SATURATION OF SWELLING IN NEUTRON IRRADIATED
MOLYBDENUM AND ITS DEPENDENCE ON IRRADIATION
TEMPERATURE AND STARTING MICROSTRUCTURAL STATE

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Saturation of Swelling in Neutron Irradiated Molybdenum and Its Dependence on Irradiation Temperature and Starting Microstructural State

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Abstract

Molybdenum and its alloys are of interest for potential fusion application due to their high melting point and relatively good thermal conductivities. The development of void superlattices during neutron irradiation appears to limit void swelling in pure molybdenum to values below 4% over a wide range of irradiation temperatures. The saturation value of swelling and the void superlattice parameter each appear to be somewhat dependent on temperature, but independent of the thermomechanical starting state. Formation of technetium and ruthenium by transmutation may also play some minor role in the microstructural evolution, but do not appear to be involved in the limitation of swelling.

Key Words: Molybdenum, neutron irradiation, loop rafts, void superlattice, swelling, transmutation

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Introduction

Molybdenum and its alloys have long been of interest for fusion and other advanced reactor concepts due to their high melting points, relatively good thermal properties and superior high temperature strength (in the absence of environmental effects). Sufficient experience on fabricability and joinability exists for molybdenum alloys such that component construction is also not a major concern. However, major issues for the use of molybdenum and its alloys for irradiation application stem from two problem areas. First, neutron-induced activation of molybdenum is a significant long term issue for maintenance, handling and disposal. Second, neutron-induced changes in mechanical properties arise from a large increase in ductile to brittle transition temperature, making molybdenum a questionable choice for structural applications in irradiation environments.

A number of irradiation studies on molybdenum and its alloys were conducted during the 1970s [1-11], but active interest waned as the potential problems mentioned earlier came to light. Interest has continued at a low level despite these concerns since molybdenum offers the best thermal conductivity among the various refractory metals and competes well with other materials with much lower melting points in situations where temperature gradients and off-normal temperature histories may cause concern.

This paper examines the swelling and microstructure of molybdenum after irradiation in FFTF as a function of starting condition, irradiation temperature and neutron dose.

Experimental

High purity molybdenum was irradiated in the Materials Open Test Assembly (MOTA) in either three or four consecutive irradiation sequences designated MOTA-1B, 1C, 1D and 1E. Five target temperatures ranging from 420 to 722°C were employed and the irradiation proceeded to doses of approximately 60 dpa at the higher temperatures and to approximately 110 dpa at 420°C. The dpa levels quoted are those for stainless steel.

The specimens were irradiated in the form of standard microscopy disks in each of two conditions: solution annealed for 1 hr at 760°C followed by aging at 320°C for 2 hrs, and a 20% cold worked condition followed by the same aging treatment. The former condition had an approximate grain size of 10 μm , and the latter 2 μm . The irradiation was carried out in weeper packets so that the specimens were in contact with the reactor sodium during irradiation. In MOTA the temperatures were controlled to within $\pm 5^\circ\text{C}$, with the single exception of an over-temperature excursion of approximately 50 min duration in MOTA-1D during FFTF cycle 7. Further details of the irradiation can be found elsewhere [12].

Transmutation production rates and levels were calculated for this irradiation experiment. Significant levels of technetium and lesser amounts of ruthenium were produced under these irradiation conditions, reaching ~1% total at 100 dpa [12,13]. The transmutant levels depend strongly on the position of irradiation in the FFTF core.

Following irradiation, swelling was measured using an immersion density technique known to be accurate to $\pm 0.2\%$ density change. Afterwards, these specimens were prepared for examination by transmission electron microscopy using a JEOL 2000CX operated at 120 kV.

Results and Discussion

The swelling measurements obtained by immersion density are compared for the solution annealed condition in Figure 1, and for the cold worked condition in Figure 2. Figure 3 shows that the cold worked and aged condition always swells at a faster rate initially than does the annealed and aged condition, but the swelling of the two conditions appears to be converging by the end of the last irradiation segment. This convergence requires that the cold worked and aged specimen must decline in swelling at the 471 and 596°C target temperatures. Note also in Figure 3 that three of the four specimen groups are converging to the same level ($\sim 2\%$). The decline probably occurs by void shrinkage.

At the lowest irradiation temperature, the microstructure consisted exclusively of loop rafts at the lower doses (see Figure 4). At the highest doses, a small number of tiny voids, with diameters < 2 nm, are observable in a microstructure that is still dominated by loop rafting. The raft structure does not coarsen with irradiation dose and is typical of other observations of loop rafts in neutron irradiated molybdenum at low homologous temperatures [1, 2]. Previous studies of rafting in molybdenum did not attempt to measure volume changes associated with the rafting structure. In the present study, the annealed and aged material shows a slight densification during irradiation that is climbing back toward a zero volume change at the highest dose. The cold worked and aged material, however, shows a sizable increase in volume at the lowest irradiation dose, then the volume change drops back toward zero at higher doses. The contribution of the small voids to swelling at the highest doses is rather small, and may be offset somewhat by density changes associated with the production of technetium and ruthenium. The initial large increase in volume in the cold worked and aged condition may be related to the higher initial sink density available in that condition. This condition possessed both smaller grain sizes and higher initial dislocation densities within grains compared to that of the annealed and aged condition.

