Irradiation Induced Structural Change in Mo₂Zr Intermetallic Phase

J. Gan^a, D. D. Keiser^a Jr., B. D. Miller^a, N. Eriksson^b, Y. H. Sohn^b, M. Kirk^c

^aIdaho National Laboratory, P. O. Box 1625, Idaho Falls, ID 83415, USA

^bUniversity of Central Florida, Orlando, FL 32816, USA

^cArgonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439, USA

Abstract

The Mo₂Zr phase has been identified as a major interaction product at the interface of U-10Mo and Zr. Transmission electron microscopy in-situ irradiation with Kr ions at 200°C with doses up to 2.0E+16 ions/cm² was carried out to investigate the radiation stability of the Mo₂Zr. The Mo₂Zr undergoes a radiation-induced structural change, from a large cubic (cF24) to a small cubic (cI2), along with an estimated 11.2% volume contraction without changing its composition. The structural change begins at irradiation dose below 1.0E+14 ions/cm². The transformed Mo₂Zr phase demonstrates exceptional radiation tolerance with the development of dislocations without bubble formation.

The high performance research reactor fuel development program (HPRR-FD) aims to develop low enrichment ($< 20\%$ ^{235}U) U-Mo fuels to ensure a safe and secure use of research and test reactors worldwide. It is well known that the microstructural development under irradiation has a strong effect on the performance of fuels and materials in the reactor. Significant efforts have been put into developing a comprehensive understanding of the U-Mo fuel microstructural evolution under irradiation. The most popular fuel format for these reactors is the plate type of fuels, either in dispersion or monolithic configuration, sandwiched with aluminum alloy Al 6061 cladding on both sides. The advantage for a monolithic fuel plate is its higher uranium loading capacity compared to a dispersion fuel. More information on these types of plate fuels can be found in the literature [1,2,3]. To mitigate the undesired strong interaction between the U-Mo fuel and the Al 6061 cladding, a Zr thin foil of $\sim 25\ \mu\text{m}$ is added as a diffusion barrier between the U-Mo and Al 6061. It is found that the Zr foil also develops reaction products at both interfaces of U-Mo/Zr and Zr/Al 6061 from the fuel plate fabrication process [4]. A comprehensive microstructural characterization is required to investigate the radiation stabilities of the relevant interaction product phases at the fuel/cladding interface.

While neutron irradiation experiments are an essential part of a fuel development program, ion irradiation experiments with a focus on a certain aspect of a fuel material property are very useful and complementary due to their cost effectiveness, quick turn-around cycle, well- controlled irradiation conditions, and negligible radioactivity of the irradiated samples. The previous ion irradiation studies on the stability of interaction product phases at the U-Mo/Al-Si interface provided useful information [5,6]. The Mo_2Zr phase has been identified as a major interaction product developed at the U-Mo/Zr interface [4,7] or in the U-10Mo- χZr ternary alloy ($\chi = 1$ to 6) [8]. In the open literature, the common crystalline structure for Mo_2Zr is MgCu_2 type (cF24, $a_0 = 0.7588\ \text{nm}$) as listed in U-Mo-Zr ternary or Mo-Zr binary system phase diagrams [9]. There is also a less common structure for Mo_2Zr phase that is bcc type (cI2, with $a_0 = 0.3185\ \text{nm}$) found in a two-phase Mo_2Zr compound where both bcc and MgCu_2 type structure co-exist [10,11]. The work by Osten shows that single phase Mo_2Zr with a bcc structure cannot be obtained without an extremely fast quenching of $10^5\ \text{K/sec}$ following the arc melt [12]. The comparison between the two structures is shown in a schematic in Figure 1. The cF24 structure of Mo_2Zr has 16 Mo and 8 Zr atoms for each cubic cell and it is ordered with all the corner and face-center sites occupied by Zr and the remaining 4 Zr and 16 Mo atoms located inside the cubic. For bcc Mo_2Zr structure, each site is $2/3$ and $1/3$ probability occupied by Mo and Zr atom, respectively. Note that the lattice parameter for bcc Mo_2Zr is similar to that of bcc Mo ($a_0 = 0.315\ \text{nm}$). The objective of this work is to investigate the radiation stability of the Mo_2Zr phase as an interaction product. This work focuses on microstructural response of the Mo_2Zr phase under Kr ion irradiation that was recorded in-situ along with more detailed

