

Effects of U_3MoSi_2 and Ti-rich layers on the diffusion between U and Al

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1. Introduction

U-Mo dispersion fuel has become a promising candidate to allow conversion from HEU (High-Enriched Uranium, all enrichments > 20% ^{235}U) to LEU (Low-Enriched Uranium, all enrichments < 20% ^{235}U) for high power research reactors.[1-7] Many efforts to identify the irradiation characteristics of the U-Mo alloys showed that the alloys with Mo contents of 7-10 wt.% have a good irradiation behavior and sufficient high intrinsic density.[8-10] However, local swelling by fission products in the high power zones was observed during some irradiation tests, and it was proved that it was caused by a formation of interaction layers (ILs) between U-Mo particles and Al matrix.[11-14] As one of remedies, Si was added to the Al matrix to stabilize the swelling behavior of U-Mo fuel during the irradiation at high fission rates, but it was insufficient to suppress the formation of ILs.[15-20] Another approach is the surface coating (or surface engineering) of U-Mo alloy particles using a PVD magnetron sputtering[21], or a pack cementation coating method developed by KAERI.[22-24] Alloying third elements to the U-Mo alloy is also proposed to reduce ILs growth, and it is considered that the third elements have a propensity to form strong compounds with Al than that of U. Transition metals such as Ti and Zr are possible candidates, and the out-of-pile test results showed that either the phase stability, or the IL growth was positively affected by the addition of those metals to U-Mo alloy.

In this study, we demonstrate the formation of silicide coating layers, U_3Si_5 , U_3Si_2 and U_3MoSi_2 , on the surface of U-7Mo and U-7Mo-1Ti powders using the pack cementation method, and the suppression of Al diffusion into the U kernel by the U_3MoSi_2 layer. The observation for the Ti addition provided that could explain the prevention of Si diffusion into the grain boundary of U-7Mo kernel by the formation of Ti-rich layer, whereas Si diffused along the grain boundary of U-7Mo kernel without the Ti addition on U-7Mo.

2. Experimental Procedure

Centrifugally atomized U-7Mo and U-7Mo-1Ti powders (90-150 μm in dia.) were prepared for the pack cementation coating. Those powders were blended with and Si powders (purity 99%, 1-5 μm in dia.) in the shaker mixer, and subsequently heat-treated in a vacuum furnace under a 10^{-5} torr at T (T = 1173 and 1273 K) for 30 min, respectively. The experimental procedure

for the pack cementation is described in detail elsewhere. [24] Heat-treated powders were compacted with Al powders (99.99%, μm in dia.) using a 5 ton press. We therefore categorized specimens into four types according to the kind of powders, and the heat-treatment conditions: U-7Mo (uranium-silicide coated at 1173K for 30 min) / Al matrix compact (#A), U-7Mo-Ti (uranium-silicide coated at 1173K for 30 min) / Al matrix compact (#B), U-7Mo (uranium-silicide coated at 1273K for 30 min) / Al matrix compact (#C), and U-7Mo-1Ti (uranium-silicide coated at 1273K for 30 min) / Al matrix compact (#D). The compacts (10 mm in dia. \times 2 mm thick) were subsequently annealed in a vacuum furnace under a 10^{-5} torr at 823 K and 873 K for 2 hr respectively. The formation of uranium-silicide layers and ILs between uranium-silicide coated powders and Al matrix were analyzed using back-scattered scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Uranium-silicide coating layers were analyzed by a powder X-ray diffract meter (XRD).

3. Results

To serve as references to the annealed samples, microstructures of as-prepared specimens are presented in Fig.1(a) and (b).

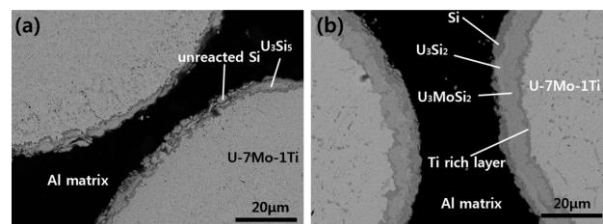


Fig. 1. SEM micrographs of as-prepared; (a) #A, and (b) #B.

