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8/3/71HIGH TEMPERATURE HEAVY
ION BOMBARDMENT OF Mo, Nb AND TZM

MASTER

by

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INTRODUCTION

The study of radiation produced defects in refractory metals has, in the past, been mainly limited to relatively low fluence ($<10^{21}$ n/cm²) and low temperature ($<0.2 T_m$) studies.⁽¹⁾ The work conducted in the 1950's and early 1960's was predominantly limited to academic considerations involving the production, migration and annihilation of single point defects. Since the late 1960's, the design of larger nuclear reactors has established the need for higher fluence ($\sim 10^{23}$ n/cm²) and higher temperature ($0.2 - 0.4 T_m$) data on refractory metals and alloys. The defect structures in these operating regimes consist mainly of "clustered" defects, such as interstitial loops and voids.⁽²⁾ Unfortunately, present day facilities are not adequate to irradiate these materials to such conditions in a reasonable amount of time. Therefore, the use of heavy ion bombardment to simulate high fluence, high temperature neutron damage was initiated in the late 1960's.⁽³⁻⁵⁾ This technique was first used for materials of interest to Liquid Metal Fast Breeder Reactors, i.e., stainless steel and nickel, but attention is now being directed to refractory metals for LMFBR's and Controlled Thermonuclear Reactors (CTR's).⁽⁶⁻⁸⁾

It is the object of this paper to present some data on heavy ion bombardment of Nb, Mo and TZM and later work will cover Ta, Re, W, V and selected Nb-Zr alloys. In this paper we will concentrate on the effect of increasing the temperature of bombardment while holding the damage level constant.

EXPERIMENTAL

The chemical compositions of the materials used for this study are given in Table I. The samples were all given pre-irradiation anneals at 1800 °C for 1/2 hour in a vacuum of 2×10^{-6} Torr prior to 5 MeV nickel ion bombardment. The irradiation temperature was varied from 650 - 1000 °C and the total ion fluence was held constant at $\sim 7 \times 10^{15}$ cm⁻² in order to produce a constant damage state of ~ 5 dpa (displacements per atom). The experimental details of the bombardment technique are described elsewhere.⁽⁶⁾ The average beam current was 1.2×10^{13} cm⁻² sec⁻¹ which resulted in a displacement rate of $\sim 8 \times 10^{-3}$ sec⁻¹.

TABLE I

PRE-IRRADIATION PROPERTIES
OF MATERIALS FOR ION BOMBARDMENT STUDIES

<u>Impurity</u>	<u>Mo</u>	<u>PPM (wt)</u> <u>TZM</u>	<u>Nb</u>
Al	<5	<300	100
C	200	100-300	30
Cd	<10		
Co	<5		
Cr	<5		60
Cu	<2		
Fe	100	<300	60
H	0.8	1-10	2
Mg	<1	<100	0.8
Mn	<2		
Mo	Bal.	Bal.	
N	1	4-15	90
Ni	<5		9
O	4.5	10-20	145
Pb	<10		
Si	<10	<300	20
Sn	<5		
Ta			200
Ti	<10	4200-4700	60
V	<5		5
W	150		80
Zr	<20	800-1100	60

The amount of displacement damage was calculated⁽⁹⁻¹⁰⁾ as a function of penetration into the solid and Figure 1 represents a typical calibration curve used for Mo and TZM in this study. The curve for Nb is only slightly different and not repeated here. The techniques for removing a fixed amount of the damaged surface are also described elsewhere,⁽¹¹⁻¹²⁾ and the resulting microstructure was observed with a model Hitachi 200 F microscope. The average void size was determined from 160,000X photomicrographs and the number density of voids was determined by stereo microscopy. The resultant volume change was calculated from the experimental data.

