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The existence of dose thresholds for void ordering (~ 2 dpa) and void superlattice formation (~ 10 dpa) in molybdenum is deduced from a compilation of heavy-ion irradiation studies, including new measurements reported here. Theories of void lattice formation are discussed and evaluated in the light of these measurements.

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Void alignment and/or the void superlattice have been previously reported in ion-bombarded⁽¹⁻¹²⁾ and neutron-irradiated⁽¹³⁻¹⁷⁾ molybdenum. Much of this experimental work was recently reviewed by Brimhall.⁽¹⁸⁾ Because of lack of experimental data, little success has resulted from efforts to understand the superlattice formation process itself. As discussed by Stoneham in his review papers,⁽¹⁹⁻²⁰⁾ theoretical efforts to understand the void superlattice have centered on its stability once formed. The objective of this note is to compare our results and those already in the literature with the predictions of the various theoretical models and if possible to eliminate those which contradict the data.

The data for heavy-ion bombarded molybdenum reported in the literature are summarized in Figures 1 and 2. Previous observations of no voids, random void arrays, void ordering, and void superlattices are given in plots of dose vs. irradiation temperature (T_{irr}) in Fig. 1 and dose vs. effective temperature (T_{eff}) in Fig. 2. The effective temperature is the irradiation temperature normalized to a dose rate of 1×10^{-3} dpa/sec by using

$$T_{eff}^{-1} = T_{irr}^{-1} + (k/Q_m^v) \ln (K_{irr}/10^{-3}) \quad (1)$$

where k is the Boltzman constant, Q_m^v is the vacancy migration energy ($= 1.5$ eV), and K_{irr} is the dose rate during the irradiation.⁽²²⁾ It was well established that doses near 10 dpa are required to form the void superlattice. However, previous data were insufficient to determine a dose threshold of void ordering in molybdenum.

Consequently, molybdenum specimens were irradiated to doses of 1-2 dpa at 700, 800, 900 and 1000°C to study the low dose region. An additional

specimen was irradiated to a dose of 19 dpa at 900°C. The high-purity molybdenum was the same material used in (11,12,23, and 24). A chemical analysis of this material has been reported in Table 1 of (24). The specimens were irradiated with 17-19 MeV Cu^{4+} ions from a tandem Van de Graaff accelerator under an ultra-high vacuum of $<10^{-6}$ Pa. The irradiation and microscopy procedures were reported in (23) and the irradiation facility was described in (25). Conventional TEM microscopy procedures were used to observe and to measure the relevant void microstructure of the irradiation specimens. Random voids were observed at 1 dpa (700, 900, and 1000°C) and also at 2 dpa (900°C). Void ordering (but not a complete superlattice) was observed at 2 dpa, (800°C). An imperfect void superlattice was observed at 19 dpa, (900°C) (Fig. 3) from which a superlattice parameter could be obtained by geometric averaging over several void rows. The results of the TEM observations are summarized in Table 1. These data have been plotted on Figs. 1 and 2 and marked with the symbol T.

The present measurements, along with the previous observations, support the existence of a dose threshold between 2 and 5 dpa for void ordering in molybdenum, at temperatures near $0.4 T_M$ ($900 \pm 50^\circ\text{C}$) where T_M is the absolute melting point. In this temperature range a random void array is formed as irradiation commences (Figs. 1 and 2). As the dose level approaches 2 dpa, some void ordering occurs, primarily in one- and two-dimensional arrays (region II of Figs. 1 and 2). As the dose is increase further, the void alignment improves until approximately 10 dpa where a three-dimensional array is formed (region III of Figs. 1 and 2). As the dose is increased above 10 dpa the perfection of the void superlattice increases. The approximate boundaries between the region of void ordering (region II) and

the void superlattice (region III) and the region of random voids (region I) and void ordering (region II) are indicated on Figs. 1 and 2. These boundaries were drawn to represent the trend of the data. No data were included that used He injection.⁽⁴⁾

The experimental evidence for molybdenum shows that the voids appear first in random array. Thus, the theories which include alignment of void nuclei as a requirement, such as spinodal decomposition (26) or nucleation on an ordered impurity gas array (3), are not relevant for molybdenum.

Stoneham (19) suggested the following sequence for void superlattice formation: 1) initial formation of many small, randomly-distributed voids; 2) growth of voids, possibly with coarsening from the growth of large voids at the expense of small ones; 3) appearance of local ordered regions where the void distribution happens fortuitously to be favorable; followed by 4) spread of order to adjacent regions. The compilation of measurements for molybdenum given in Figs. 1 and 2 supports Stoneham's suggestions, provided the irradiation temperature is near $0.4 T_M$. A theory of void superlattice creation must also explain why random voids form easily but void alignment and/or the superlattice does not at doses above 2 dpa outside regions II and III in Figs. 1 and 2.