The swelling behavior at the higher temperatures, 471 to 730°C, is dominated by the formation and growth of voids. Most importantly, void superlattices are formed early in the irradiation. Examples are shown in Figure 5, and a map of the set of irradiation conditions where void superlattices were found is shown in Figure 6. The difference in initial sink density in the two alloy conditions and its effect on the early stages of microstructural evolution probably account for this different swelling behavior. In fact, most of the specimens in the solution annealed and aged condition in this temperature range exhibited swelling that was still rising with dose at the highest doses examined. Nevertheless, it is anticipated that the swelling observed is near the peak values at these

doses and would plateau or decline at higher doses. The principal foundation for this argument is that, when void superlattices form, swelling is typically limited to 3% or less based on attainment of an equilibrium ratio of void diameter to void superlattice parameter.[14] Other investigations of neutron irradiation behavior of molybdenum where void superlattices were found [3-5] all report swelling values of less than 3%. Similar limits to swelling have also been found in ion irradiation studies of molybdenum [6-9].

Void superlattices have been found in other studies to form in molybdenum under a variety of irradiation conditions. These studies utilized either neutron or ion irradiation at temperatures ranging from as low as 430°C ($0.24 T_m$) in the neutron irradiation case [3] to temperatures as high as 1100°C ($0.48 T_m$) under ion irradiation [9]. The observed lack of void superlattice formation in the present study at an irradiation temperature of 420°C and a dose of 110 dpa indicates that there is a sharp lower temperature boundary for this phenomenon, especially when compared to the results of Sikka and Moteff [3] at $\sim 1 \times 10^{26} \text{ nm}^{-2}$ ($E > 0.1 \text{ MeV}$) and 430°C in EBR-II. It is important to note, however, that the temperatures in this early EBR-II experiment were not as well-defined or as stable as in FFTF-MOTA.

The void superlattice parameter (measured from void center to void center along the $\langle 100 \rangle$ direction) has been found in earlier studies to be dependent on irradiation temperature. Void superlattice parameters from previous neutron irradiation studies are compared to those measured in the present study in Figure 7 and are shown to be comparable. It is also noteworthy that the lattice parameters are not sensitive to the starting condition; the values for the cold worked and aged and the solution annealed and aged materials agree in all cases.

Other work on neutron-irradiated molybdenum has noted that void shrinkage seems to occur with increasing irradiation dose. The work of Bentley et al. [10] identified void shrinkage in neutron irradiated molybdenum at low doses during the early stages of microstructural evolution. More relevant to the present work is the study by Evans [11] which examined shrinkage and disappearance of voids in molybdenum irradiated to moderately high neutron fluences ($1.5, 3.5$ and $8.0 \times 10^{26} \text{ n/m}^2$, $E > 0.1 \text{ MeV}$) over a temperature range of 450 to 650°C. The void disappearance was proposed by Evans to arise from a change in the void sink bias term, possibly due to technetium segregation to void surfaces; an assumption that was not directly verified by experiment. The voids' defect biases were assumed to become attractive for interstitials, thereby resulting in void shrinkage.

It should be noted, however, that while Tc and Ru may play some minor role in determining the saturation level of swelling or the rate of approach to saturation, these elements are not a prerequisite to saturation or void shrinkage. Otherwise, saturation would not have been observed in ion bombardment studies. Evans also observed ordered void structures, similar to those found here. Evans was clearly able to demonstrate void-free zones in his highest dose microstructures, in contrast to uniform populations at lower doses. In the present study, such void-free zones were not found.

Conclusions

Both the saturation values of swelling and the void superlattice spacings that develop in pure molybdenum during neutron irradiation appear to be independent of the starting dislocation and grain microstructure. The superlattice parameter is somewhat dependent on irradiation temperature, in agreement with earlier studies, and the saturation swelling levels appear to be very slightly dependent on irradiation temperature. While transmutation of Mo to Tc and Ru may play some role in altering the details of the microstructural evolution and the swelling behavior, the saturation process appears to be controlled primarily by the processes related to superlattice formation. Dense dislocation microstructures induced by cold working appear to accelerate the onset of void growth, and sometimes cause the swelling to overshoot the saturation level. Void shrinkage then returns the swelling to the saturation level, which is always less than 4% swelling.

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List of Figures

1. Swelling in neutron irradiated molybdenum in the solution annealed and aged condition as a function of dose and irradiation temperature.
2. Swelling in neutron irradiated molybdenum in the cold worked and aged condition as a function of dose and irradiation temperature.
3. Convergence of swelling independent of starting state appears to occur at each temperature where voids dominate the microstructure.
4. Loop rafting structure observed in cold worked and aged molybdenum irradiated to 40 dpa at 420°C.
5. Void superlattice structures observed in cold worked and aged molybdenum irradiated at 569°C to 40 dpa (left) and 55 dpa (right).
6. Map of material and irradiation conditions under which void superlattices are formed.
7. Void superlattice constants as a function of reciprocal temperature.

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