RESULTS

The results of the microstructural examination are listed in Table II. Voids were found in the Mo, Nb and TZM samples after 800, 900 and 1000 °C irradiations. Figure 2 shows the typical void structures in each metal after a 900 °C irradiation. No voids were found in the Nb and Mo which were irradiated at 650 and 700 °C; only dislocation loops and segments were found. There was also some evidence for the formation of precipitation, along with voids, in the TZM alloy during 800 and 900 °C bombardments.

The average void size in the metals is shown to increase with increasing irradiation temperature in all three metals and the number density is reduced. The resultant volume change (Figure 3) goes through a maximum at 900 °C of 1% for Mo, 0.83% for Nb and 0.43% for TZM.

The morphology of the voids in Mo and TZM samples is difficult to determine because of their small size. The voids in Nb, however, grow to a sufficient size for a determination of morphology. Figure 4 shows the voids in Nb in which the foil plane is near a {110} and {111} orientation. The shape of the voids in these two positions is consistent with {100} cubes (see illustrations above prints), but there is some indication of truncation on the {110} planes.

Finally, there is evidence for a non-random configuration of voids during the 800 °C irradiation of Nb. Figure 5 shows the voids in an {110} foil orientation. The voids appear black in this picture because of absorption effects. Note the alignment of the voids along [110] direction. This arrangement and that determined for {100} indicates that the voids are arranged in a bcc superlattice. The lattice constant is ~ 350 Å.

TABLE II
VOID DATA ON ION BOMBARDED Mo, TZM AND Nb^(a)

<u>Irradiation Temp. °C</u>	<u>Ave. Void Size Å</u>	<u>Ave. Void Density x 10¹⁶/cc</u>	<u>Calc. Swelling %</u>
<u>Molybdenum</u>			
650 ^(b)	ND ^(c)	ND	--
800	50	5.2	0.34
900	75	4.7	1.0
1000	120	0.53	0.48
<u>Niobium</u>			
650 ^(b)	ND	ND	--
700	ND	ND	--
800	45	6	0.29
900	220	0.15	0.83
1000	350	0.018	0.34
<u>TZM</u>			
800	60	3.2	0.36
900	80	1.6	0.43
1000	105	0.36	0.22

(a) Damage level ~5 dpa produced by 5 MeV Ni ions except where indicated.

(b) 6 MeV Ni ions.

(c) ND - None detected.

DISCUSSION

The results of this study show that voids may be easily produced in refractory metals by high temperature, heavy ion bombardment. It is also important to note that these voids can be formed without the aid of any inert gas atoms such as helium. The exact mechanism for nucleation of voids in metals is still not known but recent experiments by Norris^(13,14) and Urban⁽¹⁵⁾ have eliminated the concept of homogeneous nucleation by displacement spikes or by the agglomeration of vacancies in a supersaturated lattice. One of the most probable remaining mechanisms is the nucleation of voids by impurity gas atoms but not necessarily by noble gases. The present results do not prove or disprove that theory, but there is certainly sufficient residual (O + H + H) gas atoms in all three metals for more than one hundred atoms per void. Future work on specially degassed samples will aid in testing this concept.

The amount of swelling in the molybdenum samples can be compared to neutron induced swelling if we take into account the shift in the effective irradiation temperature. Bullough⁽¹⁶⁾ shows that, due to the high defect production rate, ion bombardment at temperature T_i should correspond to neutron irradiation at T_n through the relationship

$$T_n = \frac{T_i}{1 + \frac{T_i k}{E_v} \ln \frac{K_i}{K_n}} \quad (1)$$

where E_v is the self diffusion energy of vacancies

k is Boltzmann's constant

K_i is the defect production rate during ion bombardment.

