re in W).
8. Post-irradiation annealing temperature.

In particular, the nature and the number density of observable irradiation induced defect clusters are determined by the use of a 200 kV transmission electron microscope (TEM). In addition, the nature and the number density of defect clusters as a function of annealing temperature is investigated principally by the use of TEM. The TEM observations are supplemented by other properties such as bulk density, electrical resistivity and length change measurements. Finally the influence of these defect clusters on the mechan-

ical properties of these metals and alloys are evaluated initially by microhardness measurements and to be followed by tensile and creep testing. A preliminary paper study on the irradiation fatigue hardening was also made.

The materials evaluated in this program include: Nb, Nb-12r, Mo and Mo-0.5Ti. The metal W and its alloy W-2.5Re are investigated only in the as-irradiated condition.

INTRODUCTION

The work performed during this period consisted of (a) detailed TEM investigations of molybdenum and preliminary TEM studies on niobium and tungsten and one alloy of each of the specimens irradiated in EBR-II at six different temperatures to a fast neutron fluence of $\sim 1 \times 10^{22}$ n cm⁻² (E > 1 MeV) in the as-irradiated condition. (b) Completion of TEM and hardness studies of Nb and Nb-1Zr specimens for different anneal conditions on one set of samples and initiation of similar work on another set. (c) Detailed recovery studies of molybdenum in which substructure (TEM), hardness and length changes were evaluated, (d) construction and calibration of a high temperature anneal furnace with associated dilatometry equipment and the subsequent measurements of length changes in neutron irradiated molybdenum. (e) Construction and calibration of a bulk density measurement apparatus and the preliminary measurements of specimens in the as-irradiated condition, and (f) detailed analysis interpretation and publication of some of the test data generated to date. A paper study on the predicted effect of neutron irradiation of the plastic fatigue properties of metals is also presented.

During this period, the principal investigator devoted approximately 20 percent effort during the academic year and 50 percent effort for the recess period. The full-time scientific investigators included (a) V.K. Sikka in the position of a Graduate Research Assistant from January 1, 1973 through June 30, 1973 and upon receiving his PhD as a Research Associate from July 1, 1973 up to the present time, (b) H. Jang, who has completed his MS Degree in August 1973 is now continuing at UC in the PhD program and (c) J. Stubbins who has initiated his PhD and will work in this area. Part time contributors include A. Malik, who has completed the draft of his thesis for the MS degree in Metallurgy and now is working on the MA in Business at UC and R. Zielinski (Mount Laboratory) who is working on his MS degree with his thesis being on the "Compressive Creep Properties of Neutron Irradiated Molybdenum." Several papers are in the process of being completed on the work which Dr. D. Michel (now at NRL) performed while he was associated with UC during the previous contract year.

This progress report was prepared by Dr. V.K. Sikka with contributions on Dilatometry (Section F6) from H. Jang, Irradiation Fatigue Interaction (Section VI) from J. Stubbins and Compressive Creep of Irradiated Molybdenum (Section VII) from R. Zielinski.

TECHNICAL PROGRAM

The technical program during this period concentrated on the nature and thermal stability of defect clusters in neutron irradiated Mo, Mo-0.5Ti, Nb and Nb-1%Zr irradiated in EBR-II at six different temperatures to a fast neutron fluence of $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) or a displacement dose of $\sim 21 \text{ dpa}$. The results reported in the literature upto the present time have been summarized.

Since the large amount of void data is available on neutron irradiated Mo, it has been used to demonstrate the effects of irradiation temperature, dpa and dpa sec^{-1} . The thermal stability of cluster defects and voids in Mo, Mo-0.5Ti, Nb and Nb-1%Zr have been carried out primarily using TEM and microhardness and supplemented by length change measurements.

The information generated from neutron irradiated Mo is used for comparison with the available ion data and for further studies on Nb and Nb-1%Zr. Explanations have been offered for most of data which has been summarized in this progress report. The data is presented according to the type of material and in the order discussed above.

I MOLYBDENUM

1. Microstructure - The fluence, temperature and impurity effect in neutron irradiated molybdenum.

Microstructure here refers to clusters and cluster agglomerates excluding voids which will be discussed in the following sections. Various materials and irradiation conditions used to investigate the effect of neutron fluence, temperature and impurity are listed below.

i) Material - Arc cast polycrystalline molybdenum in the form of 0.5 mm sheet and 1.25 mm diameter rods was investigated.

ii) Impurity Elements - Only impurity element studied was carbon. Two carbon levels used were 26 ppm and 205 ppm. The molybdenum with 26 ppm was designated ML and called low carbon and 205 ppm as MH and called high carbon.

iii) Alloying Elements - The only alloying element studied was titanium and its addition was limited to 0.5 percent (~ 1 atomic percent). The resultant material was called Mo-0.5Ti and was in the form of 1.25 mm diameter rod.

iv) Irradiation Temperatures - A wide range of temperatures were studied. They include:

- a) reactor ambient temperature ~ 70°C, irradiated in Oak Ridge Research Reactor (ORR) and the material was MH sheet.

- b) 380 and 480°C, irradiated in ORR and the materials were ML and MH sheet. The low carbon molybdenum irradiated at 380 and 480°C was designated as ML-1 and ML-2 and high carbon as MH-1 and MH-2.
- c) Six irradiation temperatures, 430, 580, 700, 800, 900 and 1000°C, irradiated in EBR-II and materials were Mo and Mo-0.5Ti rods.
- v) Neutron Fluence - For ~ 70°C irradiation, three fluences were used, 4.2×10^{19} , 1.1×10^{20} and 1.5×10^{21} n cm⁻² (E > 1 MeV). Only high carbon sheet, MH, was irradiated at ~ 70°C and three different fluences. The temperature and impurity effect was studied by irradiating ML and MH at 380°C and 480°C each and at one fast neutron fluence, 6×10^{19} n cm⁻² (E > 1 MeV) was used to irradiate Mo and Mo-0.5Ti to six different temperatures.

1.1 Fluence Effect

Typical micrographs at 100,000X, for molybdenum irradiated at ~ 70°C to three different fast neutron fluences were presented in the previous progress report⁽¹⁾. At present, the high magnification micrographs and quantitative measurements on various types of clusters have been completed. The high magnification micrographs showing the microstructure for two extreme fluences are shown in Figure 1. The microstructure for 4.2×10^{19} n cm⁻² (E > 1 MeV) shows black spot

FIGURE 1

HIGH MAGNIFICATION MICROGRAPHS OF MOLYBDENUM IRRADIATED AT REACTOR AMBIENT TEMPERATURE TO A FAST NEUTRON ($E > 1$ MeV) FLUENCE AS INDICATED. INDIVIDUAL BLACK SPOT CLUSTERS (A) AND LOOPS (B) ARE SHOWN IN (A). TWO DIFFERENT RAFT CONFIGURATIONS (c_1) AND (c_2) AND DISLOCATION SEGMENT (d) ARE PRESENTED IN (B).

clusters marked by the letter 'a' and loops marked by the letter 'b'. The low magnification micrograph in the previous progress report⁽¹⁾ showed the black spot cluster and or loop agglomeration to form rafts. But, a careful examination of high magnification micrograph in Figure 1a shows that black spot clusters and loops isolated and are the basic constituents of the microstructure, although some small groups or colonies of the black spot clusters or loops can be observed.

The high magnification micrograph for $1.5 \times 10^{21} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) in Figure 1b shows the presence of black spot clusters, loops and rafts. The rafts are of two different types and are marked as ' c_1 ' and ' c_2 '. The defect type marked by 'd' shows the dislocation line segments. The c_1 type rafts seem to have formed by grouping of black spot clusters and/or loops, whereas in c_2 type a large number of black spot clusters appear to be clinging to a dislocation loop line or dislocation line.

The cluster agglomeration has been called rafting. The rafts have been shown to form on (111) type planes and have Burgers vector of $a/2\langle 111 \rangle$ type, which is the same as for the prismatic dislocation loops in molybdenum. The rafts can be seen in edge-on orientation when observed with electron beam parallel to $\langle 110 \rangle$ direction and head-on with the

<111> direction. The rafts observed in Figure 1b are in head-on orientation.

A comparison of microstructure formed at 4.2×10^{19} n cm⁻² (E > 1 MeV) with that at 1.1×10^{20} n cm⁻² (E > 1 MeV) suggests that no cluster grouping occurs in the earlier case as opposed to the complete grouping of clusters into rafts in the latter. Such a observation suggests that the threshold fluence for raft formation at $\sim 70^\circ\text{C}$ lies between 4.2×10^{19} and 1.1×10^{20} n cm⁻² (E > 1 MeV).

The quantitative characterization of the microstructure was obtained by measuring cluster and raft densities and sizes. The cluster density and sizes were measured using a Carl Zeiss Particle Size Analyzer and are summarised in Table I. The cluster density and size was used to calculate the number of point defects associated with them. The point defect density for clusters is given by the following equation,

$$N_i = N_c (\pi r^2 b) / \Omega \quad (1)$$

where N_c is the cluster density cm⁻³

r is the cluster radius

b is the Burgers vector

Ω is the atomic volume,

and are summarized in Table I.

TABLE I

ESTIMATED DENSITY AND SIZES OF BLACK SPOT CLUSTERS AND
LOOPS IN IRRADIATED MOLYBDENUM AND MOLYBDENUM-0.5 TITANIUM

Specimen Number	Material	Irradiation Temperature °C	Neutron Fluence, $n\text{ cm}^{-2}$	Black Spot Clusters		Point Defects Associated $\# \text{cm}^{-3}$	Dislocation Density $\# \text{cm}^{-3}$	Loops Size $\text{\AA}$	Point Defects Associated $\# \text{cm}^{-3}$
				Density $\# \text{cm}^{-3}$	Size $\text{\AA}$				
871	MM	~ 70	4.2×10^{19}	2.0×10^{16}	45	6.2×10^{14}	1.4×10^{16}	50	5.0×10^{18}
926	MM ^a	~ 70	1.1×10^{20}	—	—	—	—	—	—
918	MM ^b	~ 70	1.5×10^{21}	6.6×10^{15}	53	2.7×10^{18}	—	—	—
ML-1	ML	380	6×10^{19}	—	—	—	2.6×10^{15}	110	4.7×10^{18}
MM-1	MM	380	6×10^{19}	7.2×10^{15}	83	7.3×10^{18}	—	—	—
ML-2	ML	480	6×10^{19}	—	—	—	2.1×10^{15}	92	2.6×10^{18}
MM-2	MM	480	6×10^{19}	4.0×10^{15}	63	2.4×10^{18}	4.4×10^{14}	80	4.2×10^{17}
1-A-6	MR	430	$\sim 1 \times 10^{22}$	5.5×10^{15}	70	4×10^{18}	5.5×10^{15}	70	4×10^{18}
1-B-6	Mo-0.5Ti	430	$\sim 1 \times 10^{22}$	5.8×10^{15}	80	4.8×10^{18}	2.8×10^{15}	80	3.4×10^{18}
1-B-5	Mo-0.5Ti	430	$\sim 1 \times 10^{22}$	9.8×10^{15}	81	9.4×10^{18}	4.8×10^{15}	81	4.4×10^{18}

- a. Black spot clusters and rafts are not distinctly visible. All the point defects seem to be tied up in the rafts.
- b. Black spot clusters and small dislocation loops are difficult to separate. Thus, the cluster defects are only reported as black spot clusters.

A summary of raft dimensions (thickness and density) are reported in Table II. The point defects associated with rafts were calculated using the expression,

$$N_2 = N_R(\pi b \ell t) / \Omega \quad (2)$$

where N_R is the raft density cm^{-3}
 b is the raft width
 ℓ is the raft length
 t is the raft thickness

The point defect density associated with rafts is included in Table II.

The individual and total of point defects from black spot clusters, loops and rafts have been summarized in Table III. The theoretical value of the total number of defects produced during irradiation has been calculated as follows,

$$N = N_0 v \sigma^d(E_n) \phi(E_n) t \quad (3)$$

where N_0 is the number of atoms cm^{-3}
 v is the number of displaced atoms per primary knock-on atoms
 $\sigma^d(E_n)$ is the displacement scattering cross section as a function of neutron energy
 $\phi(E_n)$ is the neutron flux as a function of neutron energy spectrum

TABLE II

SUMMARY OF RAFT PARAMETERS IN IRRADIATED MOLYBDENUM AND MOLYBDENUM-0.5 TITANIUM

Specimen Number.	Material	Irradiation Temperature °C	Neutron Fluence $n\text{ cm}^{-2}$	Foil Plane of Raft Commonly Observed	Raft Density $\#/\text{cm}^3$	Raft ^a Thickness Å	Raft Length Å	Estimated ^c number Of Point Defects $\#/\text{cm}^3$	Corrected Number Of Point Defects Associated with Rafts $\#/\text{cm}^3$
871	MH ^a	~ 70	4.2×10^{19}	(111)	—	—	—	—	—
926	MH	~ 70	1.1×10^{20}	(110)	5.2×10^{15}	65	470±70	7.5×10^{21}	1.5×10^{20}
918	MH	~ 70	1.5×10^{21}	(110)	1.3×10^{15}	65	800±200	5.5×10^{21}	1.1×10^{20}
ML-1	ML	380	6×10^{19}	(001)	3.4×10^{14}	—	1075±335	2.6×10^{21}	5.2×10^{19}
MH-1	MH	380	6×10^{19}	(111)	1.14×10^{15}	—	730±200	4.0×10^{21}	8.0×10^{19}
ML-2	ML	480	6×10^{19}	(133)+(110)	6.7×10^{14}	—	1050±200	4.8×10^{21}	9.6×10^{19}
MH-2	MH ^e	480	6×10^{19}	(111)	8.8×10^{14}	—	600±100	2.1×10^{21}	4.2×10^{19}
1-A-6	MR	430	$\sim 1 \times 10^{22}$	(133)+(110)	7.4×10^{14}	~ 100	1550±250	1.8×10^{22}	3.6×10^{20}
1-B-6	Mo-0.5Ti	430	$\sim 1 \times 10^{22}$	(110)	1.5×10^{14}	~ 100	1600±200	3.9×10^{21}	7.8×10^{19}
1-B-5	Mo-0.5Ti	430	$\sim 1 \times 10^{22}$	(110)	1.4×10^{14}	~ 100	1400±300	2.7×10^{21}	5.4×10^{19}

- a. Raft thickness of 65Å is assumed in those cases where they could not be observed in edge-on orientation.
b. Although the micrograph shows aligning tendency for defect clusters, no obvious rafts could be distinguished.
c. Numbers are overestimates, since raft configuration is assumed to be completely packed with point defects. Actually it is a open structure and so these numbers have to be corrected for the packing factor.
d. Point defect calculation is corrected by using a 2 percent packing fraction correction for defects in rafts.
e. Raft density and thus the point defect calculation refers to the uniformly distributed areas. The value of the rafts in the boundaries when calculated and the point defect concentration added on to the uniformly distributed area gives a value of $(2.1 \times 10^{15} + 1.6 \times 10^{15}) 3.7 \times 10^{15}$ defects cm^{-3} .

TABLE III

SUMMARY OF QUANTITATIVE RESULTS OBTAINED FROM BLACK SPOT CLUSTERS,
LOOPS AND THE THEORETICAL NUMBER OF POINT DEFECTS PRODUCED BY IRRADIATION

Specimen Number	Material	Irradiation Temperature °C	Neutron Fluence $n\text{ cm}^{-2}$	Displacement Dose dpa	Estimated Number of Point- ₃ Defect Associated with # cm				Theoretical Number Of Point Defects $\# \text{ cm}^{-3}$	Ratio of Estimated Theoretical %
					Black Spot Clusters	Loops	Rafts	Total		
871	MH	~ 70	4.2×10^{19}	0.168	6.2×10^{18}	5.0×10^{18}	—	1.1×10^{19}	1.1×10^{22}	0.1
926	MH	~ 70	1.1×10^{20}	0.440	—	—	1.5×10^{20}	1.5×10^{20}	2.8×10^{22}	0.6
918	MH	~ 70	1.5×10^{21}	6.0	2.7×10^{18}	—	1.1×10^{20}	1.1×10^{20}	3.9×10^{23}	0.03
ML-1	ML	380	6×10^{19}	0.24	—	4.7×10^{18}	5.2×10^{19}	5.7×10^{19}	1.5×10^{22}	0.38
MH-1	MH	380	6×10^{19}	0.24	7.3×10^{18}	—	8.0×10^{19}	8.7×10^{19}	1.5×10^{22}	0.58
ML-2	ML	480	6×10^{19}	0.24	—	2.6×10^{18}	9.6×10^{19}	9.9×10^{19}	1.5×10^{22}	0.66
14 MH-2	MH	480	6×10^{19}	0.24	2.4×10^{18}	4.2×10^{17}	4.2×10^{19}	4.4×10^{19}	1.5×10^{22}	0.29
1-A-6	NR	430	$\sim 1 \times 10^{22}$	21.0	4.0×10^{18}	4.0×10^{18}	3.6×10^{20}	3.6×10^{20}	1.4×10^{24}	0.03
1-B-6	Mo-0.5Ti	430	$\sim 1 \times 10^{22}$	21.0	4.8×10^{18}	3.4×10^{18}	7.8×10^{19}	8.6×10^{19}	1.4×10^{24}	0.01
1-B-5	Mo-0.5Ti	430	$\sim 1 \times 10^{22}$	21.0	9.4×10^{18}	4.4×10^{18}	5.4×10^{19}	6.8×10^{19}	1.4×10^{24}	0.01

FIGURE 2 CHANGES IN VARIOUS PROPERTIES AS A FUNCTION OF NEUTRON FLUENCE
SHOWING THE SATURATION EFFECT IN NEUTRON IRRADIATED MOLYBDENUM

t is the irradiation time

$v\sigma^d(E_n)$ is called the damage function

Using the appropriate values of constants and for damage function and irradiation time, theoretical values of point defect density have been obtained and listed in Table III. The last column of Table III contains the percent of the total number of theoretical defects retained in the clusters and rafts. The important point to note is that the maximum number of point defects associated with visible clusters is only 0.6% of the calculated damage.