During the heat-treatment, in the case of #A and #B, only U_3Si_5 formed on the surface of the particles while in the case of #C and #D, U_3Si_2 and U_3MoSi_2 formed. It was shown that the 5 μm thick coating layer of #A and #B was unreacted Si and uranium-silicide phases, and it was hard to distinguish them from each other. Around 10 μm thick coating layer of #C and #D was divided into two layers in common; U_3Si_2 and U_3MoSi_2 from the outside to the inside. In the case of #D, the innermost Ti-rich layer was also observed, and it was possibly formed by outward diffusion of Ti atoms from Ti precipitations located in the grain boundaries of the U-7Mo-1Ti kernel. The evolution of uranium-silicide coating layers of all specimens was confirmed by powder XRD, as shown in Figs. 2(a) and (b)..

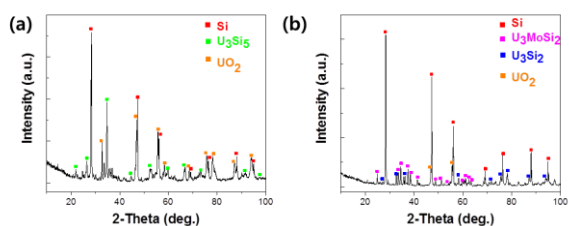


Fig. 2. XRD spectra; (a) #A, and (b) #B

As indicated in Fig. 3, after annealing for 2hr at 823K, the diffusion of Al into the kernel was effectively prevented by the coating layers in the case of #A and #B. However, few particles of #B showed discrete parts in the coating layer, and through those parts Al diffused into the kernel and formed UAl_3 phase by inter-reaction with U shown in Fig. 3(e). In the case of #C and #D, diffusion of Al into the kernel was inhibited by the coating layers, and the thickness of the coating layers was remained unchanged shown in Fig. 4(b) and (d).

In both #A and #B, formation of ILs, uranium aluminides, is observed after annealing at 873 K for 2hr, which indicates the diffusion barrier degradation. The thickness of ILs was varied with each particle, and it can be assumed that interaction was more active for smaller particles due to its larger surface area. The thickness of the coating layer, unreacted Si and U_3Si_5 , was pretty much the same as that of as-prepared #A. However, the surface of the specimen seemed to more rough than before, and a part of disconnection also found. UAl_3 is a typical uranium-aluminide intermetallic compounds (IMCs) by inter-diffusion between Al and the U-Mo alloys.

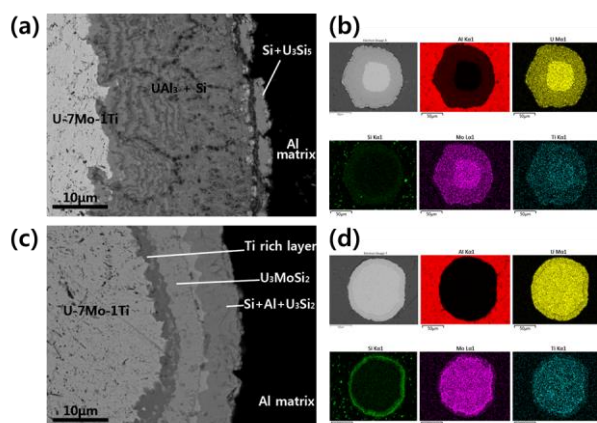


Fig. 3. SEM Micrographs; (a), (b) #A, and (c), (d) #B after annealing at 823 K for 2 hr.

