Microstructure of RERTR DU-Alloys Irradiated with Krypton Ions

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ABSTRACT

The radiation stability of the interaction product formed at the fuel-matrix interface of RERTR fuels has a strong impact on fuel performance. Three depleted uranium alloys were cast that consisted of the following 5 phases to be investigated: U(Si, Al)₃, (U, Mo)(Si, Al)₃, UMo₂Al₂₀, U₆Mo₄Al₄₃ and UAl₄. Irradiation of TEM disc samples with 500 keV Kr ions at 200°C to doses up to ~100 dpa was conducted using a 300 keV electron microscope equipped with an ion accelerator. TEM results show that U(Si, Al)₃ and UAl₄ phases remain crystalline at 100 dpa without forming voids. UMo₂Al₂₀ and (U, Mo)(Si, Al)₃ phases become amorphous at 10 dpa and ~2 dpa, respectively, and show no evidence of voids at 100 dpa. The U₆Mo₄Al₄₃ phase goes to amorphous at less than 1 dpa and reveals high density voids at 100 dpa, suggesting that this phase may be responsible for the swelling from large bubbles in the interaction layers.

1. INTRODUCTION

An important part of the fuel development program for reduced enrichment research and test reactors (RERTR) is to study fuel performance under irradiation. Radiation stability of the potential fuel-cladding interaction product can have a strong impact on fuel performance. Microstructural characterization using transmission electron microscopy (TEM) is capable of providing detailed microstructural information (crystalline structure, precipitates, defects, various interfaces and microchemistry, etc) with resolution down to the nanometer range.
A variety of phases have the potential to develop as products of the fuel/cladding interaction (FCI) in RERTR fuel. To study the effects of radiation on the potential fuel/cladding interaction product, three depleted uranium (DU) alloys were arc-cast at the Idaho National Laboratory (INL) with the compositions of 67U-5Si-28Al, 48U-5Mo-47Al and 69U-4Mo-20Al-7Si. The first alloy composition selected is close to that of a U(Al, Si)\textsubscript{3} phase. This phase has been observed to form in uranium-silicide dispersion fuels and exhibits stable performance under irradiation [1]. The second composition is near that of (U, Mo)Al\textsubscript{7}, a composition observed in interaction layers of the current version of U-Mo dispersion fuels that use aluminum as the matrix, which show poor irradiation performance at very high burnup [2]. In order to improve the performance of U-Mo dispersion fuels, the RERTR program has been investigating the use of Si additions to the aluminum cladding matrix to influence fuel/matrix interaction such that a more stable interaction product will form. By having Si participate in the interdiffusion process, it is likely that a (U, Mo)(Al, Si)\textsubscript{3} phase will form and the resultant material may remain stable under irradiation, like the U(Al, Si)\textsubscript{3} phase did in the uranium-silicide fuels [3]. As a result, the third alloy has a composition near that of a (U, Mo)(Al, Si)\textsubscript{3} phase.

Many research and test reactors are operating with a water coolant at coolant temperatures less than 100 °C. A plate-type fuel normally has a thickness of approximately 1.5 mm. A thin layer of dispersion fuel about 0.5 mm thick is sandwiched with ~ 0.5 mm thick aluminum alloy cladding on both sides. In the dispersion fuel layer, fuel particles with various diameters up to ~ 100 µm are embedded in the aluminum matrix. Typical peak fuel temperature is expected to be less than 200 °C. Radiation damage processes in the microstructure of RERTR fuels consist of damage due to neutrons and fission products. For ion irradiation studies, heavy ion irradiation with Kr ions is preferred in order to investigate microstructure response for both displacement damage and the damage associated with fission products [4,5].