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4 TEM characterization after the ion irradiation. The potential impact of the observed microstructural
5 changes under irradiation on the fuel performance is discussed.
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10 (Insert Figure 1)
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14 To investigate the radiation stability of the Mo₂Zr interaction phase, an U-10Mo-5Zr alloy was
15 cast via arc melt followed by heat treatments relevant to the fuel fabrication process to produce Mo₂Zr
16 phase for the ion irradiation experiment. The cast material was first homogenized at 900°C for 168 hours
17 and water quenched. Then, it was heat-treated at 650°C for 3 hours plus water quench, which is relevant
18 to the hot rolling process in fuel fabrication. The final step of heat treatment was carried out at 560°C for
19 90 minutes followed by air cool that is representative of the hot isostatic press (HIP) process, which is the
20 last step of fuel fabrication [13]. Scanning electron microscopy (SEM) analysis and X-ray diffraction
21 (XRD) analysis were performed to reveal the general microstructure and to confirm the presence of
22 Mo₂Zr phase in the U-10Mo-5Zr alloy. Standard 3.0 mm samples for transmission electron microscopy
23 (TEM) analysis were prepared through slicing, mechanical polishing, disc punching, and fine polishing
24 followed by electrical jet polishing to produce thin areas transparent to 200 keV electron beam. The TEM
25 sample contains high concentration large Mo₂Zr precipitates (> 1 μm) with most of them are single
26 crystals. The large Mo₂Zr precipitate with preferred crystallographic orientation for imaging condition at
27 the desired TEM foil orientation (~15 degree from ion beam) was chosen for in-situ irradiation studies.
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38 The TEM samples were irradiated with 500 keV Kr ions at 200°C to ion doses up to 2×10^{16}
39 ions/cm² using the Intermediate Voltage Electron Microscope (IVEM) equipped with a tandem
40 accelerator at Argonne National Laboratory (ANL). For 500 keV Kr ions, this corresponds to a peak
41 displacement damage of ~ 66 displacements per atom (dpa) in Mo₂Zr (~ 100 nm thick) estimated from the
42 Stopping and Range of Ions in Matter (SRIM) calculation [14,15]. The specimen chamber vacuum is
43 approximately 1.1×10^{-5} Pa (8.0×10^{-8} torr) during ion irradiation. The estimated local temperature
44 uncertainty is approximately ±10°C. With the selected ion energy of 500 keV, the retention of the injected
45 Kr ions in the electron transparent area (~100 nm thickness) of the TEM foil were estimated to be 33%.
46 The estimated Kr atomic concentration in Mo₂Zr is 57 ppm and 1.1at% at ion fluence of 1.0E+14 and
47 2.0E+16 ions/cm², respectively. The in-situ TEM analysis was performed using a Hitachi H-9000NAR
48 transmission electron microscope operating at 300 keV during the ion irradiation. Detailed post-
49 irradiation-examination (PIE) on irradiated microstructure was performed using a 200 keV JEOL-2010
50 TEM/scanning TEM (STEM) system equipped with a LaB₆ filament, a Gatan UltraSacn-1000 digital
51 camera for imaging and a Si drift detector for composition analysis with Energy Dispersive Spectroscopy
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(EDS). The TEM selected area diffraction (SAD) patterns from the major zones were used for structure analysis. The Java-version Electron Microscopy Simulation (JEMS) software developed by Stadelmann was used to assist in identifying the phase and indexing the diffraction patterns [16].

