BNWk-SA-2920
CONT-710905--2

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IRRADIATED MOLYBDENUM AND RHENIUM

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BY JH Kahn/amh
DATE 8/27/71

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INTRODUCTION

The formation of voids in metals during neutron irradiation has been extensively studied in recent years.⁽¹⁾ Most studies have concentrated on stainless steels and other fcc metals. There have been some initial studies on void formation in refractory metals,^(2,3) but quantitative data on the effect of irradiation temperature on swelling is lacking. In the work reported here, the effect of temperature on void formation on molybdenum and rhenium was studied explicitly in the temperature range 600 - 1450 °C. Using additional data from other studies, the temperature dependence of the volume change over the temperature range 50 °C to 1450 °C has been determined. These results are discussed in terms of the stabilities of the various defect configurations.

EXPERIMENTAL PROCEDURES

Three grades of molybdenum were studied: a) triple pass zone refined (Z.R.), b) commercial high purity (MRC), and c) a commercial alloy (TZM). The chemical analyses of the Z.R. and MRC are given in Table I. The TZM has approximately 0.05% Ti and 0.1% Zr. Only one purity of rhenium, 99.97%, was studied. All material was given a pre-irradiation vacuum anneal at 1800 °C for at least 1/2 hour. Samples were irradiated in either a niobium or molybdenum capsule inserted in a graphite block. The

TABLE I

CHEMICAL ANALYSIS OF ZONE REFINED AND MRC MOLYBDENUM

<u>Impurity</u>	<u>3 Pass Z.R.</u>	<u>MRC</u>
W	100	300
Ni	1	2
Cu	0.3	10
Fe	2	70
K	40	50
Si	12	20
Mn	--	2
Ca	--	3
C	3	500
O	4	5
N	1	1
H	1	1

temperature of the graphite was monitored with a thermocouple. All of the analysis of void size, density and volume change were done by transmission electron microscopy and the techniques have been described in previous publications.^(4,5) The low temperature swelling data was determined from dimensional changes of single crystals which has been described in the literature.⁽⁶⁾

RESULTS

Typical microstructures for the three grades of molybdenum irradiated at 720 °C are shown in Figure 1. The size of the voids is larger and the density smaller in the MRC molybdenum compared to the Z.R. molybdenum. Second phase precipitates, but no voids are observed in the TZM molybdenum at this irradiation temperature. An inhomogeneous distribution of voids similar in size to that observed in MRC molybdenum was observed in TZM molybdenum irradiated at a lower temperature of 615 °C. No precipitation occurred in the TZM at this temperature. The void size increases and the density decreases with increase in irradiation temperature for both the molybdenum and rhenium. Representative micrographs illustrating this behavior are shown in Figure 2 for rhenium. Very similar behavior is noted in both Z.R. and MRC molybdenum.

Plots of the volume change versus irradiation temperature for molybdenum and rhenium are shown on Figures 3 and 4. Data from other experiments by the authors⁽⁴⁾ and other investigators^(2,7) are also plotted. Some of the high temperature values have been normalized to correspond to a fluence of 2.5×10^{19} n/cm² using a linear extrapolation. The swelling at elevated temperatures is due to void formation and extends from about $0.3 T_m$ to $0.5 T_m$ (T_m = absolute melting temperature). It is

is suspected that because of the irradiation technique the temperature of 615 and 720 °C in the rhenium curves may be in error and too low. Both curves, however, also show that significant swelling can occur at very low temperature, $<0.2 T_m$, where no voids form. There appears to be a minimum in the swelling in the temperature region $0.2 T_m$ to $0.3 T_m$. The reason for this is believed to be due to the different nature of the vacancy defect structure in the different temperature regimes and this will be discussed.

DISCUSSION

Voids are the preferred vacancy defect in molybdenum and rhenium irradiated at temperatures above approximately $0.3 T_m$. Theoretical analysis shows that the decrease in swelling at high temperatures and, hence, a decrease in void formation is due to a lower supersaturation of irradiation produced vacancies because of the increased thermal equilibrium concentration. The low temperature limit of void formation is generally agreed to be due to a low vacancy mobility and increased recombination of vacancies and interstitials.

At the lower temperatures, one must also consider the relative energies and stabilities of the various defect configurations. It has been shown that vacancy dislocation loops form in molybdenum irradiated at temperatures between 200 - 575 °C.^(4,8) Actually there is an overlap region between 575 - 750 °C in which both vacancy loops and voids form.⁽⁴⁾ Since loop formation must require some vacancy motion, vacancies have at least limited mobility below the temperature at which voids form. The temperature at which voids form is then also determined by the conditions under which the void configuration becomes more stable than the loop configuration.

There is considerable evidence that gas atoms are necessary for void formation,^(1,9,10) and Bullough and Perrin⁽¹¹⁾ have shown theoretical that gas atoms are necessary to prevent a three dimensional vacancy cluster from collapsing into a planar configuration. The temperature at which vacancy clusters can be stabilized by gas atoms may be more meaningful in defining a lower temperature limit for swelling. The results shown in Figure 3 can be explained as follows. At low temperatures, vacancies are isolated or in very small clusters which contribute to the significant volume change observed. At intermediate temperature, 400 - 600 °C, vacancies are mainly in the form of dislocation loops or planar defects which contribute little to volume change. The trapping of vacancies by impurities may also be important here. Finally, at high temperatures, vacancy clusters are stabilized and form into voids resulting in substantial swelling. Direct confirmation of planar vacancy defects in rhenium irradiated at low temperatures has not been made, but the trend in the volume change is similar to molybdenum and the same reasoning should apply.

A comparison of the results from the different grades of molybdenum indicates that relatively minor differences in purity can have a significant effect on void parameters. The somewhat less pure MRC molybdenum shows a greater number but smaller size voids indicating that impurities may be serving as nucleating sites. One cannot draw too many conclusions from this one observation since distribution and type of impurities should or will also have a profound effect. In TZM molybdenum which could be considered as a very impure molybdenum, voids do not form at all above the temperature at which precipitation reactions occur.

Precipitation is generally a diffusional process requiring vacancies so the vacancies may not be available for void formation. In addition, once the precipitate has formed, the interface region can serve as a trapping site for vacancies and interstitials, resulting in their mutual annihilation at the interface.

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Z.R.

MRC

TZM

Figure 1. Micrographs of various purities of molybdenum irradiated at 720 °C to $5 \times 10^{20} \text{ n/cm}^2$ $E > 1 \text{ MeV}$. The black spots in the TZM are small precipitates.

720 °C

1050 °C

Figure 2. Micrographs of rhenium irradiated at temperature indicated and to a fluence of $5 \times 10^{20} \text{ n/cm}^2$ ($E > 1 \text{ MeV}$) illustrating effect of temperature on void size and density.

Figure 3. Swelling in molybdenum as a function of irradiation temperature. Fluence normalized to 2.5×10^{19} n/cm² ($E > 1$ MeV).

Figure 4. Swelling in rhenium as a function of irradiation temperature. Fluence normalized to 4×10^{20} n/cm²