2. EXPERIMENTS

Three DU alloys were cast using arc melting with high-purity (99.999 %) Al, Mo and Si and followed by homogenization heat treatment at 500°C for 200 hours. The composition and crystalline structure of each intermetallic phase identified in these alloys are listed in Table 1. TEM disc samples were prepared from three DU alloys through slicing, core-drilling, mechanical thinning, electrical jet-polishing and precision ion polishing. The SRIM code was used to estimate displacements per atom (dpa) for Kr ion irradiation [6]. The atomic displacement energies of 25eV, 40eV and 60eV were used for Al, U and Mo, respectively. The calculated 1-dpa Kr ion fluence is 2.3×10\textsuperscript{14}, 2.4×10\textsuperscript{14}, 2.8×10\textsuperscript{14} and 2.5×10\textsuperscript{14} ions/cm\textsuperscript{2} for UAl\textsubscript{3} type phase, UAl\textsubscript{4}, UMo\textsubscript{2}Al\textsubscript{20} and U\textsubscript{5}Mo\textsubscript{4}Al\textsubscript{33}, respectively. For simplicity, an average 1-dpa equivalent ion fluence of 2.5×10\textsuperscript{14} ions/cm\textsuperscript{2} was used for all of the five phases.
Table 1: Crystal structural information of the intermetallic phases identified in three DU alloys

<table>
<thead>
<tr>
<th>Phase</th>
<th>Alloy</th>
<th>Crystalline Structural Information [7,8,9,10,11]</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(Al, Si)$<em>3$ U$</em>{27}$Si$<em>{13}$Al$</em>{60}$</td>
<td>67U-5Si-28Al</td>
<td>Cubic, L1$_2$ ordered Cu$<em>3$Au type, a=b=c=0.424 nm, Pearson symbol: cP4, Space group: 221, $T</em>{melt}=1350$ °C for UAl$_3$</td>
</tr>
<tr>
<td>(U, Mo)(Al, Si)$<em>3$ U$</em>{27}$Mo$<em>3$Si$</em>{19}$Al$_{49}$</td>
<td>69U-4Mo-20Al-7Si</td>
<td>Cubic, L1$_2$ ordered Cu$_3$Au type, a=b=c=0.422 nm, Pearson symbol: cP4, Space group: 221</td>
</tr>
<tr>
<td>UM$<em>{25}$Al$</em>{50}$ U$_{57}$Mo$<em>2$Al$</em>{8}$</td>
<td>48U-5Mo-47Al, 69U-4Mo-20Al-7Si</td>
<td>Cubic, a=b=c=1.4506 nm, Pearson symbol: cf184, Space group: 227, $T_{melt}=1200$ °C</td>
</tr>
<tr>
<td>U$<em>6$Mo$<em>4$Al$</em>{43}$ U$</em>{12}$Mo$<em>8$Al$</em>{78}$</td>
<td>48U-5Mo-47Al</td>
<td>Hexagonal, a=b=1.0966 nm, c=1.7690 nm, c/a=1.613, $\alpha=\beta=\gamma=90^\circ$, Pearson symbol: hp106, Space group: 193, $T_{melt}=1360$ °C</td>
</tr>
<tr>
<td>UA$<em>{14}$ U$</em>{22}$Al$_{78}$</td>
<td>48U-5Mo-47Al</td>
<td>Body-centre orthorhombic, a=0.6270 nm, b=1.3710 nm, c=0.4410 nm, $\alpha=\beta=\gamma=90^\circ$, Pearson symbol: ol20, Space group: 74, $T_{melt}=730$ °C</td>
</tr>
</tbody>
</table>

Note: Both nominal and the measured specific composition in at% for each phase is listed.

The TEM discs of DU alloys were irradiated with 500 KeV Kr ions at 200 °C to doses up to 100 dpa (2.5×10$^{16}$ ions/cm$^2$) using the intermediate voltage electron microscope (IVEM) equipped with a Tandem accelerator at Argonne National Laboratory. The dose rate is estimated to be $\sim 4\times10^{-3}$ dpa/s. The ion beam has a diameter of $\sim 1.5$ mm on the specimen. The angle between ion beam for irradiation and electron beam for TEM analysis is 30 degrees. The specimen chamber vacuum is better than 4×10$^{-7}$ torr. A double-tilt high-temperature TEM specimen holder was used. With the selected ion energy, a significant portion of the injected Kr ions was retained in the material ($\sim 15\%$ for a 100 nm thick foil). The in-situ TEM analysis was performed using a Hitachi H-9000NAR transmission electron microscope operating at 300 keV at the IVEM facility. A more detailed post-irradiation microstructural characterization was conducted using a 200 keV JEOL-2010 transmission electron microscope at the INL.