The general microstructure of the TEM sample and microstructural evolution as a function of dose in Mo₂Zr phase under 500 keV Kr ion irradiation is shown in Figure 2. Low-magnification TEM overview images on the top reveal the unirradiated (g=200 for cF24) and the irradiated microstructure in the Mo₂Zr phase. The high-magnification TEM images show the details of the microstructural development at the same location. The initial unirradiated microstructure contains straight band contrast that is believed due to twin instead of stacking fault since the latter often contains fringes that are missing here [17]. The visibility of the twin dropped significantly at low dose of 1×10^{14} ions/cm² and disappeared before the ion fluence of 5×10^{14} ions/cm². Significant dislocation development can be seen even at a relatively low dose at 4×10^{13} ions/cm². Note that the reduction in local dislocation density at the highest ion fluence is likely due to stress-induced local bending off the normal two beam imaging condition for dislocation. TEM imaging with under- and over-focus conditions at high magnification during both in-situ irradiation and PIE work did not reveal any bubbles in the 500 keV Kr ion irradiated Mo₂Zr phase. It appears Mo₂Zr is quite resistant to Kr ion radiation damage in terms of bubble formation at the irradiation temperature of 200°C.

(Insert Figure 2)

One of the important findings from the detailed TEM microstructural characterization in PIE is the structural change of Mo₂Zr phase as a result of Kr ion irradiation. The TEM SAD patterns from three major zones ([001], [111] and [101]) of the Mo₂Zr phase in the unirradiated condition are compared to that of the irradiated condition (2×10^{16} ions/cm²) in Figure 3. Note that, although the SAD patterns from zone [001] and zone [111] between the two structures look somewhat similar, the corresponding indices are quite different between the two structures. For the irradiated Mo₂Zr, the missing [101] zone pattern shown in the initial cF24 structure for the unirradiated Mo₂Zr plus the presence of zone patterns from a much smaller cubic structure confirms the radiation induced structural change. The large complex cubic ($a_0 = 0.742 \pm 0.004$ nm, containing 24 atoms) in the unirradiated Mo₂Zr has changed to a small bcc cubic ($a_0 = 0.310 \pm 0.003$ nm, containing 2 atoms) in the irradiated Mo₂Zr (2×10^{16} ions/cm²). The associated volume contraction χ can be estimated by the following equation where V and v is the volume of the cubic cell calculated using the lattice constant in the literature for the initial large cubic and the irradiation-transformed small cubic, respectively:

$$x = \frac{V - \left(\frac{24}{2}\right)v}{V} = 0.112 = 11.2\%$$

(Insert Figure 3)

The transformed Mo₂Zr structure in bcc has a lattice constant close to that for bcc molybdenum ($a_0 = 0.315$ nm). Note that the single phase Mo₂Zr in bcc structure could not be obtained without an extremely fast quenching of 10^5 K/sec following the arc melt [12], the radiation-induced structural transformation for Mo₂Zr phase demonstrates that ion irradiation can quickly produce a thermodynamically metastable microstructure. Comparing to the previous work on Kr ion irradiation of U-Mo/Al-Si interaction products [5,6], excluding the structural change, the transformed Mo₂Zr phase displays exceptional radiation tolerance with clear SAD pattern and Kikuchi line pattern up to high dose of 2×10^{16} ions/cm² (~ 66 dpa). To track the structural change of the Mo₂Zr as a function of Kr ion irradiation fluence, additional in-situ irradiation under the same ion energy and irradiation temperature was performed to monitor the change of SAD pattern of zone [011] for the original cF24 structure from the same area. The results shown in Figure 4 confirm that the structural change occurs at relatively low dose below 1.0×10^{14} ions/cm². The original zone [011] pattern for a large and complex cubic structure (cF24) quickly diminishes and the newly developed bright spots are in good match with SAD pattern of zone [012] for a much smaller bcc cubic structure (cI2, $a_0 = 0.310 \pm 0.003$ nm). The angle between these two zones for a cubic structure is 18.4 degree.