The point defect density associated with cluster and rafts along with microhardness and the reported^(2,3,4) values of electrical resistivity and length change are plotted as a function of fluence in Figure 2. It is to be noted that the number of point defects and their percent based on the theoretical number of defects increase with fluence up to 1.0×10^{20} and then decrease at 1.5×10^{21} . Such a trend is similar to that observed for other properties measured by several investigators^(2,3,4). Such a saturation effect can be explained from the fact that at high fluence recombination between interstitial and vacancy become important due to their short separation distance. Furthermore, the strain fields of the clusters can overlap and coalesce them to form large loops or dislocation segments.

A detailed mechanism of raft formation has already been presented in a previous report⁽¹⁾ and additional information is included in Reference (5).

1.2 Temperature and Impurity Effect

The temperature effect is studied by comparing the microstructure developed in high carbon molybdenum for irradiation temperatures of $\sim 70^\circ$, 380° and 480°C . The impurity effect is studied by comparing the microstructure for low and high carbon at 380° and 480°C . Since the effects of temperature and impurity were obtained on the same set of samples, they are discussed together.

Typical micrographs of microstructure developed in both low and high carbon molybdenum on irradiating at 380°C to a fast neutron fluence of $6 \times 10^{19} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) are shown in Figure 3. The microstructure in both cases contains black spot clusters, loops and well defined rafts. The rafts are marked by the indices of their respective planes. The cluster, loop and raft densities and sizes are tabulated in Table I to III. The raft size for low carbon molybdenum is $1075 \text{ \AA}$ compared to $730 \text{ \AA}$ for high carbon molybdenum. This observation is in direct conflict with the observation by Brimhall and Mastel⁽⁶⁾ who showed rafts to be longer in high carbon molybdenum than the low carbon molybdenum.

FIGURE 3

HEAD-ON AND NEARLY EDGE-ON RAFTS IN (A) LOW CARBON (ML) AND (B) HIGH CARBON (MH) MOLYBDENUM IRRADIATED AT 380°C TO A FAST NEUTRON FLUENCE OF $6 \times 10^{19} \text{N cm}^{-2}$. OPERATING REFLECTIONS ARE (A) $\bar{g} = [110]$ AND PARTIALLY $\bar{g} = [130]$ AND IN (B) $\bar{g} = [011]$. RAFTS ARE CHARACTERIZED BY THE INDICES OF THEIR RESPECTIVE PLANES.

Micrographs for low carbon molybdenum irradiated at 480°C to a fast neutron fluence of $6 \times 10^{19} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) are shown in Figure 4. The rafts are marked by the indices of their respective planes and are seen in edge-on orientation in Figure 4a and in head-on orientation in Figure 4b. The cluster, loop and raft densities are listed in Tables I - III. The microstructure for high carbon molybdenum irradiated at 480°C to a fast neutron fluence of $6 \times 10^{19} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) is shown in Figure 5. The microstructure not only contains black spot clusters, loops and rafts, but boundaries or bands of rafts within the grains. The boundaries of rafts are quite similar to dislocation sub-boundaries and show regions denuded of rafts. One of the raft-boundaries has been enlarged in Figure 6. The raft size was the same for both in the boundary and area within the boundary. The selected area diffraction on different regions in Figure 5, showed no misorientation across the boundaries. Size of the raft subgrains was measured using the line intersection method, to be 1.2 and 1.4 microns at 380° and 480°C respectively, for high carbon molybdenum. Such a subgrain size is in good agreement with subgrain size observed⁽⁷⁾ in unirradiated stress relieved molybdenum.

The grain boundaries in low and high carbon samples

FIGURE 4

RAFTS FORMED IN LOW CARBON MOLYBDENUM (ML) IRRADIATED AT 480°C TO A FAST NEUTRON FLUENCE OF $6 \times 10^{19} \text{ N cm}^{-2}$. RAFTS ARE SEEN (A) NEARLY EDGE-ON, ON TWO OF THE $\{111\}$ PLANES AND (B) HEAD-ON AND EDGE-ON ON THE $\{111\}$ PLANES. OPERATING REFLECTIONS ARE (A) $\bar{g} = [01\bar{1}]$ AND (B) $\bar{g} = [1\bar{1}0]$. RAFT PLANES ARE MARKED ON THE PHOTOMICROGRAPHS.

FIGURE 5

THE COMPOSITE MICROGRAPH ILLUSTRATES THE FORMATION OF RAFT SUB-BOUNDARIES IN HIGH CARBON MOLYBDENUM (MH) IRRADIATED AT 480°C TO A FAST NEUTRON FLUENCE OF $6 \times 10^{19} \text{ N cm}^{-2}$. THE BOUNDARIES AND THE SUBGRAINS BOTH CONTAIN THE RAFTS.

FIGURE 6

RAFTS AND ENLARGED SUB-BOUNDARY OF RAFTS OBSERVED IN HIGH CARBON MOLYBDENUM (MH) IRRADIATED AT 480°C TO A FAST NEUTRON FLUENCE OF $6 \times 10^{19} \text{ N cm}^{-2}$. OPERATING REFLECTION IS $\bar{g} = [10\bar{1}]$. RAFTS ARE IDENTIFIED BY THE INDICES OF THEIR RESPECTIVE PLANES.

were found to be denuded of rafts as shown in Figure 7. The grain boundary denuded zone widths were measured and are listed in Table IV. The typical grain boundary denuded zone width for high carbon molybdenum was 2.9×10^{-5} cm which is almost twice that around the sub-boundary, 1.4×10^{-5} cm. Such a difference in the denuded zone width shows that grain boundaries are more perfect sinks for defects than the sub-boundaries.

Raft density and size for low and high carbon molybdenum have been plotted as a function of irradiation temperature in Figure 8. The raft density data point for the reactor ambient temperature was not available for the same neutron fluence, 6×10^{19} n cm⁻² as used for 380° and 480°C irradiation and so the data for 1.1×10^{20} n cm⁻² has been used. The number of point defects associated with clusters and rafts have also been included in Figure 8. The point defect density data for ~ 70°C at 6×10^{19} n cm⁻² was obtained from Figure 2, where point defect density was plotted as a function of fast neutron fluence. Some of the important points to note are:

- i) Raft density is maximum while the size is minimum at ~ 70°C.
- ii) Raft density is minimum while the size is maximum at 380°C.

ML380°C

MH380°C

ML480°C

MH480°C

FIGURE 7

GRAIN BOUNDARY DENUDED ZONE IN MOLYBDENUM IRRADIATED AT TEMPERATURES, INDICATED ON THE MICROGRAPHS, TO A FAST NEUTRON FLUENCE OF $6 \times 10^{19} \text{ N cm}^{-2}$ ($E > 1 \text{ MeV}$). (A) AND (C) REPRESENT THE LOW CARBON MOLYBDENUM AND (B) AND (D) HIGH CARBON MOLYBDENUM.

TABLE IV

GRAIN BOUNDARY DENUDED ZONE IN IRRADIATED MOLYBDENUM

Material	Irradiation Temperature °C	Neutron Fluence $n \text{ cm}^{-2}$	Denuded zone Width cm	Investigators and References
MH	~ 70	4.2×10^{19}	None	(PI) Present Investigation
MH	~ 70	1.1×10^{20}	None	PI
MH	~ 70	1.5×10^{21}	None	PI
ML	380	6×10^{19}	2.7×10^{-5}	PI
JM	380	5×10^{19}	2.2×10^{-5}	Brimhall & Mastel
ML	480	6×10^{19}	4.75×10^{-5}	PI
JM	480	5×10^{19}	4.20×10^{-5}	Brimhall & Mastel
MH	380	6×10^{19}	1.92×10^{-5}	PI
MH	480	6×10^{19}	2.9×10^{-5}	PI

Figure 8 A PLOT OF RAFT DENSITY, SIZE AND NUMBER OF POINT DEFECTS ASSOCIATED WITH RAFTS AS A FUNCTION OF IRRADIATION TEMPERATURE FOR LOW AND HIGH CARBON MO IRRADIATED TO A FAST NEUTRON FLUENCE OF $6 \times 10^{19} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

- iii) Raft density increases while the size decreases with increase in irradiation temperature from 380° to 480°C.
- iv) The point defect density associated with clusters increase up to 380°C and shows a saturation effect with essentially no further increase at 480°C.
- v) The raft size for high carbon molybdenum shows some temperature dependence, whereas in the case of low molybdenum raft size seems independent of the temperature (at least from 380° to 480°C).
- vi) The low carbon molybdenum has fewer larger rafts than high carbon molybdenum. Thus, it seems that carbon is playing an important role in nucleation of clusters making the rafts or in some indirect manner.

The small number of point defects associated with clusters at ~ 70°C could be due to the limited mobility of the defects giving rise to the formation of only a small fraction of the total damage in the sizes large enough for resolution in the transmission electron microscope. At higher temperatures, 380° and 480°C, defects become mobile and depending on conditions can lead to the formation of black spot clusters, loops, rafts, and even the voids. Furthermore, although the recombination between interstitial and vacancies would increase at the higher temperature,

the conservative climb will also be significant and so if the clusters can nucleate, they can also form rafts. Thus, one can explain the large rafts of smaller number density and still containing more point defects at 380° and 480°C than at ~ 70°C.

The effect of carbon on rafting is quite obvious from the difference in density and size between the rafts formed in low and high carbon materials. The short size and small density of rafts in high carbon molybdenum can be explained as follows: The one possibility can be seen from the expression for glide distance for clusters. Two loops lying on the same glide plane would come together by the shear stress (τ) exerted by one on the other and has been derived by Bullough and Newman⁽⁸⁾ as,

$$\tau = 3ba^3\mu/8(1 - \nu)r^4 \quad (4)$$

where a is the cluster diameter

μ is the shear modulus

ν is the Poisson's ratio

When τ becomes τ_c , the critical resolved shear stress for prismatic glide of loops, r , becomes r_c , either the initial distance over which loops of opposite sign would slip together and annihilate each other, or the critical distance at which the loops of the same sign would be re-

pelled. Eyre and Maher⁽⁹⁾ showed that the glide stress increased by a factor of 20 for impure molybdenum. Keeping in mind the increase in glide stress, the critical distance required for loops to form rafts, from Equation 4, would be much smaller for high carbon than low carbon molybdenum. Thus, one can explain small rafts in high carbon molybdenum on the basis that the 'a' cluster can only influence a few surrounding clusters to join it to form the raft and such smaller rafts of large density will be produced. In the case of low carbon molybdenum, the critical distance for the glide is extremely large and so 'a' clusters can influence many clusters in its vicinity to join in forming larger rafts and fewer in number.

The other explanation for smaller rafts and larger number in high carbon molybdenum could be that carbon atoms act as nucleation sites for stable clusters which then only bring together homogeneously nucleated clusters. Thus, the number density of rafts is predetermined by the group of carbon atoms acting as nucleation centers and the high carbon molybdenum which contains ten times more carbon atoms than low carbon molybdenum has ten times higher number of rafts. This is in good agreement with the present observations, Figure 8. The present data suggest that possibly both mechanisms could be operating simultaneously.

1.3 Calculation of Binding Energy Between Mo and C Atoms

The formation of raft bands within the grains of high carbon molybdenum and their absence in low carbon molybdenum suggests that carbon has an important role in cluster band formation. The band formation could be associated with cluster nucleation at the carbon atoms which were pre distributed along the subgrain boundaries formed during rolling. The carbon which concentrates along the sub-boundaries during rolling stays there on preirradiation annealing although dislocation boundaries are annealed out. It is those carbon atoms where Mo interstitials get trapped and form nuclei for clusters. Clusters formed at the impurity atoms are very stable and so their stress field can attract other clusters from the surrounding regions and give rise to denuded zones around them. The above hypothesis for denuding around the bands seems to be consistent with the calculated glide distance for loops of $100 - 200 \text{ \AA}$ diameter, which is $\sim 1000 \text{ \AA}$ (close to the experimental value of $1400 \text{ \AA}$).

The strong role of carbon is also reflected in smaller grain boundary denuded zone width in high carbon compared to that observed in low carbon at the same temperatures. Since the difference between the grain boundary denuded zone width for low carbon and high carbon results from only the differ-

ence in carbon impurity, it can be used to determine the binding energy between carbon and molybdenum atoms.

Brimhall and Mastel⁽⁶⁾ have shown that the grain boundary denuded zone width can be related to the interstitial migration energy by,

$$\chi^4 = \alpha \exp(-E_i^m/KT) \quad (5)$$

where χ is the grain boundary denuded zone width

E_i^m is the interstitial migration energy

α is a constant

The expression (5) for the trapped interstitial would become,

$$\chi_H^4 = \alpha \exp[-(E_i^m + B)/KT] \quad (6)$$

where χ_H is the denuded zone width in high carbon molybdenum

B is the binding energy between carbon and molybdenum.

For low carbon without significant trapping expression (5) would be,

$$\chi_L^4 = \alpha \exp[-E_i^m/KT] \quad (7)$$

where χ_L is the denuded zone width in low carbon molybdenum

For the same irradiation temperature, expression (6) and (7) can be combined to give,

$$\chi_H = \chi_L [\exp(-B/KT)]^{1/4} \quad (8)$$

For the measured values of χ_4 and χ_L (from Table IV) at 380° and 480°C, B is calculated from Equation (8) to lie between ~ 0.07 and 0.12 eV.

The direct comparison of the calculated binding energy with measured values is not possible because it is not reported in the literature. But a comparison can be made with the value of binding energy of iron interstitial with carbon atoms in α -Fe. Johnson⁽¹⁰⁾ has reported a calculated value of 0.5 eV for C-Fe interstitial binding energy. The present value of ~ 0.07 to 0.12 eV, although much smaller than 0.5 eV for C-Fe is still the right order of magnitude. A more direct comparison for C-Mo can be made with the energy change associated with the reaction⁽¹¹⁾.

$$\Delta H^0 = 4.2 \text{ Kcals}(0.18 \text{ eV})$$

The value of 4.2 Kcals or 0.18 eV shows a reasonable agreement with 0.07 - 0.12 eV calculated in the present investigation. Thus, it is quite feasible that the effect of carbon is to trap two molybdenum interstitials and form Mo_2C which can act as a nucleus for cluster formation.

1.4 Alloying Effect

The alloying effect on the microstructure was studied by the addition of 0.5 wt % Ti to molybdenum. Typical micrographs for Mo and Mo-0.5Ti, irradiated at 430°C to a fast neutron fluence of $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) are presented in Figure 9. The microstructure for both Mo and Mo-0.5Ti consisted of black spot clusters, loops, rafts and voids. The summary of black spot clusters, loops, rafts and the number of point defects associated with these clusters is given in Tables I-III. The black spot cluster and loop size and density are quite similar for both Mo and Mo-0.5Ti. The raft size for both Mo and Mo-0.5Ti is essentially the same, but raft density appears to be a factor of five greater in Mo. The effect of titanium addition when compared with the effect of carbon suggests that carbon addition increased the raft density, while titanium addition decreases it. Similarly carbon decreases the rafts size, but titanium addition has no effect on the raft size. In the earlier section it was shown that the small rafts formed in high carbon molybdenum due to two reasons; the binding between the carbon and molybdenum interstitials to form the complexes which act as nucleation sites for black spot clusters, and the increase in shear stress due to the carbon atoms, which reduces the effective glide distance for clusters to group in the

FIGURE 9

TYPICAL MICROGRAPHS OF Mo AND Mo-0.5Ti, IRRADIATED IN ROW 7 OF EBR-II AT 430°C TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22}$ N CM⁻² (E > 1 MEV).

form of rafts. Since the raft size is the same for Mo and Mo-0.5Ti, it appears that Ti atoms have no significant effect on the shear stress and thus, the glide distance. Furthermore, since titanium atoms occupy the substitutional lattice positions, no strong binding between Ti and Mo is expected to give any complexes for nucleation.

The only difference observed between the Mo and Mo-0.5Ti is in the grain size. The pre-irradiation grain size for Mo rod was 34 microns, while for Mo-0.5Ti rod was only 13 microns. Thus, it is obvious that the flux of the mobile point defect (i.e. interstitials with small migration energy) to the grain boundaries at the irradiation temperature, will be much greater in Mo-0.5Ti than Mo. The flux of interstitials, j_i , to the grain boundary can be expressed as,

$$j_i = D_i \Delta C / X \quad (9)$$

Where D_i is the interstitial diffusivity
 ΔC is the concentration gradient between the grain boundary and that within the grain
 X is the distance interstitials have to travel to reach the grain boundary

Since the concentration of interstitials at the grain boundary is zero (grain boundaries being perfect sinks for interstitials), the expression (9) becomes,

$$j_i = D_i C / X \quad (10)$$

The distance X represents half the grain size. The ratio of the interstitial flux to the grain boundary for Mo and Mo-0.5Ti for the same irradiation conditions is,

$$\frac{j_i^{\text{Mo}}}{j_i^{\text{Mo-Ti}}} = \frac{X_i^{\text{Mo-Ti}}}{X_i^{\text{Mo}}} \quad (11)$$

or the flux of interstitials in Mo-0.5Ti reaching the grain boundary in terms of the molybdenum would be,

$$j_i^{\text{Mo-Ti}} = \frac{j_i^{\text{Mo}} X_i^{\text{Mo}}}{X_i^{\text{Mo-Ti}}} \quad (12)$$

Since, $X_i^{\text{Mo}} = 17$ microns

$$X_i^{\text{Mo-Ti}} = 6.5 \text{ microns}$$

Thus, $j_i^{\text{Mo-Ti}} = 2.6 j_i^{\text{Mo}}$ (13)

The expression (13) is true only if the loss of interstitials occurs from one side of the center of the grain, but in the actual case the diffusion occurs on all sides of the grain. Then expression (13) should be multiplied by at least two to get the total loss of interstitials to the grain boundaries. Then, the loss of interstitials in Mo-0.5Ti becomes ~ 5 times the loss in Mo, which is in excellent agreement

with the observation that raft density (also point defect density) is approximately 5 times higher in Mo than in Mo-0.5Ti. The mechanism suggested above is further supported by the fact that the higher rate of loss of interstitials in Mo-0.5Ti would yield a greater degree of vacancy supersaturation and thus, should produce greater void density. Such a speculation is in excellent agreement with the observation that the void density is a factor of approximately 2 to 3 greater in Mo-0.5Ti than that observed in Mo. In conclusion, the effect of titanium addition on the as-irradiated microstructure is reflected through the reduction in the grain size of pre-irradiated alloy.

