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Article in Defect and Diffusion Forum - April 2011
DOI: 10.4028/www.scientific.net/DDF.312-315.1055

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Characterization of Interaction Layer in U-Mo-X (X = Nb, Zr) and U-Nb-Zr vs. Al Diffusion Couples Annealed at 600°C for 10 Hours

A. Ewh¹,a, E. Perez¹,b, D.D. Keiser Jr.²,c, Y.H. Sohn¹,d

¹Advanced Materials Processing and Analysis Center
Department of Mechanical, Materials, and Aerospace Engineering
University of Central Florida
4000 Central Florida Blvd., Orlando, FL 32816

²Nuclear Fuels and Materials Division
Idaho National Laboratory
P.O. Box 1625, Scoville, ID, 83415

ᵃashley ewh gmail.com, ᵇem168604@pegasus cc.ucf.edu, ᵈdennis keiser inl.gov,
³ysohn mail.ucf.edu

Keywords: Fuel-cladding interaction, metallic nuclear fuels, uranium alloys, diffusion

Abstract: U-Mo has thus far proven to be one of the most feasible metallic fuel alloys for use in research and test reactors due to its high density and stability during irradiation. However, an adverse diffusional interaction can occur between the fuel alloy and the Al based matrix. This forms an interaction layer (IL) that has undesirable thermal properties and irradiation behavior leading to accelerated swelling and reduced fuel efficiency. This study focused on the effects of ternary alloying additions on the formation of IL between U based alloys and Al. Diffusion couples of U-8Mo-3Nb, U-7Mo-6Zr, and U-10Nb-4Zr (wt.%) vs. pure Al were assembled and annealed at 600°C for 10 hours. Both thickness and phase constituent analyses were performed via electron microscopy. The major phase constituent of the IL was determined to be the UAl₃ intermetallic compound. The Nb and Zr alloying additions did not reduce growth rate of IL (1.3~1.4 µm/sec¹/²) as compared to couples made between binary U-Mo and Al (0.9~1.8 µm/sec¹/²).

Introduction

The U.S. Department of Energy launched the Reduced Enrichment for Research and Test Reactors (RERTR) program to convert research-purpose nuclear reactors from the use of highly enriched uranium (HEU) to low enriched uranium (LEU) to address safety issues associated with nuclear power [1,2]. Many uranium-based alloys have been considered for metallic nuclear fuels, but only a few have proven viable. There are many criteria to satisfy in fabricating a high performance fuel (e.g., the alloy must maintain high density and γ-U stability under irradiation). Previous studies have shown that uranium-molybdenum (U-Mo) alloys fulfill the requirements as LEU fuel for reactors by stabilizing the γ-U phase with a relatively high density [2-7].

However, the performance of the U-Mo fuels is drastically reduced due to the formation of reaction products between the fuel alloy and its Al alloy cladding. Diffusion occurs during reactor operation producing intermetallic compounds with physical and thermal properties that have adverse effects on the performance of the materials [6,8]. The reaction layer between the U-Mo and the Al matrix experiences significant volumetric expansion that can cause fracturing [9]. These compounds also have lower thermal conductivities than desired, which results in heat buildup in the fuel particles that accelerates the interdiffusion processes between the U-Mo and the Al alloys [8,10]. The growth and properties of the intermetallic compound layers that develop in the U-Mo/Al system must be controlled in order to improve the functionality and service life of the fuels.
The influence of certain alloying additions on the growth of this interaction layer has been studied. Based on a thermodynamic calculation, adding Si in the Al matrix and the transition metals such as Zr, Ti, V, and Nb to the U-Mo fuel was suggested recently by Park et al. [11]. It is suspected that the most promising candidates for additions to the U-Mo alloys are niobium and zirconium [12]. These elements were chosen based on their presumably high solubility within the U-Mo system and their potential ability to suppress the formation of the interaction layer [3,7,13]. However, these additions may result in a faster $\gamma$-U transformation rate; it appears that the decomposition of the metastable $\gamma$-U phase has a significant effect on the interdiffusion rates [7]. To evaluate the suitability of these ternary alloys as metallic nuclear fuels, U-8Mo-3Nb/Al, U-7Mo-6Zr/Al, and U-10Nb-4Zr/Al diffusion couples were annealed at 600°C for 10 hours and characterized in terms of thickness and phase constituents.