3. RESULTS

For the U(Al, Si)$_3$ phase, Kr ion irradiation resulted in loop development as shown in Figure 1. Small loops are identified at 1 dpa. At 3 dpa, some large loops with sizes greater than 50 nm are present. At 10 dpa, the densities of loops and dislocations increase and tangle between loops and dislocation segments are evident. No faulted loops are identified. The dislocations evolve to ribbon-shaped superdislocations at 100 dpa. The selected area diffraction (SAD) patterns for unirradiated and irradiated U(Al, Si)$_3$ phase indicate an ordered fcc crystalline structure (L1$_2$ type). This crystalline structure remains stable at 100 dpa with a clear Kikuchi line pattern and SAD pattern. No voids are identified. The super lattice structure with extra fine spots diminishes at very low dose ($\sim 0.2$ dpa), suggesting that it is insignificant to the microstructural stability.
For the (U, Mo)(Al, Si)_3 phase, the microstructural evolution is quite different than in U(Al, Si)_3 with no evidence of loop development before it turns amorphous at an irradiation dose as low as ~ 2 dpa. The microstructural changes as a function of irradiation dose in (U, Mo)(Al, Si)_3 are shown in Figure 2. The images on the top show the SAD patterns of zone [123] while the images on the bottom show the bright field image under g=-1,-1,1, the same condition as in Fig. 1. At a dose of 0.25 dpa, small defects developed and a diffuse ring is visible in the SAD zone pattern. At 0.5 dpa, these defects grow in size and many spots in the SAD pattern are diminished. As the irradiation proceeds to 1 dpa, the defect contrast drops to zero and the SAD pattern indicates the majority of the (U, Mo)(Al, Si)_3 has transformed to an amorphous state. At approximately 2 dpa, this phase becomes completely amorphous.
For the UM₀₂Al₂₀ phase, bright field images of high-density stacking faults for the unirradiated and 4 dpa samples and bubbles for the 1, 10 and 100 dpa samples are shown in Figure 3. The UM₀₂Al₂₀ phase begins transforming to amorphous at ~ 2 dpa and becomes fully amorphous at ~ 10 dpa. There is no significant change in small bubbles between 1 dpa and 10 dpa. No voids are found at doses up to 100 dpa. No loops were found prior to the UM₀₂Al₂₀ phase becoming amorphous.

Fig 3. Bright field images of the UM₀₂Al₂₀ phase near zone [011] shows the high-density stacking faults (left) and bubbles (right) at various doses up to 100 dpa.

For the UAl₄ phase, high-density small defects with sizes of a few nanometers were found at 1 dpa as shown in Fig. 4. These small defects are believed to be responsible for the presence of streaks in the SAD patterns. The size of these small defects increases with dose up to 10 dpa. The contrast of these defects suggests that these are likely dislocation loops. Small bubbles (~ 2 nm) at high density are found at 1 dpa. At 100 dpa, these bubbles slightly increase in size (~ 3 nm) but no voids are identified. Most of the preexisting amorphous precipitates in UAl₄ are dissolved at 100 dpa. Limited composition analysis with electron-dispersive spectroscopy (EDS) reveals Mo in these precipitates. Although the UAl₄ phase retains its crystalline structure at 100 dpa, the visibility of the Kikuchi line pattern drops to nearly zero at 10 dpa and the clarity of SAD pattern is significantly deteriorated at 100 dpa.

Fig 4. Bright field images of defects in the UAl₄ phase irradiated with 500 keV Kr at 200 °C to 1 and 10 dpa (left) and 100 dpa (right) showing high-density small defects.
For the U₆Mo₄Al₄₃ phase, Figure 5 shows a 2-beam bright field image and SAD patterns as a function of irradiation dose. The initial microstructure is clean with no sign of dislocations or precipitates. Kr ion irradiation at 200 °C quickly turns U₆Mo₄Al₄₃ amorphous at a dose as low as 1 dpa. Bubbles are found at 1 dpa, but no voids are identified at 10 dpa. At 100 dpa, high-density bubbles with size up to ~ 500 nm are present.