2. Voids - Mo and Mo-0.5Ti, irradiated in Row 7 of EBR-II reactor at six different temperatures; 430, 580, 700, 800, 900 and 1000°C to a fast neutron fluence of $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) were observed using a 200 kV JEM 200A transmission electron microscope. The details of the microstructure, excluding voids, has already been discussed in the previous section. The characteristics and their relation with irradiation temperature is the subject of this section.

2.1 Random Voids

The voids were observed in both Mo and Mo-0.5Ti at all six irradiation temperatures. Typical micrographs of voids for Mo and Mo-0.5Ti are shown in Figures 10-13. The voids shown are within the grain regions. The voids show no change in size till 700°C, and increase in size and decrease in number density with increasing temperatures. The histograms of void sizes for different irradiation temperatures are shown in Figures 14 and 15. The void density, size and swelling data for neutron irradiated molybdenum of this investigation and that reported in the literature have been summarized in Table V. The void data ranged from irradiation temperature of 425°C ($0.24 T_m$) to 1380°C ($0.57 T_m$). The voids have been observed at $\sim 0.24 T_m$, but no voids were observed at $0.57 T_m$. The void data for neutron and ion bombarded Mo-0.5Ti of this investigation along with that in the literature is summarized

430°C

580°C

700°C

500Å

FIGURE 10

TYPICAL MICROGRAPHS SHOWING VOIDS IN MO IRRADIATED IN ROW 7 OF EBR-II AT THE INDICATED TEMPERATURES (430-700°C) TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22}$ N CM⁻² (E > 1 MeV).

FIGURE 11

TYPICAL MICROGRAPHS SHOWING VOIDS IN MO IRRADIATED IN ROW 7 OF EBR-II AT THE INDICATED TEMPERATURES (800-1000°C) TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ N CM}^{-2}$ ($E > 1 \text{ MeV}$).

430°C

580°C

700°C

500Å

FIGURE 12

TYPICAL MICROGRAPHS SHOWING VOIDS IN Mo-0.5Ti IRRADIATED IN ROW 7 OF EBR-II AT THE INDICATED TEMPERATURES (430-580°C) TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ N CM}^{-2}$ ($E > 1 \text{ MeV}$).

800°C

900°C

1000°C

500Å

FIGURE 13

TYPICAL MICROGRAPHS SHOWING VOIDS IN Mo-0.5Ti IRRADIATED IN ROW 7 OF EBR-II AT THE INDICATED TEMPERATURES (800-1000°C) TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ N CM}^{-2}$ ($E > 1 \text{ MEV}$).

Figure 14 VOID SIZE HISTOGRAMS FOR Mo IRRADIATED IN ROW 7 OF EBR-II AT SIX DIFFERENT TEMPERATURES TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

Figure 15 VOID SIZE HISTOGRAMS FOR Mo-0.5Ti, IRRADIATED IN ROW 7 OF EBR-II AT SIX DIFFERENT TEMPERATURES TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

TABLE V

SUMMARY OF VOID AND SWELLING DATA FOR NEUTRON IRRADIATED POLYETHYLENE

Purity %	Reactor	Irradiation Temperature		Neutron Fluence Φ , Neutrons cm^{-2}	Displacement ^(c) Per Atom DPA	Void Concentration N_v , Voids cm^{-3}	Average Void Diameter	Total Void Volume Fraction $\Delta V/V_0$, (%)	Investigators
		T_i , °C	T/T_0						
99.9	EBR-II	425	0.24	$2.5 \times 10^{22(d)}$	~ 26	ND ^(a)	0	0	Wiffen
99.9	EBR-II	430	0.24	$\sim 1 \times 10^{22(e)}$	~ 21	5.4×10^{16}	45	0.25	Sikka and Motoff
99.97	HFR(Bel)	440(450) ^(b)	0.25	$5.5 \times 10^{20(e)}$	0.64	5.0×10^{16}	25	0.04	Elen, Hanburg, Mastenbroek
99.95	Hanford	450	0.25	$7.5 \times 10^{19(d)}$	0.07	2.4×10^{16}	20-25	0.015	Brinkhall, Simonsen, Kissinger
99.95	EBR-II	460(440) ^(b)	0.25	$8.0 \times 10^{21(d)}$	8.32	3×10^{17}	52	0.75	Brinkhall, Simonsen, Kissinger
99.9	EBR-II	500	0.29	$\sim 1 \times 10^{22(e)}$	~ 21	5.8×10^{16}	46	0.30	Sikka and Motoff
99.9	EBR-II	505(560) ^(b)	0.29	$2.5 \times 10^{22(d)}$	~ 26	7.2×10^{16}	64	1.10	Wiffen
99.97	HFR(Bel)	600	0.30	$5.2 \times 10^{20(e)}$	0.96	2.0×10^{16}	40	0.07	Elen, Hanburg, Mastenbroek
99.9	Siloe	600	0.30	$5.0 \times 10^{20(d)}$	0.46	8.0×10^{16}	20-40	0.10	Adda
-	DFR	640(615) ^(b)	0.32	$2.0 \times 10^{22(d)}$	~ 21	1.0×10^{17}	40	0.55	Eyre and Bartlett
99.95	Hanford	650(703) ^(b)	0.32	$1.5 \times 10^{20(d)}$	0.14	3.5×10^{16}	25	0.028	Brinkhall, Simonsen, Kissinger
99.95	ETR	665	0.33	$8.5 \times 10^{20(d)}$	0.79	2.0×10^{16}	35	0.07	Brinkhall, Simonsen, Kissinger
99.9	ETR	700	0.34	$1.4 \times 10^{20(e)}$	0.52	3.0×10^{16}	40	0.10	Rau, Ladd, Motoff
99.9	ESR-TI	700	0.34	$\sim 1 \times 10^{22(e)}$	~ 21	4.05×10^{16}	42	0.16	Sikka and Motoff
99.9	ETR	708	0.34	$6 \times 10^{20(d)}$	0.56	7.0×10^{15}	55	0.06	Brinkhall, Simonsen, Kissinger
99.9	ETR	715	0.35	$1.04 \times 10^{21(d)}$	1.0	6.0×10^{15}	65	0.11	Brinkhall, Simonsen, Kissinger
99.9	ETR	755	0.36	$1.37 \times 10^{21(d)}$	1.3	5.0×10^{15}	70	0.11	Brinkhall, Simonsen, Kissinger
99.9	Hanford	750(815) ^(b)	0.36	$1.5 \times 10^{20(d)}$	0.14	2.0×10^{16}	35	0.045	Brinkhall, Simonsen, Kissinger
99.97	HFR(Bel)	760(780) ^(b)	0.36	$4.4 \times 10^{20(e)}$	0.82	5.0×10^{15}	50	0.03	Elen, Hanburg, Mastenbroek
99.9	EBR-II	790(755) ^(b)	0.37	$2.5 \times 10^{22(d)}$	~ 26	5.4×10^{16}	72	1.19	Wiffen
99.9	ESR-TI	800	0.37	$\sim 1 \times 10^{22(e)}$	~ 21	1.5×10^{16}	52	0.11	Sikka and Motoff
99.9	Siloe	800(840) ^(b)	0.37	$5 \times 10^{20(d)}$	0.44	1.0×10^{16}	80	0.20	Adda
99.9	Hanford	800(870) ^(b)	0.37	$1 \times 10^{20(d)}$	0.09	1.0×10^{16}	45	0.045	Brinkhall, Simonsen, Kissinger
99.9	EBR-II	900	0.41	$\sim 1 \times 10^{22(e)}$	~ 21	6.7×10^{15}	75	0.14	Sikka and Motoff
99.95	ETR	900	0.41	$1.61 \times 10^{21(d)}$	1.5	4.0×10^{15}	65	0.09	Brinkhall, Simonsen, Kissinger
99.9	Siloe	900	0.41	$5 \times 10^{20(d)}$	0.45	3.0×10^{15}	80-200	0.240.4	Adda
99.95	ETR	970	0.43	$1.96 \times 10^{22(d)}$	1.83	6.0×10^{14}	140	0.12	Brinkhall, Simonsen, Kissinger
99.95	ETR	985	0.44	$1.26 \times 10^{21(d)}$	1.18	3.5×10^{14}	263	0.47	Brinkhall, Simonsen, Kissinger
99.9	ETR	1000	0.44	$1.30 \times 10^{20(e)}$	0.30	5.0×10^{14}	200	0.19	Rau, Ladd, Motoff
99.9	EBR-II	1000	0.44	$\sim 1 \times 10^{22(e)}$	~ 21	2.85×10^{15}	102	0.16	Sikka and Motoff
-	ETR	1050	0.45	$1.0 \times 10^{21(d)}$	1.03	1.2×10^{14}	290	0.17	Kulcinski, Mastel, Brinkhall
-	ETR	1150	0.49	$1.0 \times 10^{21(d)}$	1.03	5×10^{13}	470	0.28	Kulcinski, Mastel, Brinkhall
99.9	Siloe	1200(1080) ^(b)	0.51	$5 \times 10^{20(d)}$	0.43	1×10^{13}	300-600	0.2	Adda
99.95	ETR	1230	0.52	$1.66 \times 10^{21(d)}$	1.57	1×10^{13}	830	0.032	Brinkhall, Simonsen, Kissinger
99.95	ETR	~ 1300	0.55	$1.98 \times 10^{21(d)}$	1.85	1×10^{12}	~ 800	0.61	Brinkhall, Simonsen, Kissinger
99.95	ETR	~ 1360	0.57	$2.74 \times 10^{21(d)}$	2.56	ND ^(a)	0	0	Brinkhall, Simonsen, Kissinger

(a) Not detected.

(b) Corrected temperatures.

(c) DPA calculation were made using Kinchen and Pease theory and 37 eV for displacement energy of polyethylene.

(d) $F > 0.1$ MeV.(e) $F > 1.0$ MeV.

in Table VI. The data on Mo-0.5Ti is available only from 430°C (0.24 T_m) to 1000°C (0.44 T_m).

The void data on molybdenum due to ion bombardment is increasingly available and thus has been summarized separately from neutron data in Table VII. The advantage of ion bombardment data is that the dose effects can be studied in a much shorter time period. Although one investigation has also studied the temperature effect, data are not significant to compare with the present neutron data.

The void, black spot and loop and dislocation densities and their sizes for neutron irradiated molybdenum of the present investigation are plotted as a function of irradiation temperature in Figure 16. The black spot and loop densities decrease and sizes increase sharply with increasing irradiation temperatures. The dislocation goes through a maximum at 580°C, where no rafts had coalesced to form dislocation segments. The void density and size remained unchanged up to 700°C, whereas the density decreased and size increased exponentially with the increasing irradiation temperature. An empirical expression for the void size (d_v) and density (N_v) variation as a function of irradiation temperature above about 700°C may be written as,

$$d_v = 1.5 \exp (9.44 T/T_m) \quad (14)$$

TABLE VI

SUMMARY OF VOID AND SWELLING DATA FOR NEUTRON AND ION IRRADIATED Mo-0.5Ti AND TZM

Material	Irradiation Temperature $T_i, ^\circ\text{C}$ T/T_m		Nature Of Irradiating Particles	Fluence, ϕ Particles cm^{-2}	DPA	Void Density Voids cm^{-3}	Average Void Diameter $\text{\AA}$	Total Void Volume Fraction $\Delta V/V_o(\%)$	Investigators
Mo-0.5Ti	430	0.24	neutrons ^(b)	$\sim 1 \times 10^{22}, E > 1 \text{ MeV}$	~ 21	9.84×10^{16}	37	0.28	Sikka and Moteff
	580	0.29	neutrons ^(b)	$\sim 1 \times 10^{22}, E > 1 \text{ MeV}$	~ 21	7.75×10^{16}	46	0.44	
	700	0.34	neutrons ^(b)	$\sim 1 \times 10^{22}, E > 1 \text{ MeV}$	~ 21	5.2×10^{16}	49	0.34	
	800	0.37	neutrons ^(b)	$\sim 1 \times 10^{22}, E > 1 \text{ MeV}$	~ 21	1.9×10^{16}	53	0.18	
	900	0.41	neutrons ^(b)	$\sim 1 \times 10^{22}, E > 1 \text{ MeV}$	~ 21	6.9×10^{15}	86	0.27	
	1000	0.44	neutrons ^(b)	$\sim 1 \times 10^{22}, E > 1 \text{ MeV}$	~ 21	3.5×10^{15}	100	0.31	
Mo-0.1Ti	425	0.24	neutrons ^(c)	$2.5 \times 10^{22}, E > 1 \text{ MeV}$	~ 26	0	0	0	Wiffen
	585	0.30	neutrons ^(c)	$2.5 \times 10^{22}, E > 1 \text{ MeV}$	~ 26	2.4×10^{17}	69	4.5	
	790	0.37	neutrons ^(c)	$2.5 \times 10^{22}, E > 1 \text{ MeV}$	~ 26	6×10^{16}	72	1.3	
TZM ^(a)	800	0.37	nickel ^(d)	$E = 5 \text{ MeV}$	~ 5	3.2×10^{16}	60	0.36	Kulcinski, Brimhall and Kissinger
	980	0.41	nickel ^(d)	$E = 5 \text{ MeV}$	~ 5	1.6×10^{16}	80	0.43	
	1000	0.44	nickel ^(d)	$E = 5 \text{ MeV}$	~ 5	3.6×10^{15}	105	0.22	

(a) Contained 0.42-0.47% Ti and 0.08-0.11% Zr.

(b) Irradiation was performed in Row 7 of EBR-II where the displacement rate was $1.2 \times 10^{-6} \text{ dpa sec}^{-1}$.(c) Irradiation was performed in Row 2 of EBR-II where the displacement rate was 1.4 dpa sec^{-1} .(d) Displacement rate for nickel in bombardment varied from 1×10^{-2} to $1 \times 10^{-3} \text{ dpa sec}^{-1}$.

SUMMARY OF VOID AND SWELLING DATA FOR ION BOMBARDED MOLYBDENUM

Ion	Bombarding Temperature		DPA	Void Density N_V , Void cm^{-3}	Average Void Diameter $d, \text{\AA}$	Total Void Volume Fraction	Investigators
	$^{\circ}\text{C}$	T/T_m					
2 MeV $\text{N}^{+}(\text{c})$	400	0.23	70	ND ^(a)	0	0	Evans
	500	0.27	70	ND ^(a)	0	0	
	600	0.30	70	-	~ 15	-	
	700	0.34	70	EV ^(b)	-	-	
	800	0.37	70	EV ^(b)	-	-	
	850	0.39	70	EV ^(b)	-	-	
	900	0.41	50	1.05×10^{17}	27	0.138	
	900	0.41	70	1.19×10^{17}	26	0.15	
	900	0.41	120	1.09×10^{17}	34	0.225	
	900	0.41	200	1.67×10^{17}	39	0.438	
	900	0.41	400	-	-	0.55	
	870	0.40	100	1.9×10^{17}	40	0.60	
5 MeV $\text{Ni}^{++}(\text{d})$	800	0.37	5	5×10^{16}	45	0.23	Kulcinski, Brimhall and Kissinger
	900	0.41	5	4×10^{16}	60	0.43	
	1000	0.44	5	5×10^{15}	120	0.46	
7.5 MeV $\text{Ta}^{+++}(\text{c})$	900	0.41	1	2.5×10^{16}	45	0.12	Brimhall and Simonen
	900	0.41	1.2	2.3×10^{16}	50	0.15	
	900	0.41	2.8	2.7×10^{16}	52	0.20	
	900	0.41	3	2.45×10^{16}	50	0.16	
	900	0.41	9	4.02×10^{16}	55	0.35	
	900	0.41	10	3.53×10^{16}	59	0.38	
	900	0.41	30	4.35×10^{16}	76	1.0	
	900	0.41	90	2.86×10^{16}	100	1.5	
	900	0.41	150	2.66×10^{16}	136	3.5	
7.5 MeV $\text{Ta}^{+++}(\text{d})$	900	0.41	38	5.0×10^{16}	55	0.42	Brimhall, Simonen and Kissinger
	900	0.41	113	6.0×10^{16}	65	0.8	

(a) ND means not detected

(b) EV stands for easily visible, but still not large enough to report quantitative data.

(c) Single Crystal data.

(d) Polycrystalline data.

Figure 16 A PLOT OF BLACK SPOT AND LOOP, VOID, DISLOCATION DENSITY AND SIZE AS A FUNCTION OF IRRADIATION TEMPERATURE FOR Mo IRRADIATED IN ROW 7 OF EBR-II TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

$$N_v = 3.6 \times 10^{20} \exp (-26.9 T/T_m) \quad (15)$$

If the voids were spherical, a temperature independent vacancy concentration associated with the voids should result from the product of Equation (14) and (15) of the type $N_v d_v^3$. But, it can be seen that the empirical Equations (14) and (15) yield a slight positive temperature dependence. In order to explain the temperature independent vacancy concentration the calculation of vacancy concentration would depend on $N_v d_v^{2.9}$. Such a result can be rationalized on the basis that the voids are actually polyhedral and not spherical in most cases under investigation. Furthermore, the void volume was based on the largest size of the void projection and therefore, would yield an overestimate of the void volume. The vacancy concentration associated with voids was calculated from the measured void size and void density. The number of point defects associated with the voids were in the range of 0.75 to 1.9×10^{20} vacancies cm^{-3} and within 60 percent of the average value of 1.2×10^{20} vacancies cm^{-3} of all six irradiation temperatures as shown in Figure 17. Such a variation of vacancy concentration with irradiation is in excellent agreement with empirical results discussed above.

The void data on neutron irradiated molybdenum of the

Figure 17 A PLOT OF VACANCY DENSITY ASSOCIATED WITH VOIDS AS A FUNCTION OF IRRADIATION TEMPERATURE FOR M_0 IRRADIATED IN ROW 7 OF EBR-II TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

present investigation and that reported in the literature has been plotted in Figure 18. The only other empirical relation for temperature dependency was reported by Elen et al.⁽¹²⁾ in the range of 440 to 760°C (0.25 - 0.36 T_m) as,

$$N_v = 3 \times 10^{19} \exp (-25 T/T_m) \quad (16)$$

The factor of ten lower pre-exponent term for the data of Elen et al. is most likely due to the factor of 20 to 30 difference in the neutron fluence level. The atom displacements per atom (dpa) is also a factor of 20 to 30 lower for the case of Elen's⁽¹²⁾ data.

The void data of Adda⁽¹³⁾ Figure 18, shows some curvature at temperatures below 840°C and for the higher irradiation temperatures, the temperature dependence in the range of 840 - 1080°C may be written as,

$$N_v = 1.7 \times 10^{26} \exp (-60.4 T/T_m) \quad (17)$$

The pre-exponential term in Equation (17) is relatively high, and the exponential term suggests a very strong temperature dependence.