Experimental Details

The U-8Mo-3Nb, U-7Mo-6Zr, and U-10Nb-4Zr, in wt.%, alloys were cast using high purity DU, Mo, Nb, and Zr via arc melting at Idaho National Laboratory. These alloys were drop cast into rods, which were then homogenization annealed under argon atmosphere at 950°C for 96 hours. Disks approximately 2 mm in thickness were then sectioned from the rods and mounted in epoxy for metallographic preparation. The surfaces of the disks were then metallographically polished down to 1 µm using diamond paste. To prevent oxidation of the uranium alloys, all disk sectioning and metallographic preparation was performed in a glove box under Ar atmosphere. The Ar gas was also run through an oil-trap and air filter prior to out-gassing through a chemical fume hood to prevent airborne contamination. The composition of each of the alloys was then verified via standard-less energy dispersive spectroscopy (EDS). The phase constituents and microstructure of the alloys were examined via x-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively.

After obtaining the as-cast phase and composition information on the uranium alloys, the remaining disks were used for diffusion couple assembly. Pure aluminum disks approximately 3 mm in thickness were also sectioned, epoxy mounted and metallographically polished down to 1 µm. Both the U and Al disks were then removed from the epoxy mounts and prepared for diffusion couple assembly in the glove box under Ar. All the disks were given a final polish at 1 µm and the Al disks were treated in nitric acid to remove any oxide scale that had developed on the surface. The uranium and aluminum disks were then mated, with polished surfaces in contact, and placed between two alumina disks used as spacers. The entire set-up was then clamped between two INVAR™ stainless steel disks with screws threaded through to form a jig. Each jig was then sealed in a quartz capsule under Ar atmosphere following repeated vacuum and hydrogen purge. After encapsulation, the couples were diffusion annealed in a Lindberg/Blue™ three-zone tube furnace at 600°C for 10 hours.

Following annealing, the diffusion couples were quenched by breaking the quartz capsules in cold water. The couples were then removed from the jigs and individually epoxy mounted and cross-sectioned perpendicular to the original interface. The samples were then metallographically polished down to 1 µm and prepared for microstructural and compositional analysis via SEM, EDS, and TEM. Interaction layer thickness measurements were performed in Adobe Photoshop using two different methods. The first method used was to calculate the number of pixels in the interaction layer using a gray scale threshold and divide it by the length of the interaction layer, which provides an integrated thickness value. The second method used was to calculate the thickness of the layer in 15 evenly spaced places along the length of the interface in the micrograph and average the values. Both were done for comparison purposes and in order to provide a standard deviation for each of the layers developed.
Results

*Ternary Uranium Alloy Characterization*

The initial composition and microstructure of the three ternary alloys were examined before diffusion couple assembly. Based on the XRD patterns collected, the alloys all appeared to be single phase $\gamma$-U as expected. However, upon microstructural examination, a small volume fraction of Mo-X/Nb-Zr rich precipitates was observed. Table 1 reports the average composition of these precipitates as determined by standardless EDS for reference. Backscatter electron micrographs showing the microstructure of each of the alloys are shown in Figure 1. Further analysis of these precipitates was conducted and used to develop schematic ternary isotherms at 950°C [14].

Table 1. Precipitate compositions in the ternary U alloys determined by standardless EDS.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>U (at.%)</th>
<th>Mo (at.%)</th>
<th>Nb (at.%)</th>
<th>Zr (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-8Mo-3Nb</td>
<td>2.0 ± 0.5</td>
<td>58.8 ± 1.0</td>
<td>39.1 ± 0.7</td>
<td>-</td>
</tr>
<tr>
<td>U-7Mo-6Zr</td>
<td>1.9 ± 0.6</td>
<td>28.8 ± 0.7</td>
<td>-</td>
<td>69.2 ± 0.7</td>
</tr>
<tr>
<td>U-10Nb-4Zr</td>
<td>6.1 ± 1.8</td>
<td>-</td>
<td>11.4 ± 0.5</td>
<td>82.6 ± 2.2</td>
</tr>
</tbody>
</table>

Interaction Layer Microstructure

For the three diffusion couples annealed at 600°C for 10 hours, cross-sectional backscatter electron micrographs of the IL were collected to observe the microstructure. Figure 2 shows the micrographs of typical sections of the IL developed in each of the couples. As shown, the interaction layer developed in each of the diffusion couples is relatively consistent, but non planar. In the U-7Mo-6Zr vs. Al couple, the reaction product penetrated into grain boundaries visible in the U-7Mo-6Zr alloy as shown in Figure 2(b). Higher magnification micrographs within the IL show the presence of the Mo-X/Nb-Zr rich precipitates. Representative micrographs of the U-7Mo-6Zr vs. Al IL are shown in Figure 3. The Mo-Zr rich precipitates are visible within the IL, but there are also acicular structures visible below the IL in the U-7Mo-6Zr alloy. Some grains are shown to be consumed by the reaction product. The high magnification images also reveal regions of different contrast within the IL suggesting the presence of multiple phases.