![Fig 5. SAD (top) and bright field images (bottom) in U₆Mo₄Al₄₃ irradiated at 200°C.](image)

4. DISCUSSION

Irradiations of TEM disc samples with 500 keV Kr ions at 200 °C to various doses up 100 dpa result in different microstructural response in the five phases investigated. The results from this work indicate that the microstructural stability of these five phases, ranking from the stable to the unstable, are U(Al, Si)₃, UAl₄, UMo₂Al₂₀ₙ, (U, Mo)(Al, Si)₃ and U₆Mo₄Al₄₃. Although small bubbles of ~ 2 nm are found in some of these phases, large voids or gas bubbles are only found in U₆Mo₄Al₄₃ at 100 dpa. These findings provide insight to a better understanding of the role of irradiated microstructure on fuel performance and the possible mechanism of the Si addition to the Al alloy matrix on stabilizing the microstructure of the fuel-cladding interaction product under irradiation.

The irradiation behavior of U(Al, Si)₃ is consistent with literature data [1]. In addition to its ordered fcc structure (L1₂), the super lattice structure in the unirradiated condition has not been previously reported. Since the super lattice diffraction spots are diminished at a very low dose (around 0.2 dpa), the role of this super lattice structure on the microstructural performance of U(Al, Si)₃ under irradiation is expected to be insignificant. Considering the melting temperature of ~ 1350 °C, that large loops developed at a relatively low irradiation temperature suggests high mobility of point defects in this phase. The effect of superdislocation development at high doses (> 50 dpa) on the microstructural stability under irradiation does not appear to be problematic. At 100 dpa, the U(Al, Si)₃ phase remains crystalline structure without significant degradation on the Kikuchi line pattern or SAD pattern. This finding disagrees with the results reported by Ryu et al based on x-ray diffraction that the interaction layers in silicide fuel (U₃Si₂ in Al matrix), that containing the U(Al, Si)₃ phase [12,13], will become amorphous after irradiation [14].
The \((U, Mo)(Al, Si)_3\) phase, with a crystalline structure similar to \(U(Al, Si)_3\), showed a very different response to Kr ion irradiation under similar conditions. The crystal became amorphous at a dose of \(\sim 1\) dpa. In comparison between the \(U(Al, Si)_3\) and \((U, Mo)(Al, Si)_3\) phases, the measured composition in Table 1 indicates that the latter has an extra 3 at.% Mo with a stoichiometry of heavy element \((U, Mo)\) to light element \((Al, Si)\) as 1:2.3, rather than 1:3 for a stable \(Cu_3Au\) type ordered structure. Kim reported that the addition of Mo to the interaction layer of \(U-Mo/Al\) reduces the stability of the interaction layer \[15\]. This result indicates that approximately 5 at% of \(U\) or Mo atoms cannot occupy their normal lattice sites at the corners in a \(Cu_3Au\) type ordered fcc crystalline structure. This may be responsible for the \((U, Mo)(Al, Si)_3\) phase going amorphous at a low dose. The lack of void or large bubbles at 100 dpa in the amorphous \((U, Mo)(Al, Si)_3\) suggests that the amorphous phase is not necessarily a leading cause of the bubble swelling in the interaction layers.

The microstructural response of the \(UMo_2Al_{20}\) phase under Kr ion irradiation is consistent with the literature data. This crystal has a very large simple cubic cell with 184 atoms in a complex arrangement \[16\]. The high-density stacking faults found in this phase indicate low stacking fault energy in the unirradiated \(UMo_2Al_{20}\) phase. The lack of defect feature development except for stacking faults may be related to its complex structure. This phase begins amorphization at \(\sim 2\) dpa and shows only an amorphous ring in SAD at 10 dpa. No voids or large bubbles are identified at 100 dpa, indicating that \(UMo_2Al_{20}\) phase, which tends to develop near the end of interaction layer close to Al alloy matrix, may not be the leading cause of the formation of large bubbles in the interaction layers.