The void density data from various reactors and investigators, Figure 18, as a function of temperature shows a range of variation at lower temperatures and merge into a

Figure 18 VOID DENSITY DATA OF THE PRESENT INVESTIGATION AND THOSE REPORTED IN THE LITERATURE AS A FUNCTION OF IRRADIATION TEMPERATURE FOR NEUTRON IRRADIATED Mo.

line at the higher temperature. The difference in data between the various investigators at lower irradiation temperatures is possibly due to the following reasons;

- i) The difference in material purity.
- ii) The fluence or displacement per atom (dpa) difference.
- iii) The flux or displacement per atom rate (dpa sec^{-1}) difference.
- iv) The neutron spectrum difference from reactor to reactor.
- v) The uncertainties in the temperature monitoring during irradiation.
- vi) The uncertainties introduced during transmission electron microscopy.

The most important and significant difference between the present investigation and that of the other investigations is the displacement dose. The dose factor can be corrected if one plots the void density data normalized to the dpa. A plot of voids $\text{cm}^{-3} \text{ dpa}^{-1}$ as a function of temperature is shown in Figure 19. The normalization of the void density data to dpa, Figure 19, has separated the data obtained from different reactors, with EBR-II curve being the lower most and Hanford curve the upper most. Such a separation of data into reactor categories suggest that the void density is a sensitive function of the reactor spectrum, which is reflected by the dose rate, dpa sec^{-1} . Thus, the void density per dpa

Figure 19 VOID DENSITY PER DISPLACEMENT DOSE AS A FUNCTION OF IRRADIATION TEMPERATURE FOR NEUTRON IRRADIATED Mo.

from Figure 19 was multiplied by the dpa sec^{-1} of the respective reactors. The data so obtained was in terms of voids $\text{cm}^{-3} \text{ sec}^{-1}$ and has been plotted as a function of irradiation temperature in Figure 20. Most of the data fell within 30 percent band up to 1000°C and then merged into a line at higher temperatures. The only exception to the 30 percent band is the data of Adda⁽¹³⁾ at 600 and 840°C and that of Rau, Ladd and Moteff⁽¹⁴⁾ at 700°C . The reason for such differences are not quite clear at the present time, although impurity and microscope techniques used could account quite well for it.

The big scatter ($\sim 30\%$) in the void data of all investigators at the lower range of the irradiation temperature could be associated to extremely small void size and large void densities. Such small sizes and large void densities introduce significant errors in the void density measurement due to the void overlapping. The other error could be due to difference in the foil thickness measurements. The later error can be supported by the fact that the ordered void lattice parameter, which requires no knowledge of foil thickness at 580°C for the present investigation compared extremely well with that reported by Wiffen¹⁵ at 585°C but the void densities at the same temperature are different by ~ 25 percent. Thus, one can tenta-

tively conclude that the void number density,

- i) is a strong function of irradiation temperature for a constant dpa.
- ii) is a function of reactor spectrum when normalized to dpa.
- iii) follows a 30 percent band on correcting for the fast neutron spectrum.

2.2 Alloying Effect on Void Parameters

The void size and density for both Mo and Mo-0.5Ti are plotted as a function of irradiation temperature in Figure 21. The void size is much smaller and void density much higher at 430°C in Mo-0.5Ti than Mo for identical irradiation conditions. For other five irradiation temperatures, void size is quite similar to Mo, but void densities are slightly higher in Mo-0.5Ti. The vacancy concentration associated with voids is higher in Mo-0.5Ti than Mo and it remains essentially constant over the range of irradiation temperatures, similar to the observation made for Mo. The temperature dependency of void size and density in the temperature range of 700 - 1000°C is in excellent agreement with the empirical relations derived for Mo in Equations (14) and (15).

The smaller size and higher void density in Mo-0.5Ti can be explained easily on the basis of suggestion made in

Figure 21 VOID DENSITY AS A FUNCTION OF IRRADIATION TEMPERATURE FOR MO AND MO-0.5Ti IRRADIATED IN EBR-II TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

Section 1.4. It was shown in Equation (13) that the flux of interstitial going to the grain boundary sinks (due to the small grain size of Mo-0.5Ti) is 2.6 times that reaching for Mo. Thus, a preferential loss rate of interstitials in Mo-0.5Ti would be expected to yield a higher degree of vacancy supersaturation, and thus the nucleation rate. Such a hypothesis should produce numerous voids of smaller size and is consistent with the observation made in Figure 21. Thus, it appears that the effect of titanium, although not beneficial in reducing void swelling results indirectly from a smaller grain size in Mo-0.5Ti.

2.3 Void Swelling

The most important concern for materials due to neutron irradiation at high temperatures ($0.24 - 0.57 T_m$) is the void volume swelling. In a recent paper, Johnston et al.⁽¹⁶⁾ have shown that void swelling in stainless steels (annealed and cold-worked) can go up as high as 100-150 percent. The data on neutron and ion bombardment of molybdenum is presented here to show that molybdenum is relatively prone to high degrees of swelling.

The calculated void volume fraction of the present investigation and those reported in the literature for neutron irradiated molybdenum over a range of temperatures, is plotted as a function of displacement per atom in Figure 22. The

Figure 22 A PLOT OF VOID VOLUME SWELLING AS A FUNCTION OF DIS-
PLACEMENT PER ATOM FOR NEUTRON IRRADIATED Mo.

temperature effect is ignored because it was shown in the previous section that vacancy concentration associated with voids remain essentially constant over the range of temperatures ($0.24-0.44 T_m$). The whole set of data of neutron irradiated molybdenum can be best fitted within a band to the following expression,

$$(\Delta V/V)\% = \alpha(dpa)^{1/2} \quad (18)$$

where $\alpha = 0.023 - 0.45 \quad (0.2365 \pm 0.2135)$

The void volume swelling data due to N^+ , Ni^{++} and Ta^{+++} ions for both single crystals and polycrystalline molybdenum is plotted as a function of dose in Figure 23. The ion data from different investigators⁽¹⁷⁻²⁰⁾ can be best fitted to the following expression,

$$(\Delta V/V)\% = \beta(dpa)^{2/3} \quad (19)$$

where $\beta = 0.21$ for single crystal Ta^{+++} ions at $900^\circ C$.
 $\beta = 0.078$ for polycrystalline Ta^{+++} ions at $900^\circ C$.
 $\beta = 0.021$ for single crystal N^+ ions at $900^\circ C$

The single crystal and polycrystalline data of Brimhall et al.^(17,18) for Ta^{+++} ions follows the same general behavior as N^+ ion data of Evans^(19,20) but the value of the constant is a factor of 10 lower in the later case. Thus, swelling in Ta^{+++}

Figure 23 A PLOT OF VOID VOLUME FRACTION AS A FUNCTION OF DISPLACEMENT DOSE FOR Mo ION BOMBARDED AT 900°C.

ion bombarded samples appears to be at least 10 times that produced due to N^+ ions. The polycrystalline molybdenum at the same temperature and bombarding ions (Ta^{++}) swell only 3.7 times that of single crystal molybdenum. The lower swelling in polycrystalline molybdenum could be associated with the presence of grain boundary sinks.

Brailsford and Bullough²¹ derived a void volume swelling-dpa relationship based on sink densities as,

$$(\Delta V/V)\% \leq 1/4 \text{ (dpa)} \quad (20)$$

Thus, the values of the constants, α and β , in Equations (18) and (19) should be 0.25 from Equation (20) and a linear void volume swelling-dose dependence. The experimental results on neutron irradiation yielded a square root dependence whereas, ion bombardment gives a 2/3 power dependence. The values of α and β constants differs for neutron and ion bombardment and for single crystal and polycrystalline molybdenum. The reason for the difference between neutron and ion bombardment and theory are hard to explain at the present time due to meager amount of data available.

Attempts were made to determine void density and void size dependence on displacement per atom (dpa) and are plotted for ion data in Figures 24 and 25. The void size, d_v , for

Figure 24 A PLOT OF VOID SIZE AS A FUNCTION OF DISPLACEMENT DOSE FOR Mo ION BOMBARDED AT 900°C

Figure 25 A PLOT OF VOID DENSITY AS A FUNCTION DISPLACEMENT DOSE FOR Mo ION BOMBARDED AT 900°C

Ta⁺⁺⁺ and N⁺ bombardment at 900°C can be described as,

$$d_v = A (\text{dpa})^{2/9} \quad (21)$$

where $A = 40 \text{ } \overset{\circ}{\text{A}}$ for single crystal Mo and Ta⁺⁺⁺ ions.
 $A = 24 \text{ } \overset{\circ}{\text{A}}$ for polycrystalline Mo and Ta⁺⁺⁺ ions.
 $A = 12 \text{ } \overset{\circ}{\text{A}}$ for single crystal Mo and N⁺ ions.

From Equations (19) and (21), the void number density dose dependence can be expressed as,

$$N_v = B (\text{dpa})^0 \quad (22)$$

The plot of N_v as a function of dpa, Figure 25, clearly suggests no dose dependence consistent with Equation (22).^o The values of B for different cases are:

$B = 3 \times 10^{16} \text{ voids cm}^{-3}$ for single crystal Mo
and Ta⁺⁺⁺ ions.

$B = 5.5 \times 10^{16} \text{ voids cm}^{-3}$ for polycrystalline
Mo and Ta⁺⁺⁺ ions.

$B = 1.1 \times 10^{17} \text{ voids cm}^{-3}$ for single crystal
Mo and N⁺ ions.

Although void number density shows a zero dose dependence for all cases listed above, the higher number density and

smaller void size for N^+ ion bombarded single crystal Mo at 900°C, compared to Ta^{++} ion irradiation is rather strange. The only possible explanation must be the effect of bombarding ions on the nucleation and growth of voids. The present data suggests that N atoms might be acting as nucleation sites in N^+ ion bombardment study.

The overall conclusions from neutron and ion bombardment data can be listed as follows:

- i) The void volume swelling even up to a displacement dose of 400 dpa ($\sim 2 \times 10^{23}$ n cm⁻², $E > 1$ MeV) would be approximately 0.6 - 6 percent.
- ii) The void swelling shows a square root dose dependence for neutron irradiation over a temperature range of 425-1300°C and a 2/3 power dependence for ion bombardment at 900°C.
- iii) The difference in void swelling dose dependence between neutron and ion bombardment is probably due to a factor of approximately 10^{14} difference in their displacement rate.
- iv) The void density is independent of the dose.
- v) The void size has a 2/9 power dose dependence.
- vi) The neutron data suggests a void swelling independent of temperature over the temperature range of 430 - 1000°C.

2.4 Void Ordering

Voids formed during neutron and ion bombardment have a tendency to align themselves into three dimensional lattice.

The void lattice so formed has been shown to be BCC for BCC host metal and FCC for FCC host metal. The void lattice was observed in Mo for all six irradiation conditions. Typical micrographs showing (110) void lattice projection are shown in Figure 26. The void ordering is relatively well defined at three lower temperatures, as compared to the higher temperatures. The ordered void lattice parameter values of this investigation and that reported in the literature for neutron and ion bombardment of Mo are summarized in Table VIII.

Voids in neutron and ion irradiated Mo-0.5Ti also showed the void ordering. Typical micrographs showing the (110) projections are shown in Figure 27. The void ordering was limited to only three lower temperatures (430, 580 and 700°C). The void ordering at 580 and 700°C was relatively well defined than that observed at 430°C. The ordered void lattice parameter values for both the neutron and ion bombarded Mo-0.5Ti are summarized in Table IX.

The ordered void lattice parameter for both Mo and Mo-0.5Ti have been plotted as a function of irradiation temperature in Figure 28. The values reported by Wiffen¹⁵ for EBR-II irradiation are in reasonable agreement with the present investigation. The void lattice parameter is linear with irradiation temperature in the range of 430 - 700°C and extrapolates to

FIGURE 26

TYPICAL MICROGRAPHS SHOWING VOID ORDERING IN Mo IRRADIATED IN ROW 7 OF EBR-II AT THE INDICATED TEMPERATURES (430-1000°C) TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

TABLE VIII

SUMMARY OF DATA ON ORDERED VOID LATTICES IN MOLYBDENUM

Irradiation Temperature		Fluence Φ , Particles cm^{-2}	Void Lattice Constant $a, \text{\AA}$	Average Void Diameter $d, \text{\AA}$	Investigator(s)
$T, ^\circ\text{C}$	T/T_m				
650 $\pm$ 30	0.32	$3 \times 10^{22(a)}$	340	~ 40	Eyre and Evans
430	0.24	1×10^{22}	220	45	Sikka and Moteff
580	0.29	1×10^{22}	270	46	Sikka and Moteff
700	0.34	1×10^{22}	320	42	Sikka and Moteff
800	0.37	1×10^{22}	390-410	52	Sikka and Moteff
900	0.41	1×10^{22}	470	73	Sikka and Moteff
1000	0.44	1×10^{22}	660	100	Sikka and Moteff
585	0.30	$2.5 \times 10^{22(b)}$	265	64	Wiffen
790	0.37	2.5×10^{22}	328	72	Wiffen
870		Nitrogen Ions ^(c)	240	~ 40	Evans
900		Tantalum Ions ^(d)	230	60	Kulcinski and Brimhall

(a) Energy E greater than 1 MeV

(b) Energy E greater than 0.1 MeV

(c) Energy E equal to 2 MeV

(d) Energy E equal to 7.5 MeV

(e) P.I. indicates present investigation

FIGURE 27

TYPICAL MICROGRAPHS SHOWING VOID ORDERING IN Mo-0.5Ti IRRADIATED IN ROW 7 OF EBR-II AT THE INDICATED TEMPERATURES (430-700°C) TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ N CM}^{-2}$ ($E > 1 \text{ MeV}$).

TABLE IX

SUMMARY OF DATA ON ORDERED VOID LATTICES IN Mo-0.5Ti

Irradiation Temperature $T_i, ^\circ\text{C}$ T/T_m		Fluence ϕ , Particles cm^{-2}	Void Lattice Constant $a, \text{\AA}$	Average Void Diameter $d_v, \text{\AA}$	Investigators
430	0.24	$\sim 1 \times 10^{22} \text{(a)}$	~ 190	37	Sikka and Moteff
580	0.29	$\sim 1 \times 10^{22}$	230	46	Sikka and Moteff
700	0.34	$\sim 1 \times 10^{22}$	290	49	Sikka and Moteff
585	0.29	$2.5 \times 10^{22} \text{(b)}$	215	69	Wiffen
790	0.37	2.5×10^{22}	315	72	Wiffen
870		Nitrogen Ions (c)	220	~ 60	Evans

(a) Energy E greater than 1 MeV.

(b) Energy E greater than 0.1 MeV.

(c) Energy E equal to 2 MeV.

Figure 28 ORDERED VOID LATTICE PARAMETER AS A FUNCTION OF IRRADIATION TEMPERATURE FOR NEUTRON IRRADIATED Mo AND Mo-0.5Ti

0°K. The linear dependence breaks at $\sim 0.37 T_m$ to another linear behavior up to 1000°C. The reason for such a change is not clear at the present time. The void lattice parameter for Mo-0.5Ti is also linear in the temperature range fo 430 - 700°C, but the values are lower by $\sim 40 \text{ \AA}$.

The ordered void lattice observed to form in EBR-II irradiation and ion bombarded Mo, Mo-0.5Ti and other metals has been extensively reported, but no one explanation is available to properly account for all the observed facts. A review of the existing models and their comparison with the present data has been made in a recent publication⁽²²⁾ (Damage in Neutron Irradiated Molybdenum, Part I by V.K. Sikka and J. Moteff).

The importance of the void ordering in Mo and Mo-0.5Ti exists due to the fact that it changes linearly with irradiation temperature and thus, can be used in temperature monitoring. The void volume fraction for ordered void structure can be expressed in terms of void lattice parameters as,

$$(\Delta V/V)\% = 4/3\pi r^3 \times \frac{2}{a^3} \times 100 \quad (23)$$

where $(2/a^3)$ represents the void number density per unit volume, based on two voids per unit cell of BCC structure.

From Equation (23),

$$(\Delta V/V)\% \approx 800\left(\frac{r}{a}\right)^3 \quad (24)$$

The (a/r) ratio for molybdenum varied over the range of irradiation temperature as; 9.8, 11.7, 15.2, 15.4, 12.9, 12.9. Thus, the void volume swelling can reach a maximum of 0.849 percent and a minimum of 0.219 percent. The maximum and minimum values obtained from the random void count were 0.28 to 0.11 percent suggesting the void lattice occupancies of the order of ~ 50 percent. But in any case, it appears that void ordering would introduce a saturation type of effect in void nucleation, growth and void swelling. The maximum void swelling from Equation (24) should reach ~ 1 percent, which is within the acceptable limits for reactor design. Similar upper limits for void volume fraction will also be expected for Mo-0.5Ti.

3. Void Annealing - A limited quantity of information on the stability of voids in BCC metals is available and has been summarized, along with the data of the present investigation in Table X. The important point to note is that the work reported earlier is associated with the low fluence irradiation (smaller number of vacancies retained in the voids) as compared to the present case. Furthermore, the

TABLE X

SUMMARY OF VOID ANNEALING TEMPERATURES FOR THE BCC METALS, Mo, Nb, AND V

Material	Irradiation Conditions		Annealing Temperature		Complete Void Removal		Investigators and References
	Neutron Fluence $\phi_n, n\text{ cm}^{-2}$	Displacements $\phi_d, \text{disp atom}^{-1}$	T, °C	T/T _m	T, °C	T/T _m	
Mo	3.5×10^{20} (E > 1.0 MeV)	0.64	440 ^(a)	0.25	1300	0.55	Elen (11)
			600	0.30			
			800	0.37			
			1000	0.44			
			1200	0.51			
			1300	0.55			
Mo	$\sim 1 \times 10^{22}$ (E > 1 MeV)	21.0	430 ^(a)	0.24	1450	0.60	Sikka and Moteff (Pl) ^(d)
			550 ^(a)	0.29			
			700 ^(a)	0.34			
			800 ^(a)	0.37			
			900 ^(a)	0.41			
			1000 ^(a)	0.44			
			1100	0.48			
			1200	0.51			
			1300	0.54			
			1350	0.56			
			1450	0.60			
Nb	3.9×10^{20} (E > 1.0 MeV)	~ 0.70	470 ^(a)	0.27	1100	0.50	Elen (11)
			600	0.32			
			800	0.39			
			900	0.43			
			1000	0.46			
			1100	0.50			
Nb	2.5×10^{22} (E > 0.1 MeV)	26.0	425 ^(a)	0.26	1230	0.56	Michel and Moteff (12)
			585 ^(a)	0.31			
			790 ^(a)	0.38			
			1230	0.56			
			1380	0.61	1380 ^(c)	0.61	
V	4.2×10^{20} (E > 1.0 MeV)	-	420 ^(a)	0.32	1000	0.59	Elen (11)
			600	0.40			
			700	0.45			
			800	0.50			
			1200	0.59			

(a) Represents the irradiation temperature, as well as, one of the annealing temperatures.