Figure 2. Low magnification backscatter electron micrographs of ILs developed in a) U-8Mo-3Nb vs. Al b) U-7Mo-6Zr vs. Al and c) U-10Nb-4Zr vs. Al diffusion couples.
Interaction Layer Thickness

In order to compare the ILs developed within each of the systems thickness values were determined. Two different methods were used to calculate the thickness of the ILs. The first method was to calculate the total number of pixels within the IL and divide it by the length of the IL giving an average integrated thickness. The second involved measuring the thickness of a series of fifteen evenly spaced lines across the IL and averaging those values, which also produced a standard deviation for analysis. The results from the two methods are reported in Table 2. The values calculated using the different methods agree relatively well. With thicknesses of approximately 250 microns, the ILs developed in the diffusion couples were all comparable.

Table 2. IL thickness measurements calculated using integrated and average line methods.

<table>
<thead>
<tr>
<th>Side 1</th>
<th>Side 2</th>
<th>Integrated Thickness (µm)</th>
<th>Average Line Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-8Mo-3Nb</td>
<td>Al</td>
<td>264.7</td>
<td>271.8 ± 18.7</td>
</tr>
<tr>
<td>U-7Mo-6Zr</td>
<td>Al</td>
<td>242.9</td>
<td>251.9 ± 32.8</td>
</tr>
<tr>
<td>U-10Nb-4Zr</td>
<td>Al</td>
<td>247.8</td>
<td>265.2 ± 28.7</td>
</tr>
</tbody>
</table>

The main purpose of this study, however, was to determine whether or not the addition of a third alloying element would have an advantage over the binary U-Mo alloy in reducing the rate of IL growth. In a separate study, diffusion couples between binary U-Mo vs. pure Al were assembled and annealed for 24 hours as opposed to 10 hours. Parabolic growth constants accounting for the difference in anneal time were calculated for comparison with the ternary U-Mo-X vs. Al couples. The values are summarized in Table 3. No significant change was observed between the ternary and binary systems with growth constants ranging from approximately 1.3~1.4 µm/sec^{1/2} and 0.9~1.8 µm/sec^{1/2}, respectively.
Table 3. Calculated growth constants for binary and ternary U alloys vs. Al.

<table>
<thead>
<tr>
<th>Diffusion couple</th>
<th>Thickness (μm)</th>
<th>K Value (μm/sec^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-7Mo vs. Al</td>
<td>265</td>
<td>0.90</td>
</tr>
<tr>
<td>U-10Mo vs. Al</td>
<td>542</td>
<td>1.84</td>
</tr>
<tr>
<td>U-12Mo vs. Al</td>
<td>362</td>
<td>1.23</td>
</tr>
<tr>
<td>U-8Mo-3Nb vs. Al</td>
<td>265</td>
<td>1.40</td>
</tr>
<tr>
<td>U-7Mo-6Zr vs. Al</td>
<td>243</td>
<td>1.28</td>
</tr>
<tr>
<td>U-10Nb-4Zr vs. Al</td>
<td>248</td>
<td>1.31</td>
</tr>
</tbody>
</table>

Interaction Layer Phase Constituents

Identification of the phase constituents present within the ILs was another aspect considered within this study. An average composition over the thickness of the IL was obtained using EPMA to collect a concentration profile. As shown in Figure 4, the concentration across the U-7Mo-6Zr vs. Al IL is relatively constant with little gradient. The Al to (U+Mo) ratio is approximately 4 with slightly over 80 percent Al. This composition and profile is typical of ILs developed within these systems. In order to verify the phases present a TEM sample was taken from the IL in the U-7Mo-6Zr vs. Al couple. Figure 5(a) shows the FIB site from where the sample was lifted and Figure 5(b) is a STEM image of the TEM sample. Regions of different contrast were observed in the IL and acicular structures that were identified as pure Zr were observed in the U-7Mo-6Zr alloy side of the TEM sample as shown in Figure 5(b). Selected area diffraction patterns were collected from a region of the IL that appears to be the majority phase based on contrast. Representative electron diffraction patterns are shown in Figure 6, which were indexed to identify the IL phase as solid solution phase of UAl₃.