(Insert Figure 4)

STEM characterization in PIE on a sample irradiated to 2×10^{16} ions/cm² reveals multiple small cracks around the interface between a large Mo₂Zr precipitate (~ 5 μm) and U-Mo-Zr alloy matrix. It is speculated that the volume contraction (11.2%) from radiation-induced structural change in Mo₂Zr phase may create a tensile stress exceeding the bond strength at the large precipitate and matrix interface. Interface cracks were not found for the small precipitates despite the similar volume contraction, indicating less tensile stress built up at the small precipitate and matrix interface. It is well known that the crack development or excess amount of bubble accumulation along the fuel cladding interface for a monolithic fuel plate could have negative impact on fuel performance in a reactor. Perez et al. found that the Mo₂Zr precipitates developed at the interface of U-Mo and Zr barrier layer as a result of fuel fabrication process tend to be quite small [4]. Therefore, the crack development at the precipitate and matrix interface for the large Mo₂Zr as a result of radiation-induced structural change reported in this

work may not be a concern for the U-10Mo/Zr/Al-6061 monolithic fuel plate, as long as the fuel fabrication process does not introduce large Mo₂Zr precipitates at the U-10Mo fuel and Zr barrier interface.

Further work is needed to investigate the temperature dependence of the radiation-induced structural transformation and thermal stability of the transformed bcc Mo₂Zr. Based on its exceptional radiation stability at 200°C, the transformed Mo₂Zr in bcc structure is speculated to be relatively stable thermally. Since the structural transformation is well developed at low fluence of 1.0E+14 ions/cm² where the estimated Kr trapped in Mo₂Zr is only 57 ppm, the effect of Kr concentration on transformation is negligible. The corresponding atomic displacements is 0.33 dpa, this could be significant and it is likely that Kr ion irradiation-induced cascade mixing is the driving force to transform from a large, complex and ordered structure, typically unstable under irradiation, to a simple bcc structure with Mo and Zr atom interchangeable, usually quite stable under irradiation. It is known that stable phase, that could not be produced thermally, could be produced by heavy ion irradiation as a result of cascade mixing and dissolution and enhanced kinetics during irradiation^[18].

In summary, the Mo₂Zr phase that develops at the U-10Mo/Zr interface in monolithic fuel plates as a result of fuel fabrication has an MgCu₂ type complex cubic structure. Under 500 keV Kr ion irradiation at 200°C to a fluence as low as 1×10^{14} ions/cm², this phase changes its structure to a much smaller bcc cubic associated with a volume contraction of 11.2%. The transformed Mo₂Zr with bcc structure remains stable up to 2×10^{16} ions/cm². The irradiated defect structure mainly consists of dislocation tangles and network. Excluding the radiation-induced structural change, the Mo₂Zr phase shows exceptional radiation tolerance on suppressing bubble formation and maintaining crystalline structure up to a high dose of ~66 dpa.

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Figure 1. Schematics showing cubic cell for Mo_2Zr phase in its common structure (MgCu₂ type, cF24, $a_0 = 0.7588 \text{ nm}$) on the left and the less common structure (bcc type, cI2, $a_0 = 0.3185 \text{ nm}$) on the right.

Figure 2. Micrographs showing (1) STEM image of general microstructure of U-10Mo-5Zr TEM sample consisting of many large Mo_2Zr precipitates (top-left), (2) TEM overview of microstructure in a Mo_2Zr precipitate before and after irradiation with 500 keV Kr ions at 200°C up to 2×10^{16} ions/cm² (top-center and -right), (3) the detailed TEM views from the same area showing the development of dislocations vs. doses (middle and bottom) starting with $g=200$ for the unirradiated condition.

Figure 3. Comparisons of SAD zone patterns for Mo_2Zr phase in unirradiated (cF24 structure) (left) and irradiated (cI2 structure, 2×10^{16} ions/cm²) (right) conditions at zone [001] (top), [111] (middle), and [101] (bottom).

Figure 4. Evolution of SAD patterns from the same area revealing structural change vs. ion fluence for Mo_2Zr from the zone $[011]$ of unirradiated condition (cF24 structure, $a_0 = 0.742 \text{ nm}$) to the zone $[012]$ of the irradiated condition (cI2 structure, $a_0 = 0.310 \text{ nm}$).

Mo_2Zr (common structure)
cF24 (MgCu₂ type)
 $a_0 = 0.75875 \text{ nm}$

Structural change under
Kr ion irradiation

11% volume contraction

Mo_2Zr (less common)
cI2 (bcc)
 $a_0 = 0.3185 \text{ nm}$