(b) Complete void removal for only the 425° and 585°C irradiation condition.

(c) Complete void removal for only the 790°C irradiation condition.

(d) Present Investigation.

irradiation conditions used by Elen²³ did not produce any ordered void structure. In the present investigation, the as-irradiated structure contained higher number of vacancies in the voids and in addition, an ordered void structure. The void annealing was carried out at temperatures of 425, 550, 700, 800, 900, 1000, 1100, 1200, 1300, 1350 and 1450°C. The changes produced on annealing were followed by transmission electron microscopy and the microhardness measurements.

A set of micrographs showing the changes in void size and distribution for 430°C and 1000°C irradiation conditions are shown in Figures 29-31. The lowest irradiation temperature is selected to compare the results with that reported by Elen for 440°C irradiation temperature, but a factor of 40 lower fluence. The highest irradiation temperature is selected to determine if larger size voids would anneal out differently than the smaller ones. The void size distribution histograms were drawn after each anneal and are shown in Figures 32 and 33 for 430°C and 1000°C irradiation respectively.

The ordered void lattice parameter was also measured after each anneal temperature and is listed in Table XI. The void lattice parameter was found to be essentially constant for various annealing temperatures. A plot of the

430°C

550°C

500Å

700°C

800°C

FIGURE 29

TYPICAL MICROGRAPHS SHOWING CHANGES PRODUCED AFTER ONE HOUR POST-IRRADIATION ANNEAL TREATMENT AT THE INDICATED TEMPERATURES (430-800°C) FOR Nb IRRADIATED IN ROW 7 OF EBR-II AT 430°C TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ N CM}^{-2}$ ($E > 1 \text{ MeV}$).

900°C

1000°C

500Å

1100°C

1300°C

FIGURE 30

TYPICAL MICROGRAPHS SHOWING CHANGES PRODUCED AFTER ONE HOUR POST-IRRADIATION ANNEAL TREATMENT AT INDICATED TEMPERATURES (900-1300°C) FOR MO IRRADIATED IN ROW-7 OF EBR-II AT 430 TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ N CM}^{-2}$ ($E > 1 \text{ MeV}$).

FIGURE 31

TRANSMISSION ELECTRON MICROGRAPHS SHOWING THE EFFECT OF ONE HOUR ANNEALS AT VARIOUS TEMPERATURES ON THE VOID SIZE IN MOLYBDENUM IRRADIATED IN EBR-II AT 1000°C TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ N cm}^{-2}$ ($E > 1 \text{ MeV}$). (A) AS-IRRADIATED (B), (C) AND (D) ANNEALED AT 1100, 1200 AND 1300°C RESPECTIVELY.

Figure 32 VOID SIZE HISTOGRAMS FOR Mo IRRADIATED AT 430°C TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) AND POST-IRRADIATION ANNEALED AT THE INDICATED TEMPERATURES.

Figure 33 VOID SIZE HISTOGRAMS FOR Mo IRRADIATED AT 1000°C TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) AND POST IRRADIATION ANNEALED FOR ONE HOUR AT THE INDICATED TEMPERATURES.

TABLE XI

SUMMARY OF VOID ANNEALING IN NEUTRON IRRADIATED
MOLYBDENUM ORDERED VOID LATTICE PARAMETER

Irradiation Temperature T_i , °C	Ordered Void Lattice Parameter, Å										
	Anneal Temperature, T_a , °C										
	430	550	700	800	900	1000	1100	1200	1300	1350	1450
84 430	220	223	232	217	224	242	216	—	Random	Few Voids	Anneal Out
580	270	270 ^(a)	262	260	274	260	—	—	Random	Few Voids	Anneal Out
1000	—	—	660	—	640	660 ^(a)	668	660	Random	Random	Anneal Out

(a) Same number as obtained in as-irradiated sample at $580 \pm 20^\circ\text{C}$.

void size, density, volume fraction and the ordered void lattice parameter are plotted in Figure 34. The complete void removal temperature is shown to be 1450°C ($0.60 T_m$) for both Mo and Mo-0.5Ti, as compared to $0.55 T_m$ reported by Elen. Michel and Moteff²⁴ have shown that complete void removal temperature in niobium for EBR-II irradiation is $\sim 0.56 T_m$ for 425 and 585°C and $\sim 0.61 T_m$ for 790°C irradiation as opposed to the $0.50 T_m$ reported by Elen for 470°C irradiation to a fast neutron fluence of $3.9 \times 10^{20} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

The higher annealing temperature for EBR-II irradiation as opposed to low fluence studies could be due to excessive vacancies stored in EBR-II samples. The excessive vacancies stored in the EBR-II irradiated samples is determined by void volume fraction, which is a factor of ~ 25 higher in the case of niobium and ~ 10 higher in the case of molybdenum, compared to the results under approximately similar irradiation temperature conditions by Elen. A void volume fraction increase in niobium by a factor of ~ 25 requires a further increase of $\sim 0.06 T_m$ in the complete void removal temperature. Molybdenum as compared to niobium for a factor of ~ 10 higher void volume fraction should require about a $0.02 T_m$ increase in annealing temperatures as opposed to $0.05 T_m$ value observed in this investigation.

Figure 34(A) VOID DENSITY AS A FUNCTION OF ANNEAL TEMPERATURE FOR Mo IRRADIATED AT 430°C TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

Figure 34(B) SIZE AND ORDERED VOID LATTICE PARAMETER AS A FUNCTION OF ANNEAL TEMPERATURE FOR Mo IRRADIATED AT 430°C TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

Figure 34(C) SWELLING CHARACTERISTICS AS A FUNCTION OF ANNEAL TEMPERATURE FOR Mo IRRADIATED AT 430°C TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

but, the irradiation under the present conditions have produced an ordered void structure and thus, $0.03 T_m$ being the difference between the predicted and observed values could be due to the stability of the ordered void structure.

The higher complete void removal temperature in the case of niobium (with no ordered void structure at 425°C) and molybdenum (with ordered structure) irradiated to fluence of $2.5 \times 10^{22} \text{ n cm}^{-2}$ ($E > 0.1 \text{ MeV}$) and $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) has already been explained semi-quantitatively in a recent publication²⁵ (Stability of the Defect State in Neutron Irradiated Molybdenum by V.K. Sikka and J. Moteff). The basic idea used was that the emission of a vacancy from a void requires energy, which is the binding energy of the vacancy to the void and is given by,

$$E_b^V = E_f^V - 2\gamma\Omega/r \quad (25)$$

where E_f^V is the vacancy formation energy in the normal lattice and

$\frac{2\gamma\Omega}{r}$ is the energy required for a vacancy to leave a void of radius, r .

γ a constant, is the surface energy and

Ω is the atomic volume.

From Equation (25) it becomes clear that the binding energy is small for a smaller void and large for a larger void. Thus,

the smaller voids should lose vacancies faster than the larger voids in relative terms.

In order for a void to shrink, it should emit vacancies and vacancies should be able to migrate away to sinks. The number of vacancies leaving per void then is,

$$\frac{\pi r^2}{a^2} v \exp [-(E_b^v + E_m)/KT] \quad (26)$$

where v is the jump frequency, E_m is the vacancy migration energy and a , is the lattice parameter. While the voids are losing vacancies, they have a certain probability to absorb vacancies from the surroundings and this is given by,

$$\frac{\pi r^2}{a^2} v C_v \exp(-E_m/KT) \quad (27)$$

where C_v is the vacancy concentration in the matrix.

Thus, the net loss rate of vacancies from a void surface is given by,

$$\frac{dN_v}{dt} = - \frac{\pi r^2}{a^2} v [\exp -(E_b^v + E_m)/KT - C_v \exp(-E_m/KT)] \quad (28)$$

At the temperatures which are near complete void removal,

the vacancy emission from the void surface and subsequent migration away to sink predominates. In such a circumstance, for the case of the smaller voids generated at lower fluence and the larger voids generated at the higher fluence in which the voids completely disappear, the vacancy loss should become maximum and be equal, in a first approximation, for the two initial size distribution. For such a condition,

$$\frac{E_b^{v1^0} + E_m}{T_1} = \frac{E_b^{v2^0} + E_m}{T_2} \quad (29)$$

Where T_1 and T_2 are the annealing temperatures for average voids radius of r_1 and r_2 and binding energy,

$$E_b^{v1^0} = E_f^v - \frac{2\gamma\Omega}{r_1} \text{ and } E_b^{v2^0} = E_f^v - \frac{2\gamma\Omega}{r_2}$$

In the case of ordered void structure, Equation (29) needs an additional binding energy term and becomes,

$$\frac{E_b^{v1^0} + E_m}{T_1} = \frac{E_b^{v2^0} + E_b^0 + E_m}{T_2} \quad (30)$$

For only the size increase in EBR-II samples, the values of T_2 was calculated to be $0.57 T_m$ as opposed to $0.60 T_m$ ob-

served experimentally. The difference between $0.60 T_m$ and $0.57 T_m$, from Equation (30) has been shown to give a value of 0.25 eV for the binding energy of the ordered void structure. The value of 0.25 eV for the ordered void structure based on the approximate calculation is not unrealistic and shows reasonable agreement with 0.5 eV calculated by Tewary and Bullough⁽²⁶⁾.

A similar calculation for niobium, based on Equation (29) gave the value for complete void removal as $0.54 T_m$, closer to the value of $\sim 0.56 T_m$ reported by Michel and Moteff⁽²⁴⁾.

Equations (25) through (30), although satisfactorily near the complete void removal temperature, assumes a very simple approach. In actual practice, one can see from Equation (25) that the vacancy concentration in equilibrium with each void would vary and the vacancy gradients would be set up between the voids of different sizes. A schematic diagram showing the concentration gradients, random void distribution and the ordered void structure is shown in Figure 36. Thus, one needs to set up equations for a diffusion controlled growth of large voids at the expense of small ones as a function of annealing temperature and this can be done from the most commonly used diffusion equation based on the spherical configuration,

$$dr/dt = D_s/r [C_v/C_o - \exp(2\gamma\Omega/rKT)] \quad (31)$$

(a) Vacancy gradient
between two voids.

(b) Dispersed voids

(c) Ordered voids

FIG. 36 REPRESENTATION OF THE VOID SYSTEM USED
FOR BULK DIFFUSION MECHANISM,

where C_v/C_o represents the vacancy supersaturation and D_s is the self diffusion coefficient. Equation (31) suggests that an essential condition for void growth is the supersaturation of vacancies in the surrounding lattice. Moreover, it follows that for any given values of $C_v/C_o \neq 1$, a critical void radius can be defined such that,

$$\begin{aligned} dr_{\text{crit}}/dt &= 0 \\ r_{\text{crit}} &= 2\gamma\Omega/KT_a \ln C_v/C_o \end{aligned} \quad (32)$$

The critical void radius, r_{crit} , defining the boundary between growth and shrinkage of voids has been evaluated as a function, C_v/C_o , for various annealing temperatures using Equation (32) and plotted in Figure 37. The family of curves in Figure 37 show that for a fixed value of vacancy supersaturation, smaller voids would be going into solution and larger ones would be growing. A detailed set of calculations for void shrinkage rates and dissolution times have been made and reported in the thesis⁵ (The Nature and Thermal Stability of Defects in Neutron Irradiated Mo and Mo-0.5Ti, PhD Thesis, 1973).

4. Grain Boundary Denuding - Voids

Voids were observed at all six temperatures (425, 580,

FIG. 37

CALCULATED CRITICAL VOID RADIUS AS A
FUNCTION OF THE VACANCY SUPER SATURATION
FOR MOLYBDENUM.

700, 800, 900 and 1000°C) in Mo and Mo-0.5Ti. They were uniformly distributed within the grain and near the grain boundary at three lower irradiation temperatures. At three higher irradiation temperatures, void free regions or zones were observed near the grain boundaries and are shown in Figures 38 and 39 for both Mo and Mo-0.5Ti. The summary of the grain boundary denuding zone width is presented in Table XII. The void denuded zone is expected to form at and/or above the temperature of vacancy migration, with vacancies going to the grain boundary sinks. The void denuded zones expand on annealing and their values for various annealing temperatures are listed in Table XIII.

The void denuded zones are possibly formed by the flux of vacancies reaching the grain boundary. In such a process, a greater degree of vacancy supersaturation would occur at a certain distance from the grain boundary (determined by the vacancy migration distance). Thus, the voids near the void denuded zone show a higher void density and larger void size compared to the overall (including both inside the grain and near the grain boundary) void parameters. Two such examples are presented in Figures 40 and 41 for irradiation temperatures of 900 and 1000°C respectively and on post irradiation annealing. The void density and size for irradiation temperature of 900°C are 18 and 12 percent

FIGURE 38

TYPICAL MICROGRAPHS SHOWING GRAIN BOUNDARY VOID DENUDING IN Mo IRRADIATED IN ROW 7 OF EBR-II AT THE INDICATED TEMPERATURES TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ N CM}^{-2}$ ($E > 1 \text{ MeV}$).

FIGURE 39

TYPICAL MICROGRAPHS SHOWING GRAIN BOUNDARY VOID DENUDING IN Mo-0.5Ti IRRADIATED IN ROW 7 OF EBR-II AT THE INDICATED TEMPERATURES TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ N CM}^{-2}$ ($E > 1 \text{ MeV}$).

TABLE XII

GRAIN-BOUNDARY VOID DENUDING FOR MOLYBDENUM AND MOLYBDENUM-0.5%
TITANIUM, IRRADIATED AT VARIOUS TEMPERATURES, IN EBR-II, TO A
FAST NEUTRON DOSE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$)

Irradiation Temperature °C	Molybdenum Specimen Number A-Series	Grain Boundary Void Denuding Å	Molybdenum-0.5% Titanium Specimen Number B-Series	Grain Boundary Void Denuding Å
430±5	1-A-6	None	1-B-6	None
580±20	2-A-6	None	2-B-6	None
700	3-A-6	None	3-B-6	83±16
800	4-A-6	483±17	4-B-6	325±8
900	6-A-6	579±21	6-B-6	533±33
1000	5-A-6	830±20	5-B-6	716±35

TABLE XIII

SUMMARY OF VOID ANNEALING IN NEUTRON IRRADIATED
MOLYBDENUM - GRAIN BOUNDARY VOID DENUING WIDTH

Irradiation Temperature °C	Grain Boundary Void Denuding Zone Width Å										
	430	550	700	800	900	1000	1100	1200	1300	1350	1450
430	None	None	None	None	-	260	-	-	Very Large	Anneal Out	Anneal Out
900	-	-	-	-	580 525	-	600	842	1575	1760	Anneal Out
1000	-	-	783	-	633	833 850	770	867	1255	4340 ^(a)	Anneal Out

(a) Denuding width varied from 2267 - 9334 Å in different grains.

Figure 40 PLOT OF VOID DENSITY AND SIZE AS A FUNCTION OF ANNEALING TEMPERATURE SHOWING THE DIFFERENCE BETWEEN THE OVERALL AND NEAR THE GRAIN BOUNDARY VOID PARAMETERS FOR Mo IRRADIATED IN EBR-II AT 900°C TO A FAST NEUTRON FLUENCE OF $\sim 10^{22} \text{ n cm}^{-2}$ ($E > 1\text{-MeV}$).

Figure 41 PLOT OF VOID DENSITY AND SIZE AS A FUNCTION OF ANNEALING TEMPERATURE, SHOWING THE DIFFERENCE BETWEEN THE OVERALL AND NEAR THE GRAIN BOUNDARY VOID PARAMETERS, FOR MO IRRADIATED IN EBR-II AT 1000°C TO A FAST NEUTRON FLUENCE OF $\sim 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

higher than overall, whereas they were 28 and 14 percent higher than the overall for 1000°C.

The void denuded zone width should be related to the vacancy migration distance given by:

$$\chi = \sqrt{6Dt} \quad (33)$$

Since $D = D_0 \exp (-E_m/KT)$, Equation (33) can be expressed as:

$$\chi^2 = 6D_0 t \exp (-E_m/KT) \quad (34)$$

A plot χ^2 versus $1/T^\circ K$, for a fixed time of irradiation or annealing should give the activation energy for vacancy migration. A plot of void denuded zone as a function inverse irradiation temperature is plotted in Figure 42a and as a function of inverse annealing temperature in Figure 42b. Reasonable straight lines have been drawn through both the irradiation and annealing data and activation energy determined. The activation energy values for χ plot are 0.32 eV and for χ^2 plot should be 0.64 eV. The value of 0.64 eV is hard to explain because vacancy migration energy for Mo is ~ 1.95 eV. Although rationalization of the activation energy value of 0.64 eV is not possible, it is interesting to note that there is no difference

GRAIN BOUNDARY VOID
DENUDED ZONE WIDTH, χ , Å

GRAIN BOUNDARY VOID
DENUDED ZONE WIDTH, χ , Å

Figure 42 GRAIN BOUNDARY VOID DENUDED ZONE WIDTH AS A FUNCTION OF INVERSE TEMPERATURE, (a) IRRADIATION, (b) ANNEALING FOR Mo AND Mo-0.5Ti.

between the process occurring during irradiation or annealing. Furthermore, the straight line relationship can possibly be used in reactor temperature monitoring.

The other important aspect of grain boundary denuding is on the nature of failure in service. One can imagine the void denuded zone and grain interior as a composite of hard and soft material zones. The flow stress for the denuded zone would be much smaller than for the grain interior (due to void hardening, see next section) and so some deformation can occur in the void denuded zone before failure. Thus, a material with the void denuded zone would more likely fail with some ductility and avoid possible catastrophic failure. More work is necessary to determine the best void denuded zone width conditions to obtain utmost advantage of this effect.