Figure 4. EPMA Concentration profile of IL from U-7Mo-6Zr vs. Al annealed at 600°C for 10 hours.
Discussion

With regard to IL thickness, the addition of the third element to the U alloy does not appear to slow down the interaction. The parabolic growth constants calculated for the diffusion couples including the ternary U alloy are not significantly lower than those calculated for the diffusion couples with the binary U-Mo alloy. One of the reasons for suggesting the use of Nb and Zr as alloying additions in U based fuel alloys was that these elements were thought to remain in solid solution with $\gamma$-U [12]. In the binary systems, these elements do remain in solution $\gamma$-U according to the phase diagrams, however, based on the characterization of the ternary alloys there is a limited solubility of the alloying additions. The formation of the Mo-X/Nb-Zr rich precipitates may be part of the reason the alloying additions do not reduce the growth of the interaction layer.

Another possible reason that the additions are not effective in mitigating the interaction is the fact that they cause a more rapid transformation from $\gamma$ to $\alpha$-U. It is known that U-Zr cannot be retained in the $\gamma$ phase and U-Nb can be retained in the $\gamma$ phase only at large Nb concentrations. The presence of the $\alpha$ phase allows for faster diffusion and typically nucleation of $\alpha$-U occurs at grain boundaries [12]. In particular, U-Zr alloys martensitically transform from $\gamma$-U to $\alpha$-U + $\alpha$-Zr, which is acicular in nature [15]. This agrees well with the microstructure observed in the U-7Mo-6Zr vs. Al couple where the reaction product penetrated into grain boundaries and the acicular $\alpha$-Zr formed in the $\gamma$ + $\alpha$ phase region. TTT diagrams show U-10Nb-4Zr starting to transform after 10 hours, which agrees with the micrographs collected showing IL penetrating into grain boundaries and enveloping grains [16]. The U-8Mo-3Nb also appears to have started transforming based on the micrographs where some reaction product is penetrating into the grain boundaries. Therefore, one method recommended to reduce the interaction layer thickness is to choose U alloys with high $\gamma$ stability. However, it has also been suggested that the decomposition of the $\gamma$ phase is a diffusion controlled process and a possible strategy for delaying the transformation is to choose elements that slow the rate of interdiffusion in U alloy systems as alloying additions.
While the growth kinetics of the interaction are an important aspect, the phase constituents of the interaction layer must also be considered. Based on the backscatter electron micrographs, regions of varying contrast were observed in all of the ILs suggesting the presence of multiple phases. After performing EPMA and obtaining the concentration profile across the U-7Mo-6Zr vs. Al IL, it appeared that the major phase constituent was UAl$_4$, which is the less preferred phase because of its properties. Many concentration profiles have been published with a similar composition distribution of about 80 percent Al [3,11,17]. However, selected area electron diffraction patterns identified the phase as the preferred UAl$_3$. Multiple phases have been identified in diffusion couples between U-Mo and pure Al via electron diffraction including UAl$_3$ and other more Al rich compounds such as UMo$_2$Al$_{20}$ and U$_6$Mo$_4$Al$_{43}$ [17]. The presence of these other phases could account for the unexpectedly high Al content on the concentration profiles as the values are an average composition. It is possible that these phases also appear in the diffusion couples investigated in this study, but they have not been identified via diffraction.

Summary

Diffusion couples between U-8Mo-3Nb, U-7Mo-6Zr, and U-10Nb-4Zr and Al were assembled and annealed at 600°C for 10 hours. The couples were examined in terms of interaction layer microstructure, thickness, and phase constituents. With thicknesses consistently around 250 µm, the alloying addition did not appear to reduce the interaction layer development as compared to diffusion couples assembled with binary U-Mo alloys. The parabolic growth constants for the systems with ternary U alloys (1.3–1.4 µm-sec$^{1/2}$) were not significantly lower than those calculated for the systems with the binary U-Mo alloys (0.9–1.8 µm-sec$^{1/2}$) and in some cases were higher. Possible reasons that the alloying addition was not beneficial may be that the elements did not remain in solid solution in the $\gamma$-U phase and hence could not influence the diffusion process as much as suspected. Another possible reason is that the additions increased the $\gamma$ to $\alpha$ transformation rate. While the interaction layer growth was not reduced by the alloying additions, electron diffraction was used to identify that the preferred UAl$_3$ phase appears to be the major phase constituent of the interaction layer, though other phases are present.

Acknowledgements

This work was performed with financial support from U.S. Department of Energy (DE-AC07-05ID14517) through Subcontract No. 00062267 administered by Battelle Energy Alliance, LLC and Idaho National Laboratory.

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