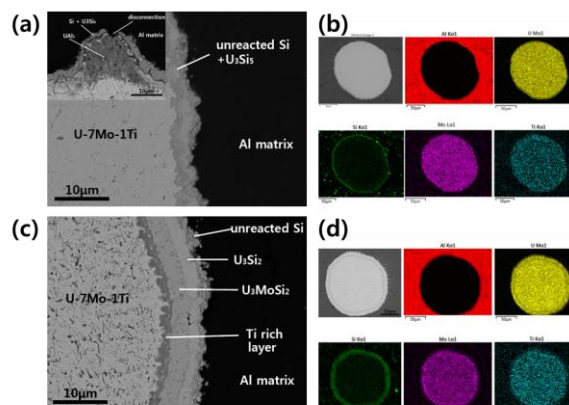


Fig. 4. SEM Micrographs; (a), (b) #A, and (c), (d) #B after annealing at 873 K for 2 hr.

4. Discussion

Formation of the IMCs can be explained in terms of the susceptibility to diffusion of Al into the uranium-silicide coating layer. A.E. Dwight. reported that U_3Si_5 marks the compositions at which the silicides begin to take Al into a solid solution, and U_3Si_5 is the only phase in which Si-Si bond is not present. In other words, a ternary element (e.g. Al) can easily enter an empty lattice or displace the Si atoms. [25] Interestingly, the coating layers still remained at the outermost layer of a particle. For unreacted Si, there are no IMCs between the Al and Si, and thus Al should pass the Si layer in some way to interact with U-7Mo-1Ti alloys. A possible explanation for this phenomenon is cracks of the outermost thin Si layer caused by the compaction process or the annealing. The compaction or annealing can frequently cause the cracks of the coating layer of U-7Mo-1Ti particles, and once initiated cracks can be a diffusion path for Al atoms into U-7Mo-1Ti. Diffused Al atoms reacted or passed by thin uranium-silicide coating layers first, and then reacted with the core of U-7Mo-1Ti alloys. The final transformed phase was a UAl_3 phase, and small quantity of Si found in that phase. In some #A, U-7Mo-1Ti particles were fully transformed into UAl_3 , and in others, a transformed 30-40 μm thick UAl_3 layer was observed, as shown in Figs. 4(a) and 4(b).

In the case of #B, although Al diffused into the outermost coating layer like #A, Al did not react with the core of U-7Mo-1Ti particles, as shown in Figs. 4(c) and 4(d). The U-7Mo-1Ti core was protected by the U_3MoSi_2 layer while small quantity of Al was found in the outermost layer, U_3Si_2 phase. This result showed good agreement with the annealing experiments on U_3Si_2 / Al matrix dispersion fuel[26-29], which showed a formation of UAl_3 or $U(Al,Si)_3$ at the interface between the U_3Si_2 and Al, and the growth of UAl_3 obeyed classical diffusion kinetics.

For consideration of the interruption of Al diffusion by the U_3MoSi_2 layer presented above, the knowledge of the crystal structure for U_3MoSi_2 is needed. According to JCPDS card Nos. 47-1070 and 51-0999, the U_3Si_2 phase is tetragonal and the U_3MoSi_2 phase is cubic respectively. A tetragonal phase is more open to diffusion of different elements such as Al than a cubic phase due to its lower packing factor at the same temperature. It can also be assumed that the heat-treatment temperature 1273 K was high enough to overcome the activation energy (Q) for U or Si replacement by Mo in the U_3Si_2 phase, and it resulted in the formation of U_3MoSi_2 . On the other hand, in the U_3MoSi_2 phase, a high Q is necessary for the substitutional diffusion of Al against Mo which pre-occupied U or Si sites in the U_3Si_2 phase, but the annealing temperature of 873 K was not high enough to overcome Q.

5. Conclusions

In this sense, Al diffusion into the core of U-7Mo-1Ti was interrupted by U_3MoSi_2 , and it could be concluded that the effect of U_3MoSi_2 phase as a diffusion barrier for Al is valid for the annealing at 873 K for 2 hr. There is no higher temperature process in regard of the fabrication of nuclear fuel, thus U_3MoSi_2 can be a possible candidate for the surface engineering of U-Mo alloy powders. However, the results of the irradiation test should be considered in the near future.

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