5. Irradiation-Induced Length Change

The changes in linear dimensions of commercially pure molybdenum rods upon fast neutron irradiation were measured using the high vacuum dilatometer which is described in the next section. The specimens were irradiated to a fast neutron fluence range of $1.1 \times 10^{19} \text{ n cm}^{-2} \sim 1 \times 10^{22} \text{ n cm}^{-2}$ at the irradiation temperature of $70^\circ\text{C} \sim 480^\circ\text{C}$. All the specimens studied showed an increase in length after neutron irradiation, the amount of increase being varied from

0.018 to 0.325 percent according to the irradiation condition. The length changes of the specimens irradiated at the reactor ambient temperature increased as a function of fluence, approaching a saturation value of ~ 0.06 percent at about 10^{21} n cm $^{-2}$. The specimens irradiated to the same fluences showed smaller length changes as the irradiation temperature became higher. It should be noted that the specimen irradiated in EBR-II (1×10^{22} n cm $^{-2}$ at 430°C) showed an increment which was 5 to 18 times larger than those irradiated in ORR (1.1×10^{19} n cm $^{-2}$ at 70 - 480°C). The irradiated specimens were annealed in high vacuum ($\sim 10^{-7}$ torr) up to 1620°C. The ORR specimens showed four recovery regions: at about $0.16 T_m$ (Stage III), $0.22 T_m$ (Stage IV), $0.31 T_m$ (Stage V) and $0.36 T_m$ (Stage VI). With the help of transmission electron microscope, it is suggested that the point defects, cluster defects and dislocation loops are responsible for these recovery stages. The EBR-II specimen showed only two recovery stages: one at $0.36 T_m$ (Stage VI) and the other at $0.54 T_m$ (Stage VII). The stage at $0.54 T_m$ is believed to be attributed to the voids present in the specimen.

5.1 Fluence Effect in Neutron Irradiated Molybdenum

The irradiation condition, sample dimensions and irradi-

ation induced length changes are shown in Table XIV. In the table, the total fractional length change, $\Delta l/l$, was calculated by subtracting the length of the post-irradiation annealed specimen from that of the as-irradiated specimen as follows:

$$\frac{\Delta l}{l} = \frac{l_i - l}{l}$$

where l_i = Length of as-irradiated specimen.
 l = Length of post-irradiation annealed specimen (up to 1620°C).

All the specimens examined in this study showed an increase in length after neutron irradiation. At the same irradiation temperature (70°C), the irradiation induced length changes increased with the fast neutron fluences. Their trends are plotted in Figure 43 on semi-log scale, along with other data obtained from Adam et al. (1958)²⁷ and Kissinger et al. (1968).²⁸ This figure shows that the rate of length increments increases with the fluence up to about $1 \times 10^{19} \text{ n cm}^{-2}$ and then decreases at the higher fluences approaching a saturation level of 0.06 percent at $10^{21} \text{ n cm}^{-2}$ or higher. The saturation effect of irradiation-induced length increments was also observed in the early studies by

TABLE XIV

IRRADIATION-INDUCED LENGTH CHANGES OF MOLYBDENUM AND RECOVERY PEAK TEMPERATURES

Mo Specimen Number	Irradiation Condition Fluence, ϕ (n, cm^2)	Irradiation Condition Temperature ($T_i, ^\circ C$)	Sample Dimension (mm)	Total Length Change (%)	Peak Temperature of Recovery Spectra				
					Stage III 0.16 T_m	Stage IV 0.22 T_m	Stage V 0.31 T_m	Stage VI 0.36 T_m	Stage VII 0.54 T_m
504(a)	1.1×10^{19}	70	51.0x3.0	0.023	175°C	320°C	635°C	785°C	Not Observed
2284(a)	7×10^{19}	70	47.6x3.0	0.041	180°C	320°C	635°C	770°C	Not Observed
925(a)	1.5×10^{21}	70	50.7x3.0	0.056	175°C	420°C	640°C	760°C	Not Observed
2275(a)	5×10^{19}	380	47.6x3.0	0.020	Not Observed	Not Observed	655°C	800°C	Not Observed
2285(a)	5×10^{19}	480	47.6x3.0	0.018	180°C	Not Observed	695°C	775°C	Not Observed
1A-4(b)	1×10^{22}	430	47.6x1.3	0.325	Not Observed	Not Observed	Not Observed	795°C	1,280°C

(a) Other specimens irradiated in ORR.

(b) Irradiated in EBR-II.

Figure 43 THE EFFECT OF FAST NEUTRON FLUENCE ON THE LENGTH CHANGES OF MOLYBDENUM IRRADIATED AT 70°C

Kissinger et al.²⁸ The small data scatter, shown in the figure, between this study and those of earlier workers is believed to be due for the most part to the difference in the irradiation temperature and in the impurity content of the specimens. A typical as-irradiated microstructure of molybdenum irradiated at 70°C consists of a high density of black spots; small dislocation loops and rafts. The nature of the microstructure for different fluences is the same, but the density and the size of the defects (specifically the rafts) vary from one fluence to another (Sikka,⁽⁵⁾ 1973). The raft density decreases with higher fluence, while the size increases with the fluence. This suggests that the ratio of point defects to cluster defects decreases with the fluence. If this is the case, the saturation effect of irradiation-induced length increments can easily be explained since the specific contribution of the defects to the length change decreases exponentially as the defect size increases (Damask,⁽²⁹⁾ 1963).

5.2 Effect of Irradiation Temperature

Figure 44 shows the effect of the irradiation temperatures on the irradiation induced length increments. The values at 380° and 480°C were obtained from the specimens irradiated to a fast neutron fluence of $5 \times 10^{19} \text{ n cm}^{-2}$ and the one at 70°C was obtained from the interpolation of

Figure 44 THE EFFECT OF IRRADIATION TEMPERATURE ON LENGTH CHANGES OF MOLYBDENUM IRRADIATED TO A FAST NEUTRON FLUENCE OF $1 \times 10^{19} \text{ n cm}^{-2}$ (THIS STUDY) AND $2.5 \times 10^{19} \text{ n cm}^{-2}$ (BRIMHALL ET AL.)

Figure 43. For comparison, other data obtained from Brimhall et al.³⁰ (1972) are plotted in the same figure. The lower values of Brimhall's³⁰ data are believed to be due to the lower fluences ($2.5 \times 10^{19} \text{ n cm}^{-2}$). The length increments became smaller at higher temperatures suggesting that more defects are annealed out during irradiation at higher temperatures and/or more point defects convert to the cluster defects which contribute less to the length changes.

Although not included in the figure, the specimen irradiated in EBR-II ($1 \times 10^{22} \text{ n cm}^{-2}$ at 430°C) showed an irradiation-induced length increment of 0.325 percent, which is about 15 times higher than those irradiated in ORR ($5 \times 10^{19} \text{ n cm}^{-2}$ at 380° and 480°C). It is likely that this high value is due to the presence of voids. The presence of voids was confirmed in this study using transmission electron microscope in the specimen annealed at 900°C . This suggests that the voids are not only good sinks for the vacancies, but also very stable at the irradiation temperature. Consequently, the presence of the voids decreases the self-irradiation annealing and much higher length changes are resulted, compared to those without the voids. In Figure 44, the Brimhall's³⁰ data suggest that the point defects could contribute to the length changes as significantly as

the voids. This statement may be true for the low fluence and low temperature level. In the high fluence and high temperature regime, the voids are believed to be the most dominant factor which contributes to the length changes.

5.3 Annealing Behavior of Irradiation-Induced Length Changes

The irradiated specimens were heated continuously with a linear heating rate of $0.5^{\circ}\text{C}/\text{min.}$ from 70° to 900°C , and then held at the highest temperature for two hours before cooling. The temperature and length change of the specimens were continuously plotted on the X-Y recorder, and then the specimens were isochronal-annealed for one hour at each annealing temperature from 1000° to 1600°C . The irradiation-induced length increments of the ORR specimens were recovered during the linear continuous heating annealing (up to 900°C), and no further recovery was observed in the isochronal annealing temperature range (1000° - 1600°C). Some of the typical annealing curves of these specimens are plotted in Figure 45. These annealing curves show four major recovery stages: $0.16 T_m$ (Stage III), $0.22 T_m$ (Stage IV), $0.31 T_m$ (Stage V), and $0.36 T_m$ (Stage VI). The irradiation-induced length increment of the EBR-II specimen showed only two recovery stages; one at $0.36 T_m$ (Stage VI) and the other at $0.54 T_m$ (Stage VII), See Figure 46 When annealed at 900°C

Figure 45 RECOVERY OF FAST NEUTRON IRRADIATION INDUCED LENGTH INCREMENT OF RECRYSTALLIZED MOLYBDENUM AS A FUNCTION OF ANNEALING TEMPERATURE.

for two hours, the microstructure of this specimen revealed dislocation segments and small voids. The voids were not observed in the specimen annealed at 1600°C. Therefore, it is believed that the voids are responsible for the recovery stage at $0.54 T_m$. This recovery stage was not observed in any of the ORR specimens. In Figure 46, the recovery curve of one of the ORR specimens is plotted along with that of EBR-II specimen. This figure suggests that the cluster defects mainly contribute to the irradiation-induced length increments in the ORR specimens, and the cluster defects and the voids each contribute 50 percent to the irradiation-induced length increments in the EBR-II irradiated specimens to $1 \times 10^{22} \text{ n cm}^{-2}$ at 430°C. At higher irradiation temperatures and fluences, it is likely that the voids are the dominant factor which contributes to the length changes, since the voids are stable up to $0.54 T_m$.

6. Dilatometry

6.1 Description of Dilatometer

The dilatometer system constructed in this laboratory capable of measuring small length changes of about 2 inches, long rod shaped specimens with an accuracy of one part in 10^5 over a temperature range of RT - 1000°C in a high vacuum of 10^{-7} torr. The length changes are continuously plotted

Figure 46 RECOVERY OF FAST NEUTRON IRRADIATION INDUCED LENGTH INCREMENT FOR RECRYSTALLIZED Mo AS A FUNCTION OF ANNEALING TEMPERATURE.

on a chart as a function of temperature. The test apparatus, as noted in Figure 47, consists of a linear variable differential transformer, a high vacuum heating furnace, a temperature programmer-controller, an oscillator/demodulator unit, and an X-Y recorder.

The specimen holder is made of clear fused quartz, and consists of a closed outer tube, an inner tube, and a quartz spacer. The dimensions of the outer and inner tubes are 0.33 in. OD, 0.25 in. ID, 10.5 in long, and 0.24 OD, 0.16 ID, 9.5 in. long, respectively. The specimens are small cylinders in shape from 1.7 to 2 inches long and from 50 mil. in diameter. The specimen is inserted into a spacer and then placed in a closed outer quartz tube with an inner quartz

tube seated on the top of the specimen, as illustrated in Figure 48. The outer tube is clamped to the supporting housing of the differential transformer while the inner tube inside it is connected to the armature rod of the transformer. A pair of 10 mil chromel-alumel thermocouple wires is placed at the midpoint of a specimen through the inner tube.

The specimen is heated up to 1000°C in a 560 watt resistance type furnace with a programmed linear continuous heating rate of 0.5°C/min. The furnace is placed inside a

Figure 47
ASSEMBLY OF LVDT TRANSDUCER
AND SPECIMEN HOLDER

Figure 48 SCHEMATIC DIAGRAM OF DILATOMETER

tantalum heat shield chamber to obtain a wide temperature controlled zone. This chamber is cylindrical in shape with a wall thickness of one inch. Its bottom is blocked completely and its top is covered with a one inch thick lid, which has a small hole in its center for the insertion of the quartz tubes. The heating furnace and the heat shield chamber are placed in a high vacuum chamber which gives a vacuum of 10^{-9} torr or higher.

6.2 Calibration of Dilatometer

To insure that the dilatometer system was capable of meeting the desired sensitivity and accuracy requirements, a series of measurements and calibrations were conducted on the system and its components. First the linear variable differential transformer, thermocouples and other components were calibrated, and then the entire system was calibrated as a whole unit. The linear variable differential transformer was calibrated by using a calibration kit. The calibration kit consists of a precision micrometer and a dial gage, and the resolution of both the micrometer and the dial gage is 0.0001 in. The LVDT coil and its armature were placed between the micrometer and the dial gage, with one end of the armature shaft touching the micrometer and the other end touching the dial gage. The LVDT was connected

Figure 49 CALIBRATION MEASUREMENTS OF STANDARD Al, Cu AND Mo

to a potentiometer through the demodulator. The armature displacements of a series of known distances were done by turning the micrometer knob and these were double checked with the dial gage and the corresponding output millivoltage of the LVDT was read from the potentiometer. The thermocouples were calibrated by a comparison technique, using the thermocouple 10404TE P/N 5K0140L of the Thermo-Electric Company as a standard. The X-Y recorder was checked by placing accurate millivoltage signals on the X and Y terminals from an L & N 8686 potentiometer.

The dilatometer was calibrated as an integrated measurement system using several standard specimens of known chemistry. The standard specimens were 99.999 percent aluminum, 99.999 percent copper, and commercially pure, 99.98 percent, recrystallized molybdenum. These specimens were subjected to a linear continuous heating ($0.5^{\circ}\text{C}/\text{min}$) and the changes in length versus temperature were plotted on the X-Y recorder as shown in Figure 49. Several runs were conducted for each material and the results were examined for consistancy and for accuracy. The reproducibility was excellent and the coefficients of linear thermal expansion of the standard specimens calculated from the calibration measurements were in good agreement with the published values. The results are summarized in Table XV along with the published values.

TABLE XV
COEFFICIENTS OF LINEAR THERMAL EXPANSION

MATERIAL	TEMPERATURE RANGE (°C)	COEFFICIENT (in./in./°C)	OBSERVERS
Aluminum (99.95%)	20-100	23.8×10^{-6}	Nat. Bureau of Standards ⁴
	20-100	23.6×10^{-6}	Fink et al ⁴
	20-100	23.7×10^{-6}	Dick ⁴
	(99.996%) 20-100	23.6×10^{-6}	Metals handbook ⁷
	(99.999%) 40-100	23.8×10^{-6}	This Study
	(99.95%) 20-300	25.7×10^{-6}	Nat. Bureau of Standards ⁴
	(99.996%) 20-300	25.5×10^{-6}	Metals handbook ⁷
(99.999%)	85-338	26.0×10^{-6}	This Study
Copper (Electrolytic)	25-100	16.3×10^{-6}	Nat. Bureau of Standards ⁴
	at 20°C	16.5×10^{-6}	Metals handbook ⁷
	(99.999%) 45-100	16.4×10^{-6}	This Study
Molybdenum	0-100	5.2×10^{-6}	Argent et al ⁸
	at 20°C	5.1×10^{-6}	Reactor handbook ⁹
	(99.98%) 107-271	5.1×10^{-6}	This Study

II NIOBIUM - NIOBIUM - 1% ZIRCONIUM

1.1 Voids

Sheet specimens of Nb and Nb-1Zr, irradiated in Row 2 of EBR-II reactor at 425, 585 and 790°C to a fast neutron fluence of $2.5 \times 10^{22} \text{ n cm}^{-2}$ ($E > 0.1 \text{ MeV}$) have been observed in the as-irradiated and post-irradiation annealed condition. Voids were observed in Nb at all three irradiation temperatures, but were only present at 790°C in Nb-1Zr. The void ordering in to a three dimensional BCC lattice was also observed at in Nb, but only at 790°C. The BCC void lattice parameter was $\sim 660 \text{ \AA}$. The void parameters for Nb and Nb-1Zr in the as-irradiated condition of this investigation and those reported in the literature are summarized in Table XVI. The summary of complete void removal temperature has been included in Table X. Details of voids and their thermal stability has recently been published²⁴ (Voids in Neutron Irradiated and Annealed Niobium and Niobium-1% Zirconium Alloy by D. J. Michel and J. Moteff).

A mechanism which can suppress void nucleation in these alloys has been recently proposed by Smidt and Sprague.³¹ The basic feature of the mechanism is a reduction of the vacancy supersaturation by vacancy trapping at oversize solute atoms. To illustrate the effectiveness of this mechanism in the

SUMMARY OF VOID AND SWELLING DATA FOR NEUTRON AND ION BOMBARDED Nb AND Nb-1Zr

Material	Purity	Irradiation Temperature		Nature of Radiation	Neutron Fluence $\phi, n\text{ cm}^{-2}$	Particle Energy MeV	Displacement Per Atom DPA	Void Concentration $N_v, \text{voids cm}^{-3}$	Average Void Diameter $d, \text{\AA}$	Total Void Volume Fraction $\Delta V/V, (\%)$	Investigators
		$T, ^\circ\text{C}$	T/T_m								
Nb	-	470	0.27	neutrons	3.9×10^{20}	>1.0	~ 0.6	3×10^{16}	20	0.01	Elen, Hamburg and Mastenbroek
		650	0.34	neutrons	5.5×10^{20}	>1.0	~ 0.9	8×10^{15}	60	0.09	
		750	0.37	neutrons	4.1×10^{20}	>1.0	~ 0.6	5×10^{14}	125	0.05	
Nb	99.998	600	0.33	neutrons	5.0×10^{20}	>0.1	~ 0.4	10^{16}	50-60	0.1-0.2	Adda
		900	0.44	neutrons	5.0×10^{20}	>0.1	~ 0.4	0	0	0	
Nb		425	0.26	neutrons	2.5×10^{22}	>0.1	~ 26	1.6×10^{17}	70	3.1	Wiffen
		585	0.31	neutrons	2.5×10^{22}	>0.1	~ 26	2.1×10^{17}	71	4.8	
		790	0.38	neutrons	2.5×10^{22}	>0.1	~ 26	2.8×10^{15}	186	1.04	
Nb	99.91	650	0.34	nickel	-	6	-	0	0	0	Kulcinski, Brimhall and Kissinger
		700	0.36	nickel	-	5	~ 5	0	0	0	
		800	0.40	nickel	-	5	~ 5	2×10^{16}	45	0.100	
		900	0.44	nickel	-	5	~ 5	1.5×10^{15}	220	0.83	
		900	0.44	tantalum	-	7.5	~ 8	2.4×10^{15}	200	1.00	
		1000	0.47	nickel	-	5	~ 5	1.5×10^{14}	350	0.34	
Nb	99.91	800	0.40	tantalum	-	7.5	1	6×10^{15}	38	0.04	Brimhall and Kulcinski
		800	0.40	tantalum	-	7.5	3	8×10^{15}	45	0.09	
		800	0.40	tantalum	-	7.5	30	1.8×10^{16}	56	0.65	
		800	0.40	tantalum	-	7.5	60	2.0×10^{16}	66	1.5	
		800	0.40	tantalum	-	7.5	90	3.0×10^{16}	105	3.5	
		800	0.40	tantalum	-	7.5	300	3.5×10^{16}	106	4.5	
Nb	99.985	800	0.40	tantalum	-	7.5	15	1.6×10^{16}	70	0.65	Brimhall and Kulcinski
		800	0.40	tantalum	-	7.5	45	2.0×10^{16}	75	1.0	
		800	0.40	tantalum	-	7.5	115	3.2×10^{16}	96	3.5	
Nb	99.91	900	0.44	tantalum	-	7.5	1	1.1×10^{16}	35	0.07	Brimhall and Kulcinski
		900	0.44	tantalum	-	7.5	3	8×10^{15}	55	0.13	
		900	0.44	tantalum	-	7.5	10	7.5×10^{15}	120	1.20	
		900	0.44	tantalum	-	7.5	25	2×10^{15}	165	0.90	
		900	0.44	tantalum	-	7.5	50	5.5×10^{15}	180	3.0	
		900	0.44	tantalum	-	7.5	100	2.0×10^{15}	210	3.0	
		900	0.44	tantalum	-	7.5	300	5.5×10^{15}	245	4.0	

TABLE XVI (CONT.)