The \(UAl_4\) phase is the low melting point phase among the five phases investigated. The irradiation temperature of 200 \(^{\circ}\)C may be too high \((T_{irr}/T_m=0.47)\) for it to undergo an amorphous transformation. Significant radiation damage in this phase is evident as the visibility of Kikuchi line patterns drops to zero and clarity of SAD patterns is degraded at 10 dpa. It is rather surprising that the \(UAl_4\) retains crystallinity at a high dose of \(\sim 100\) dpa. No voids are found at 100 dpa. The heavy ion irradiation study by Wieschalla et al. using 120 MeV iodine ions at 200 \(^{\circ}\)C in dispersion fuel \((U-6Mo\) or \(U-10Mo\) dispersed in Al) indicated that the irradiation-induced fuel/cladding interaction layer contains multiple phases of \(UAl_2, UAl_3\) and \(UAl_4\) \[17\]. They concluded that the large fraction of the brittle \(UAl_4\) phase that tends to crack under stress in the interaction layers is responsible for the breakaway swelling observed in the reactor-irradiated dispersion fuel.

The \(U_6Mo_4Al_{43}\) phase was the most unstable phase among the five phases irradiated using Kr ions. The initial microstructure of this phase is clean and featureless. Irradiation-induced amorphization occurred at quite a low dose and the phase became fully amorphous at \(\sim 1\) dpa. While no voids or large bubbles are identified at 10 dpa, high-density bubbles, some greater than 50 nm, are found at 100 dpa. This phase may be responsible for the aggressive bubble swelling observed in the FCI in the irradiated dispersion fuels.

Keiser et al. reported the presence of the \((U, Mo)(Al, Si)_3\) phase in the interaction layer of the as-fabricated dispersion fuel \[18\]. The recent results by Keiser et al. on the irradiated dispersion fuel with \(\sim 50\%\) burnup, \(\sim 100\) \(^{\circ}\)C peak temperature and \(\sim 3.5 \times 10^{21}\) fission/cm\(^3\) show clear correlation between Si content and fission gas bubbles \[19\]. Fission gas bubbles are found in the Si depleted zone but not in the neighboring zones with relatively high Si content in the interaction layer. It may be possible that Si atoms in the \(U(Al, Si)_3\) type interaction layer reduce the mobility of fission gaseous atoms. The high Si
content in the interaction layer may also increase the material surface energy, thus inhibiting bubble growth. These effects may compete with the effects of amorphization and slow down the swelling driven by fission gas. Another possible mechanism of Si effect on stabilizing microstructure in FCI layers against aggressive bubble swelling is the impact of Si in the Al alloy on suppressing the formation of the U₆Mo₄Al₄₃ phase in the interaction layers [20,21].

Rest has shown that the viscosity of an irradiated amorphous material depends on the composition [22]. Rest has also related the gas-driven swelling of the amorphous material to the materials viscosity [23]. A relatively high Si content may increase the viscosity of the irradiated materials and thus limit the growth of the fission gas bubbles.

Hofman [24] proposes that for U-Si fuels, which also go amorphous during irradiation, the additional Si bonds in U₃Si₂ relative to U₃Si results in an improvement in irradiation performance. These additional bonds reportedly have a large effect on the amount of free volume in the material, which affects the fluidity of the fuel and the fission gas diffusivity and swelling behavior. For the U₃Si₂, which behaves well during irradiation, the increase in free volume during amorphization is negligibly small, and for U₃Si, which behaves poorly during irradiation, the increase in free volume during amorphization is relatively large. This means that just because a material goes amorphous it is not guaranteed that there will be a large swelling increase unless there is a significant increase in free volume.

5. CONCLUSION

The three DU alloys cast contain five phases relevant to the fuel/cladding interaction product in RERTR dispersion fuels. The effectiveness of the use of Kr ion irradiation to investigate the irradiation-induced damage to the microstructure from fission has been demonstrated. Among the five phases investigated, U(Al, Si)₃ is identified as the most stable phase up to 100 dpa with a well-developed dislocation microstructure. The U₆Mo₄Al₄₃ phase is identified as the problematic phase that turns fully amorphous below 1 dpa and develops high-density large bubbles at 100 dpa. The UAl₄ phase is relatively stable and retains its crystalline structure up to 100 dpa with significant degradation in SAD zone patterns. The ternary phase UMo₂Al₂₀ becomes fully amorphous at ~ 10 dpa. The (U, Mo)(Al, Si)₃ phase becomes amorphous at a dose of ~ 1 dpa, but shows no voids or large bubbles at 100 dpa.

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