K_n is the defect production rate during neutron irradiation

Using values for the self diffusion energy of 4.1 eV⁽¹⁷⁾ and $K_n \sim 10^{-6} \text{ sec}^{-1}$, we find that the present 650 °C heavy ion bombardment of Mo should correspond to a neutron irradiation temperature of ~510 °C, 800 °C to 615 °C, 900 °C to 690 °C, and 1000 °C to 750 °C. The threshold for void formation in terms of effective temperatures is then ~600 °C, close to what Brimhall finds for the same stock material.⁽²⁾ The lack of void induced swelling at 650 °C in the ion bombarded samples can then be explained on the basis that no voids have yet been discovered after neutron irradiation at 510 °C. The magnitude of the swelling in this study is comparable to the neutron irradiated material if it is normalized on the basis of equivalent dpa values. Brimhall⁽¹⁸⁾ finds the volume change ranges from 0.07 to 0.08% over the 650 - 750 °C temperature range for a $1.5 \times 10^{21} \text{ n/cm}^2$ ($E > 0.1 \text{ MeV}$) irradiation. This neutron fluence would amount to a dpa value of ~1.5 if a Kinchen and Pease⁽¹⁹⁾ model is valid. If the swelling increase in Mo follows roughly the 3/2 dependence on fluence,⁽¹⁶⁾ then the neutron irradiated samples would swell 0.4 - 0.5% at 5 dpa and 650 - 750 °C. This swelling is reasonably close to the 0.4 - 1.0% swelling over the 615 to 750 °C "effective" temperature range for the present experiment.

It is not possible to compare the Nb and TZM swelling to neutron irradiated material because of the lack of experimental information. It would be expected that the temperature threshold for Nb would be somewhat lower than Mo because of its lower melting temperature, but the threshold for TZM should be close to Mo. Brimhall,⁽²⁰⁾ et al, have reported that voids form in neutron irradiated TZM at 615 °C, but that only precipitates, not voids, were formed during 750 and 900 °C studies. We found both precipitates and voids in ion bombarded TZM in this temperature range and speculate that the time of irradiation may account for the differences. It would be expected that if the precipitates form by long term aging process, in which they absorb the vacancies produced by neutron irradiation, then the higher supersaturation present during ion bombardment might provide enough vacancies for both the precipitates and voids to form.

The morphology of voids in Nb after the 1000 °C bombardment was expected to be somewhat the same as that reported for bcc Mo after high temperature

neutron irradiation but it turned out to be slightly different. Rau, et al⁽²¹⁾ and Kulcinski, et al,⁽²²⁾ found that the void morphology in neutron irradiated Mo is consistent with $\{110\}$ octahedra with $\{100\}$ truncations. The situation is somewhat reversed in Nb where the voids take the shape of $\{100\}$ cubes with $\{110\}$ truncation (see Figure 4). It is quite possible that the rate at which defects are produced in the metals may alter the morphology, and studies of higher temperature irradiated Mo may provide more information on this point.

The alignment of the voids in Nb is consistent with ion bombardment results on Ni,⁽¹²⁾ Mo,^(7,8) and neutron irradiation results on Mo and Nb.⁽²³⁾ The fact that the alignment occurs in both types of studies which have widely differing defect production rates establishes that such structures do not solely result from ion bombardment. Also the lack of inert gas atoms in the ion bombardment experiments rules out inert gas nucleation phenomena. It has been suggested⁽⁸⁾ that the alignment of voids is due to the elastic anisotropy of the materials. The anisotropy ratio, $2C_{44}/(C_{11} - C_{12})$, is 2.52, 0.78 and 0.51 for Ni, Mo and Nb, respectively.⁽²⁴⁾ (A value of 1 is completely isotropic.) The exact mechanism by which such anisotropy might cause the voids to form the aligned structures is not known at this time.

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FIGURE CAPTIONS

1. Displacement Damage from 5 MeV Nickel Ions as a Function of Penetration into Molybdenum Metal. Fluence is 7×10^{15} Ions/cm².
2. Voids in Nb, Mo and TZM After Ion Bombardment to 5 dpa at 900 °C
3. Effect of Irradiation Temperature on the Void Induced Swelling in Nb, Mo and TZM. Damage Level is 5 dpa.
4. Morphology Determination of Voids in Nb after 1000 °C Ion Bombardment.
5. Aligned Voids in Nb After 800 °C Irradiation.