SUMMARY OF VOID AND SWELLING DATA FOR NEUTRON AND ION BOMBARDED Nb AND Nb-1Zr

Material	Purity	Irradiation Temperature		Nature of Radiation	Neutron Fluence $\phi, n\text{ cm}^{-2}$	Particle Energy MeV	Displacement Per Atom DPA	Void Concentration $N_v, \text{voids cm}^{-3}$	Average	Total Void Volume Fraction $\Delta V/V, (\%)$	Investigators			
		$T_i, ^\circ\text{C}$	T/T_m						Void Diameter $\bar{d}, \text{\AA}$					
Nb	-	500	0.29	nickel	-	3.0	50	-	-	-	Loomis, Taylor, Klippert and Gerber			
		600	0.32	nickel	-	3.0	50	--	-					
Nb	-	500	0.29	nickel	-	3.0	50	-	-	O ₂ ppm		Loomis, Taylor Klippert and Gerber		
		600	0.32	nickel	-	3.0	50	-	-	10	68		400	900
		700	0.36	nickel	-	3.0	50	-	-	0.001	-		-	0.001
		800	0.40	nickel	-	3.0	50	-	-	0.02	-		-	0.011
		900	0.44	nickel	-	3.0	50	-	-	0.15	-		-	0.015
		1000	0.47	nickel	-	3.0	50	-	-	0.8	-		-	0.22
										3.5	2.0		2.0	2.0
Nb	-	425	0.26	neutrons	2.5×10^{22}	$E > 0.1$	~ 26	2.5×10^{16}	55	0.23	Michel and Moteff			
		585	0.31	neutrons	2.5×10^{22}	$E > 0.1$	~ 26	2.9×10^{16}	61	0.37				
		790	0.38	neutrons	2.5×10^{22}	$E > 0.1$	~ 26	3.7×10^{14}	152	0.21				
Nb	-	430	0.26	neutrons	$\sim 1 \times 10^{22}$	$E > 1$	~ 21	3.2×10^{16}	46	0.163	Sikka and Moteff			
		560	0.31	neutrons	$\sim 1 \times 10^{22}$	$E > 1$	~ 21							
		700	0.36	neutrons	$\sim 1 \times 10^{22}$	$E > 1$	~ 21							
		800	0.40	neutrons	$\sim 1 \times 10^{22}$	$E > 1$	~ 21							
		900	0.44	neutrons	$\sim 1 \times 10^{22}$	$E > 1$	~ 21							
		1000	0.47	neutrons	$\sim 1 \times 10^{22}$	$E > 1$	~ 21							
Nb-1Zr	-	425	0.26	neutrons	2.5×10^{22}	$E > 0.1$	~ 26	$< 2 \times 10^{14}$	510	< 1.4	Wiffen			
Nb-1Zr	-	425	0.26	neutrons	2.5×10^{22}	$E > 0.1$	~ 26	0	0	0	Michel and Moteff			
		585	0.32	neutrons	2.5×10^{22}	$E > 0.1$	~ 26	0	0	0				
		790	0.38	neutrons	2.5×10^{22}	$E > 0.1$	~ 26	1.8×10^{14}	575	2.78				

niobium-1% zirconium alloy, vacancy concentration calculations were performed using the proposed model.⁽³¹⁾ Figure 50 shows the results of these calculations for conditions typical of a fast reactor environment. The parameters employed in the calculation were those for niobium and include a 0.4 eV vacancy binding energy, a dislocation density of 10^7 disl/cm², a 1.3 eV interstitial migration energy, a 1.9 eV vacancy migration energy, and a 2.2 eV vacancy formation energy.³² Comparable results, on the basis of homologous temperature, to those in Figure 50 were previously determined for iron using the model.⁽³¹⁾

Figure 50 shows that the free vacancy concentration at all temperatures is reduced by at least one order of magnitude as the result of vacancy trapping. This figure also indicates that vacancy trapping should be effective in suppressing void formation in the niobium-1 wt.% zirconium-alloy during irradiation at temperatures up to $\sim 0.55 T_m$ (1230°C). The formation of voids in the alloy specimen irradiated at 790°C ($0.39 T_m$) is therefore considered anomalous and must be related to effects other than vacancy trapping.

It has been suggested that to be effective in void nucleation an impurity atom must produce a decrease in surface energy of niobium. A direct indication that impurity migration was responsible for the void formation in the

Figure 50 FREE VACANCY CONCENTRATION AS A FUNCTION OF TEMPERATURE CALCULATED FOR Nb FOR THE CASES OF NO TRAPPING AND 0.4 eV BINDING ENERGY BETWEEN VACANCIES AND Zr SOLUTE ATOMS. CALCULATION BASED ON THE MODEL BY Smidt and Sprague.

Nb-12r alloy during irradiation at 790°C is provided by computing the arrival rate ratio for impurity atoms and vacancies, B_X/B_V , where B_X is the arrival rate for impurity atoms and B_V is the arrival rate for vacancies for void formation per unit area and unit time. Assuming the conditions for simultaneous impurity atom and vacancy migration, the relationship between D_X and D_V , the diffusivities of impurity atoms and vacancies, respectively can be expressed by,

$$\frac{D_X}{D_V} = \exp [(H_X - H_V)/KT] \quad (35)$$

where H_X and H_V are the impurity atom and vacancy migration energies, K is the Boltzmann constant and T is the °K. The arrival rate ratio is then approximated by, ⁽³³⁾

$$\frac{B_X}{B_V} = \frac{D_X C_X}{D_V C_V} \quad (36)$$

where C_X and C_V are the respective impurity atom and vacancy concentration.

Equations (35 and (36) applied to the present results at both the 585°C (0.31 T_m) and 790°C (0.39 T_m) irradiation temperatures to determine the B_X/B_V ratios for the case of

oxygen. The oxygen migration energy (H_o) used in the calculation was taken as 1.17 eV. The vacancy migration energy used for Nb was 1.9 eV. The vacancy concentration at 585 and 790°C was taken from Figure 50 for the case of no trapping and when trapping was present. The oxygen concentration of the alloy was 200 ppm by weight (1162 ppm atomic). The calculated values for B_o/B_v are listed in Table XVII.

The results in Table XVII show that the maximum arrival-rate ratio occurs at 790°C when the vacancy concentration is decreased by vacancy trapping. Where no trapping is involved (i.e. pure Nb) the results indicate that oxygen could be slightly effective in the void nucleation process during irradiation at 790°C. The calculations also show that oxygen migration had no effect on void nucleation at 585°C or lower temperatures where vacancy migration is dominant. The effect of nitrogen and carbon is also listed in Table XVII and discussed by Michel and Moteff.⁽²⁴⁾

1.2 Microstructure

Although the study of sheet specimen of Nb and Nb-1Zr has been completed, (See Sec. 1.1) it is only limited to three irradiation temperatures. A systematic and detailed study on Nb and Nb-1Zr specimens 50 mil (1.25 mm) in diameter irradiated in row 7 of EBR-II reactor at six different temperatures, 430, 580, 700, 800, 900 and 1000°C to a

TABLE XVII

ARRIVAL-RATE RATIOS FOR IMPURITY ATOMS AND VACANCIES
IN Nb AND Nb-1Zr

Temperature (°C)	Nb (No Vacancy Trapping)			Nb-1Zr (Vacancy Trapping)		
	O	N	C	O	N	C
585	7.6×10^{-4}	2.7×10^{-5}	1.8×10^{-3}	1.4×10^{-2}	5.0×10^{-4}	3.4×10^{-2}
790	7.8×10^{-2}	3.5×10^{-3}	9.4×10^{-2}	9.2×10^{-1}	4.0×10^{-2}	1.1

fast neutron fluence of $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) has been initiated and some preliminary results are presented here.

A typical micrograph for niobium irradiated at 430°C to a fast neutron fluence of $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) is shown in Figure 51. The micrograph plane is (110) and the $\bar{g}$ vector of [001]. The various types of defect agglomerates are marked by the letters a - e and are described under separate headings.

a-type - are the black spot clusters, similar to that reported by Loomis et al.³⁴ for room temperature irradiation in the neutron fluence range of $3 \times 10^{17} - 1.5 \times 10^{19} \text{ n cm}^{-2}$ ($E > 0.1 \text{ MeV}$). The black spot size is $\sim 50\text{-}60 \text{ \AA}$ and represents only a small fraction of the total defect cluster density at $430 \pm 5^\circ\text{C}$. Molybdenum neutron irradiated at $430 \pm 5^\circ\text{C}$ to the fast neutron fluence of $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) also showed similar black spot clusters.

b-type - represent dislocation loops. The size of the loops is $\sim 100\text{-}150 \text{ \AA}$ and are similar to that observed during room temperature irradiation by Loomis et al.³⁴ The loop density appears to be slightly greater than the black spot cluster density

c-type - identified defect cluster agglomerate rafts. These types of defects are similar to those observed in neutron

figure 51 REPRESENTATIVE MICROGRAPH OF NIOBIUM IRRADIATED AT $430 \pm 5^\circ\text{C}$ TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

irradiated molybdenum by Brimhall and Mastel⁽⁶⁾, Elen et al.,⁽¹²⁾ and Sikka and Moteff⁽³⁵⁾; and in tungsten by Sikka and Moteff;⁽³⁶⁾ and in vanadium by Elen et al.⁽¹²⁾. The defect agglomerate, type a and b, represent the planar defect clusters, whereas rafts, c-type are the the agglomeration of a large number of black spot clusters and/or loops. Rafts in niobium have not been reported earlier.

d-type - identifies dislocation segments which might have been produced by coalescence of small loops or represent the pre-irradiation condition.

e-type - represent the three dimensional cluster defect voids. The voids parameters have been determined as listed in Table XVI.

The void density at 430°C was 3.22×10^{16} voids cm^{-3} and average void size of 46 Å. The void density decreases and size increased with increasing irradiation temperature and is shown in Figure 52. It is interesting to note that the very large voids were present even at 1000°C for EBR-II irradiation, where as Adda¹⁵ reported no voids at 900°C for a neutron fluence of 5.0×10^{20} n cm^{-2} ($E > 0.1$ MeV).

The more detailed study on as-irradiated and post-irradiated annealed microstructure and hardening are in progress.

430 C

700 C

500A

900 C

1000 C

FIGURE 52

TYPICAL MICROGRAPHS SHOWING VOIDS IN Nb IRRADIATED IN ROW 7 OF EBR-II AT THE INDICATED TEMPERATURES (430-1000°C) TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ N CM}^{-2}$ ($E > 1 \text{ MeV}$).

III TUNGSTEN AND TUNGSTEN -25% RHENIUM

The study on W and W-25Re irradiated in Row 7 of EBR-II reactor at six different temperatures, 430, 580, 700, 800, 900 and 1000°C to a fast neutron fluence of $\sim 1 \times 10^{22} \text{ n cm}^{-2}$, in only as-irradiated condition is in progress. The microstructure in the as-irradiated condition has shown the presence of voids in W for all six temperatures and their absence in W-25Re. Such a statement was supported by bulk density measurements, which showed essentially no swelling for W-25Re, See Figure 53. The microstructure of W-25Re consisted of precipitates whose details are presented in a recent paper by Sikka and Moteff.³⁸ More work is underway to characterize in detail the as-irradiated structure of W and W-25Re.

Figure 53 A PLOT OF SWELLING DATA AS A FUNCTION OF IRRADIATION TEMPERATURE FOR W AND W-25Re IRRADIATED IN ROW 7 OF EBR-II TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

IV IRRADIATION HARDENING

It is commonly accepted that the mechanical properties of metals are primarily governed by the movement of dislocations. The plastic flow of the metal is related to the ease of dislocation movement through the lattice. The flow stress necessary to move the dislocations in the metal can be modified by the frictional stress produced by the interaction of moving dislocations with any and/or combination of barriers. The elevated temperature (irradiation temperature $T_i > 0.19 T_m$) neutron irradiations in the BCC metals (Mo, Nb, V, W...) and alloys (Mo-0.5Ti, Nb-1Zr, W-25Re....) may produce any or all of the following types of observable defect clusters.

- i) Black spots (vacancy or interstitia type; diameter d , $< 70-80 \text{ \AA}$).
- ii) Loops (vacancy or interstitial type; $d > 70-80 \text{ \AA}$).
- iii) Rafts (agglomerates of black spot clusters and small loops; exist on $\{111\}$ type planes and pointing in $\langle 110 \rangle$ direction. The rafts are about $60-100 \text{ \AA}$ thick, $1000-2000 \text{ \AA}$ in length and width.
- iv) Dislocations (segments of large loops).
- v) Voids (vacancy clusters; $d \geq 30-40 \text{ \AA}$, randomly distributed or having ordered void structure).

vi) Precipitates (W-Re).

vii) Transmutation atoms (helium, hydrogen, rhenium, etc.)

The relative magnitudes of the above defect densities will, of course, depend on variables such as the neutron flux densities, neutron fluence levels, neutron spectrum (displacement rate, dpa sec^{-1}), irradiation temperatures, initial substructure of irradiated material including the impurity level and the post-irradiation annealing temperature.

Thus, it can be stated that the elevated temperature neutron irradiations can, in general, increase the frictional stress due to the interaction of mobile dislocations with some or all of the above mentioned defect clusters. The result of the dislocation interactions with irradiation induced defects, excluding in-reactor radiation enhanced diffusion, is to increase the strength, but at the cost of a large reduction in the low temperature ductility. The loss of ductility associated with an increase in the irradiation strength is a significant concern from a design point of view and therefore, an understanding of the hardening mechanisms is very important.

A detailed review of the hardening models and their applicability to irradiation hardening has been presented

in a recent paper⁽³⁹⁾ [The Influence of Irradiation Temperature on the Hardening Behavior of the Refractory BCC Metals and Alloys by J. Moteff, D. J. Michel and V. K. Sikka]. The following three equations were used to calculate the hardening contributions from the three classes of cluster defects,

$$\Delta H_{\text{loops}} = 3\mu b \sqrt{N_L d_L} \quad (39)$$

$$\Delta H_{\text{disl.}} = 3\mu b \sqrt{\rho} \quad (40)$$

$$\Delta H_{\text{voids}} = 6\mu b \sqrt{N_V d_V} \quad (41)$$

where, N_L and d_L are the loop density and size, ρ is the dislocation density and N_V and d_V are the void density and size. b is the Burgers vector.

The total experimental observed hardening is the sum of hardness increments due to each of three classes of cluster defects and is given by the following equations,

$$\Delta H_{\text{total}} = \Delta H_{\text{loops}} + \Delta H_{\text{disl.}} + \Delta H_{\text{voids}} \quad (42)$$

$$\Delta H_{\text{total}} = [\Delta H_{\text{loops}}^2 + \Delta H_{\text{disl.}}^2 + \Delta H_{\text{voids}}^2]^{1/2}$$

The cluster parameters for Mo, Mo-0.5Ti, Nb and Nb-12Zr for irradiation conditions are presented in Table XVIII and XIX. The cluster parameter for Mo irradiated at 430°C to a

Radiation Induced Defect Densities^(a)

TABLE XVIII

Irradiation Temperature $T_i, ^\circ\text{C}$	Loops		Voids		Dislocations
	Average Size $d_L, \text{\AA}$	Density $N_L, \text{Loops cm}^{-3}$	Average Size $d_V, \text{\AA}$	Density $N_V, \text{Voids cm}^{-3}$	$N_D, \text{Dislocation cm}^{-2}$
<u>Mo</u>					
430	66	1.1×10^{16}	45	5.4×10^{16}	3.9×10^9
580	130	2.5×10^{14}	46	5.8×10^{16}	2.0×10^9
700	450	1.2×10^{13}	42	4.1×10^{16}	8.6×10^8
800	-	-	52	1.5×10^{16}	8.8×10^8
900	-	-	73	6.7×10^{15}	5.5×10^8
1000	-	-	100	2.9×10^{15}	
<u>Mo-0.5Ti</u>					
430	80	8.6×10^{15}	37	9.8×10^{16}	2.9×10^9
580	130	3.3×10^{14}	46	7.8×10^{16}	2.1×10^9
700	260	4.2×10^{13}	49	5.2×10^{16}	1.0×10^9
800	-	-	53	1.9×10^{16}	1.4×10^9
900	-	-	86	6.9×10^{15}	
1000	-	-	100	3.3×10^{15}	1.5×10^9

(a) EBR-II, Row 7 irradiations to a fast neutron fluence of about $1.0 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1.0 \text{ MeV}$).