Unlike niobium (27), the creation of the superlattice in molybdenum appears not to be sensitive to small amounts of interstitial impurity since the material used in this and other (11,12) studies readily forms the superlattice even though it contains ≤ 70 at. ppm of C, N, or O and was irradiated under ultra-high vacuum. This molybdenum is pure enough that Nolfi's solute segregation mechanism (28) is probably not applicable. Thus, the comments of Chen and Ardell (29) on the role of solute segregation in non-random nucleation of voids in nickel alloyed with small ($\sim 1\%$) amounts of aluminum are

probably not relevant. Benoist and Martin's model (30) may qualitatively explain the observed dose dependence, but Brailsford (31) has recently estimated that a dose level of ~ 300 dpa for molybdenum is needed to form the void superlattice with the mechanism proposed in (30). Any role proposed for impurities in ordering during void growth should be consistent with the rather low impurity concentrations in molybdenum.

The formation of a void superlattice has an analogy in the alignment of precipitates during coarsening to minimize strain field interactions.⁽³²⁾ This involves motion of the precipitates by one side "coarsening" at the expense of the other. Given the similar interaction between voids^(33,34), surface migration of atoms from higher to lower energy sides of the void would readily explain how voids move. Since this mechanism requires pre-existing voids, it does not contradict the data presented in Figs. 1 and 2.

Foreman's suggestion of a flux of interstitials along specific crystal directions can also explain the formation of the void lattice out of a random array. Any such array will contain localized regions where a few voids are ordered. The interstitial flux out from this region will be peaked along the channels (close packed direction) of the ordered region according to Foreman's model. A corresponding decrease in the interstitial flux along a line of voids will also occur. Since the vacancy flux is isotropic, this could give rise to net shrinkage of neighboring voids not aligned with the void rows and growth of those which are aligned. Voids will either move in response to the anisotropic interstitial flux or nucleate and grow preferentially on lattice positions adjacent to the lattice "nucleus" causing it to grow.

Both the above models explain the lack of ordering at high temperatures as being due to the larger inter-void spacing implied by larger void sizes

and lower nucleation rates. This would make a strain interaction, which is dependent on distance, too weak to be effective. In Foreman's model the larger distances would be beyond the range of long range interstitial motion. As has frequently been pointed out, such interstitial motion does not seem likely except at cryogenic temperatures. (Furthermore the appearance of a void lattice under electron irradiation (35) makes this model unlikely.) Nevertheless until such crowdion motion is experimentally eliminated the model remains viable to explain the molybdenum data.

In summary, the present measurements, along with those previously published, indicate a threshold for both void ordering (~ 2 dpa) and for void superlattice formation (~ 10 dpa) in molybdenum. Theoretical attempts to deal with the creation of the superlattice in molybdenum are thus constrained not to use either void nucleation on a preexisting solute atom array or void nucleation in an ordered array. Instead, the voids must first form in random arrays from which void ordering and finally the void superlattice evolve. Presently this sequence can be described to be either selective growth and void motion in response to a void-void interaction⁽³⁴⁾ or to Foreman's crowdion mechanism⁽²¹⁾ but these theories must be formulated on a more quantitative basis before detailed comparison with experiment can be accomplished.

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Table 1
Void Microstructure and Irradiation Parameters
for the Copper-Irradiated Molybdenum Specimens

| $T_{irr}(^{\circ}C)$ | Calculated Dose (dpa) \pm Error | Dose Rate (dpa/sec) | Avg. Void Radius (nm) | Void Density (m^{-3}) | Void Volume Fraction(%) \pm Error | Void Ordered Array Spacing (nm) |
|----------------------|---|---------------------------|--------------------------|---------------------------------|---|---------------------------------------|
| 1000 | 1.3 ± 0.3 | 6×10^{-4} | 12.6 | 5.8×10^{20} | 0.76 ± 0.15 | a |
| 900 | 1.0 ± 0.2 | 6×10^{-4} | 3.9 | 6.0×10^{21} | 0.17 ± 0.03 | a |
| 900 | 1.9 ± 0.4 | 4×10^{-4} | 4.9 | 6.6×10^{21} | 0.39 ± 0.08 | a |
| 800 | 2.2 ± 0.5 | 3×10^{-4} | 2.2 | 1.7×10^{22} | 0.11 ± 0.06 | 35 ± 5 |
| 700 | 1.0 ± 0.2 | 6×10^{-4} | 2.4 | 1.0×10^{22} | 0.08 ± 0.04 | a |
| 900 | 19 ± 4 | 3×10^{-4} | 3.8 | 3.0×10^{22} | 0.87 ± 0.17 | 40 ± 5 |

^ano void ordering observed

Figure Captions

- Figure 1 Experimental observations of the void superlattice (filled circles), void ordering (half-filled circles), random voids (open circles), and no voids (crosses) in heavy-ion irradiated molybdenum plotted in dose-irradiation temperature (T_{irr}) space. The references from which the data points were taken are indicated on the figure. The present measurements are marked with a T. The approximate boundaries between the region of void superlattice formation and void ordering (solid curve) and between the random void and void ordering regions (dashed curves) are indicated on the figure. The curves are the result of empirical observation and do not result from a theoretical calculation.
- Figure 2 Same as Fig. 1 except the abscissa is T_{eff} (the irradiation temperature normalized to a dose rate of 1×10^{-3} dpa/sec using Eq. 1).
- Figure 3 Molybdenum specimen irradiated to a dose of 19 dpa at 900°C with Cu^{4+} ions. The void superlattice shown in the micrograph was observed to be bcc parallel with the BCC crystal structure of the host metal.