TABLE XIX

Irradiation Temperature $T_i, ^\circ\text{C}$	Loops		Voids		Dislocations
	Average Size $d_L, \text{\AA}$	Density $N_L, \text{Loops cm}^{-3}$	Average Size $d_V, \text{\AA}$	Density $N_V, \text{Voids cm}^{-3}$	$N_D, \text{Dislocation cm}^{-2}$
<u>Nb</u>					
425	27	2.6×10^{15}	55	2.3×10^{16}	3.2×10^9
585	44	1.4×10^{15}	61	2.9×10^{16}	2.4×10^9
790	51	4.4×10^{14}	150	8.7×10^{14}	2.0×10^9
<u>Nb-12r</u>					
425	100	7.3×10^{16}	-	-	2.1×10^9
585	110	1.3×10^{16}	-	-	1.7×10^9
790	330	7.1×10^{13}	580	1.6×10^{14}	1.7×10^8

(a) EBR-II, Row 2 irradiations to a fast neutron fluence of about $2.5 \times 10^{22} \text{ n cm}^{-2}$ ($E > 0.1 \text{ MeV}$).

fast neutron fluence of $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) and post-irradiation annealed at various temperatures are summarized in Table XX. Using the values of modulus and Burgers vector and the cluster parameters from Tables XVIII through XX, individual contributions for three classes of cluster defects have been calculated from Equations (39) through (41) and total contributions from Equation (42) and (43). The values of the individual hardening and total hardening for Mo, Mo-0.5Ti and Nb, Nb-1Zr are plotted as a function of irradiation temperature in Figures 54, 55 and 56. The individual and total hardening for Mo irradiated at 430°C is plotted as a function of annealing temperature in Figure 57.

The experimental results for total irradiation hardening are in excellent agreement with the sum of individual hardening based on Equation (43). The relative hardening contribution from three classes of cluster defects are shown as a function of homologous temperature in Figure 58. Among the three classes of clusters, voids seems to contribute maximum to the hardening and are the most stable defect clusters. More details on thermal stability of hardening due to various types of clusters are available in the paper⁽²⁵⁾ (Stability of the Defect State in Neutron Irradiated

TABLE XX

SUMMARY OF CLUSTER DENSITY FOR Mg IRRADIATED AT 430°C AND
POST IRRADIATION ANNEALED FOR ONE HOUR AT VARIOUS TEMPERATURES

Annealing Temperature $T_A, ^\circ\text{C}$	Rafts $N_R, \text{Rafts cm}^{-3}$	Average Size $d_L, \text{\AA}$	Density $N_L, \text{Loops cm}^{-3}$	Average Size $d_V, \text{\AA}$	Density $N_V, \text{Voids cm}^{-3}$	Dislocations $N_D, \text{Dislocations cm}^{-3}$
430(a)	7.4×10^{14}	66	1.1×10^{16}	45	5.4×10^{15}	1.2×10^9
550	7.4×10^{14}	69	1.1×10^{16}	43	4.2×10^{16}	-
700	ND(b)	80	8.3×10^{15}	47	4.0×10^{16}	-
800	ND(b)	125	6.2×10^{14}	46	3.8×10^{16}	2.54×10^{19}
900	ND(b)	388	6.4×10^{13}	47	3.1×10^{16}	1.51×10^9
1000	ND(b)	456	1.9×10^{13}	56	2.1×10^{16}	1.59×10^9
1100	ND(b)	ND(b)	ND(b)	59	1.1×10^{16}	1.72×10^9
1300	ND(b)	ND(b)	ND(b)	81	1.7×10^{15}	-
1350	ND(b)	ND(b)	ND(b)	220	8.5×10^{13}	

(a) Represents the as-irradiated densities.

(b) ND means not detected.

Figure S4 Comparison of the calculated hardness increment with experimental data as a function of irradiation temperature for Mo irradiated at $\sim 1 \times 10^{22} \text{ n cm}^{-2}$, $E > 1.0 \text{ MeV}$.

Figure 55

Comparison of the calculated hardness increment with experimental data as a function of irradiation temperature for Mo-0.5Ti irradiated at $\sim 1 \times 10^{22} \text{ n cm}^{-2}$, $E > 1.0 \text{ MeV}$.

Figure 56 Comparison of the calculated hardness increment with experimental data as a function of irradiation temperature for Nb and Nb-12Zr irradiated at $\sim 2.5 \times 10^{22} \text{ n cm}^{-2}$, $E > 1.0 \text{ MeV}$.

Figure 57 COMPARISON OF THE CALCULATED HARDNESS INCREMENT WITH THE EXPERIMENTAL DATA AS A FUNCTION OF ANNEALING TEMPERATURE FOR Mo IRRADIATED AT 430 TO A FAST NEUTRON FLUENCE OF $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

Figure 58 Schematic showing the recovery of the irradiation induced hardening following annealing heat treatments. Typical of molybdenum irradiated at $\sim 430^\circ\text{C}$ ($0.24 T_m$) to a neutron fluence of about $10^{22} \text{ n cm}^{-2}$. Transmission electron microscopy of the observable defects suggest the regions where the defects may contribute to the hardening.

Molybdenum by V. K. Sikka and J. Moteff).

V. RADIATION ENHANCED PROCESSES

On comparison of post-irradiation annealed microstructure at a temperature to that formed during irradiation, it is noticed that the processes are enhanced or occur at a lower temperature during irradiation than during annealing. Some of the examples of such enhanced processes are listed below:

- i) Rafts were observed in Mo irradiated in EBR-II at 430°C to a fast neutron fluence of $\sim 1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) and no rafts were observed at 580°C, when irradiated under the identical conditions. Rafts formed at 430°C when subjected to one hour post-irradiation anneals at various temperatures were only removed at 700°C. Thus, it seems that at least a 100°C lower temperature is necessary for raft elimination in reactor than outside.
- ii) Black spot clusters formed in Mo irradiated in EBR-II at 430°C to a fast neutron fluence of $\sim 1 \times 10^{22} \text{ n cm}^{-2}$, were absent at 700°C irradiation under the identical conditions. The one hour post-irradiation anneals removed black spot clusters and small loops only at 800°C. Thus, one observes again a 100°C difference between in-reactor and outside.
- iii) Brimhall et al.¹⁸ showed that upper limits for void forma-

tion in Mo is $\sim 1380^{\circ}\text{C}$. We have annealed voids formed at 430°C at various temperatures and shown that complete void removal occurs only at 1450°C . Thus, there is $\sim 100^{\circ}\text{C}$ difference in no void temperature between in-reactor and outside.

Details of radiation enhanced processes are being studied.

VI IRRADIATION FATIGUE INTERACTION

(Preliminary Study)

1.1 Introduction

In the past several years, concern over the interaction between processes which affect the mechanical properties of materials in service environments has increased sharply. Studies are advancing in stress corrosion, corrosion fatigue, irradiation creep, and the interaction between creep and fatigue, to name a few. Nowhere are these interactions more important than in nuclear reactor environments, for not only are there several processes operating simultaneously (irradiation damage, corrosion, creep, fatigue and high temperature) but the magnitude of each changes from position to position in the reactor. Materials selection in design considerations must then be based on how a given material reacts when a number of competing processes are imposed which may be drastically different from how a material reacts to each process separately.

An interaction process which will be very important in the design of controlled thermonuclear reactors (CTR), especially those using laser pulses to induce fusion, is the interaction between radiation damage and fatigue. Of the six CTR designs presently envisioned⁽⁴⁰⁾, half are to be

operated in a pulsed mode. This means reactor structural members will have to withstand both periodic loading and a radiation field. Several refractory metals have been mentioned for use in environments such as this, the most promising of which are molybdenum, vanadium, and niobium. A preliminary study has been made to determine the important factors involved in the interaction between simultaneous irradiation and fatigue.

1.2 Development

A very limited number of studies have been directed toward understanding the fatigue properties of BCC metals⁽⁴¹⁻⁴⁴⁾. Some of these studies have shown that the fatigue properties of BCC metals are significantly different from properties exhibited by the group of well studied FCC metals. In particular, the fraction of fatigue life spent in initiating a fatigue crack always accounts for a large part of the total fatigue life in Mo, while initiation time is significantly only for very long fatigue lives in FCC metals. In addition, Stage I crack growth (i.e. crack growth along planes aligned with the maximum resolved shear stress) is absent in Mo, while in FCC metals it accounts for a significant portion of the fatigue life at intermediate to long fatigue lives. The difference in fatigue properties can probably be related directly to actual physical properties

such as stacking fault energy, operating slip systems and Peierls forces, though there remains a good deal of work to be done to understand the actual relationships involved.

The mechanical and microstructural changes in BCC metals due to irradiation are described in several places, including this report. In general, irradiation produces defect clusters whose type, size and distribution depends on several factors including the fluence, the irradiation temperature, and the presence of impurities. The resulting effect on mechanical properties is to reduce ductility, shift the DBTT to higher temperatures and consequently, increase the yield strength and ultimate tensile strength.

The fact that cycling causes hardening through dislocation-dislocation interaction, and irradiation induces hardening through dislocation-defect cluster interaction provides a common ground on which to pursue to interaction between simultaneous irradiation and cycling. The possibilities are: (1) There is a net gain or enhancement of hardening due to both mechanisms working together, (2) a net loss or recovery of hardening due to the hardening mechanisms working against each other, or (3) no discernable change from regular fatigue properties.

It is common in evaluating fatigue results to separate the total strain component into its elastic and plastic com-

ponents⁽⁴⁵⁾,

$$\Delta\epsilon_{\text{tot}} = \Delta\epsilon_E + \Delta\epsilon_P \quad (44)$$

(See Figure 59)

Each component can then be separately related to its effect on fatigue life, N_f (cycles to failure). The elastic strain is related through the Basquin relationship⁽⁴⁶⁾ as,

$$\Delta\epsilon_E = A[N_f]^{-b} \quad (45)$$

where A and b are the fatigue strength coefficient and the fatigue strength exponent respectively.

The plastic strain is related through the well known Manson Coffin relationship as,

$$\Delta\epsilon_P = B[N_f]^{-c} \quad (46)$$

where B and C are the fatigue ductility coefficient and the fatigue ductility exponent respectively.

Combining the elastic and plastic components we have

$$\Delta\epsilon_t = A[N_f]^{-b} + B[N_f]^{-c} \quad (47)$$

Where A , b , B and c are constants for the entire range of $\Delta\epsilon_t$.

Figure 59 STRAIN COMPONENTS VERSUS FATIGUE LIFE

Figure 60 PLASTIC STRAIN VERSUS FATIGUE LIFE

At large total strains, or equivalently, short fatigue lives, the relationship between the total strain and cycles to failure is represented very well by the plastic strain portion alone. In this region the ductile properties of a material have a great effect on the materials ability to withstand fatigue: ductile metals are better able to withstand plastic strains than hard brittle ones. To take the effect of a competing radiation field into account, there must be some determination of its effect on the retention or loss of ductility.

If hardening is enhanced by irradiation, there will be a quicker loss of ductility and a reduction of the fatigue life at a given plastic strain. If hardening is recovered, there will be an accompanying recovery of some ductility and the fatigue life will be longer. (See Figure 60).

For small total strains or long fatigue lives the total strain is well represented by the elastic component. Strength properties are important in this range and irradiation may have the following effects. Enhanced hardening, increase in strength, will cause better fatigue lives while, radiation induced recovery of hardening will degrade the fatigue life (See Figure 61).

These two effects can be combined (See Figure 62) and Equation (47) can be rewritten as,

Figure 61 ELASTIC STRAIN VERSUS FATIGUE LIFE

Figure 62 TOTAL STRAIN VERSUS FATIGUE LIFE

$$\Delta \varepsilon_t = A'(t, \psi) [N_f]^{-b} + B'(t, \psi) [N_f]^{-c} \quad (48)$$

to take into account the effect of irradiation fatigue interaction. The effect could be accounted for by varying either the exponents or coefficients or both. Varying the coefficients alone results in the simplest form of the equation with no loss of generality.

In the range of interest of materials for reactor design, strains will be in the elastic region or:

$$\Delta \varepsilon_t = \Delta \varepsilon_E = A'(t, |\psi|) [N_f]^{-b} \quad (49)$$

this can be rewritten as,

$$[N_f]^b \Delta \varepsilon_E = A'(t, \psi) \quad (50)$$

and $A'(t, \psi)$ has the following boundary and initial conditions,

$$A'(t, \psi) |_{\psi=0} = A \quad (51)$$

and

$$A'(t, \psi) |_{t=0} = A \quad (52)$$

A reasonable functional form for $A'(t, \psi)$ is,

$$A'(t, \psi) = A + \int_0^t D_I(t) \psi(E_n, t) dt \quad (53)$$

where D_I is defined as the interaction damage function and will depend on several other variables, as well as, time. Remembering that,

$$N_f = (t_f)(r) \quad (54)$$

where r is the cycling rate (cycles/sec) and t_f is the time to failure (sec), we can arrive at a transcendental form for the fatigue life. From Equations (50), (53) and (54), we have,

$$[r]^b [t]^b \Delta \epsilon_E = A + \int_0^t D_I(t) \psi(E_n, t) dt \quad (55)$$

which determines the fatigue life. The t where the LHS of Equation (55) equals the RHS is the fatigue life. Equation (55) is amenable to experimental determination. The coefficient A and the exponent b are arrived at from the simple fatigue life curve and the integral is then found as the difference between the simple fatigue curve and the irradiation fatigue curve. In the case of a time invariant flux the integral reduces to,

$$\int_0^t D_I \psi dt \rightarrow |\psi| \int_0^t D_I dt \quad (56)$$

and the damage interaction function, $D_I(t)$, can be determined for a particular case.

The preceding equations were developed on the basis of hardening, even though the equations are general and in practice can and will take other effects into account. Some of the other effects that may possibly be important in radiation fatigue interaction should be mentioned. There is evidence that the presence of voids due to irradiation can cause a significant loss in the elastic properties of a metal⁽⁴⁷⁾. A decrease in Young's modulus relates directly to a decrease in the crack extension force. The beneficial effect that cluster hardening may show could then be offset by a decrease in crack growth resistance. Another effect that defect clusters may have is to provide preferred nucleating sites for cracks. For irradiation below $.5 T_m$ the supersaturation of vacancies due to irradiation may play an important role in nucleating cracks. Finally, the presence of helium may be important depending on whether it segregates to the grain boundaries or forms bubbles in the matrix. The effect of helium implanted in TZM has been studied⁽⁴⁸⁾.

1.3 Testing

Mechanical testing to evaluate the irradiation fatigue interaction is becoming possible with the advent of high

energy neutron sources like the one at Livermore. Fatigue testing machines, like the MTS, are well developed and can offer a wide range of loadings and a good deal of diversity in loading patterns allowing simulation of actual reactor loading conditions. An induction furnace mounted with the MTS can approximate service temperatures. Several design studies^(40,49) have attempted to pin down operating conditions of CTR's so that experiments can be designed to simulate future service conditions.

A test to simulate one CTR design⁽⁴⁹⁾ might be set up as follows. A MTS with an induction furnace and a neutron source with a reasonably high flux would be used. The test temperature would be fixed by the inner wall operating temperature at about 400°C. The cycling rate would be fixed by the operating pulse rate of the reactor at one cycle per second. A cylindrical specimen would be used in an axial strain controlled test. A test matrix is shown in Figure 63, where specimens along the diagonals would be fatigued to failure both with and without a radiation field. The data from these tests would determine A, b, and $D_I(t)$ in Equation (55).

The specimens above the diagonals would be cycled or cycled and irradiated at the same strains as the test above, but these tests would be interrupted before rupture. A set

UNIRRADIATED

DAYS AT 1 CPS (1.2 DAYS = 10^5 CYCLES)									$\Delta\epsilon$
.0012		.012		.12		1.2	4.0	12.0	$\Delta\epsilon_1$
							4.0		$\Delta\epsilon_2$
.0012		.012		.12		1.2			$\Delta\epsilon_3$
					.40				$\Delta\epsilon_4$
.0012		.012		.12					$\Delta\epsilon_5$
			.04						$\Delta\epsilon_6$
.0012		.012							$\Delta\epsilon_7$
	.004								$\Delta\epsilon_8$
.0012									$\Delta\epsilon_9$

IRRADIATED

.0012		.012		.12		1.20	4.0		0
.0012		.012		.12		1.20	4.0	12.0	$\Delta\epsilon_{10}$
							4.0		$\Delta\epsilon_{11}$
.0012		.012		.12		1.20			$\Delta\epsilon_{12}$
					.4				$\Delta\epsilon_{13}$
.0012		.012		.12					$\Delta\epsilon_{14}$
			.04						$\Delta\epsilon_{15}$
.0012		.012							$\Delta\epsilon_{16}$
	.004								$\Delta\epsilon_{17}$
.0012									$\Delta\epsilon_{18}$

Figure 63. IRRADIATION FATIGUE TEST MATRIX

of specimens would be irradiated at zero strain to match the times of the cycled specimens. This set of specimens would then be tensile tested to observe the effects of irradiation alone, cycling alone, and irradiation and cycling on the ductility and strength of the material. This information would be important in determining the irradiation fatigue interaction effect on hardening.

Post test investigation would include a thorough microstructural study of the specimens using transmission electron microscopy and rupture surface characterization using scanning electron microscopy.

1.4 Conclusions

The importance of irradiation fatigue interaction in the design of pulsed laser thermonuclear reactors, and in many other reactors, cannot be understated. Economic and safety considerations will be based to a large extent on the reactor material to stand up to conditions such as this. The ability to determine the dual effects of irradiation and fatigue has become available with the advent of high energy neutron sources, and these studies should be carried out.

VII COMPRESSIVE CREEP OF IRRADIATED MOLYBDENUM

Compressive creep studies on neutron irradiated molybdenum have been initiated. The first series of specimens that will be tested have been irradiated to a fast neutron fluence of $5 \times 10^{19} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) at a temperature of 480°C .

The tests are being conducted using a SATEC model D creep tester equipped with a high temperature vacuum furnace. The load train has been modified to permit the use of a compressive creep fixture.

The first specimen is being tested at 700°C with a stress of 18 kg mm^{-2} . The atmosphere for the test is approximately $8.3 \times 10^{-6} \text{ torr}$.

Figure 64 is the creep curve recorded to date for the first specimen.

Other specimens in this series of tests will be tested at 600 and 800°C with the same initial applied stress.

• Figure 64 COMPRESSIVE CREEP CURVE FOR Mo NEUTRON IRRADIATED AT $\sim 70^\circ\text{C}$ TO A FAST NEUTRON FLUENCE OF $5 \times 10^{19} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$).

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Damage in Neutron Irradiated Molybdenum, Part IV, Influence of Solute Atoms.

Dimensional Stability in Neutron Irradiated Molybdenum.

Neutron Radiation Effects in Tungsten

Periodic Void Arrays