PHASE STABILITY AND DIFFUSION CHARACTERISTICS OF U-MO-X (X=SI, AL, ZR) ALLOYS

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ABSTRACT

As a means to reduce the reaction between the U-Mo and Al in U-Mo/Al dispersion fuels, a third element addition to U-Mo was proposed recently by Argonne National Laboratory. As preliminary tests before an in-reactor irradiation, we investigated by laboratory tests the efficacy of an addition of an X (= Si, Al, or Zr) element to U-7Mo in light of the gamma phase stability and diffusion reaction behavior. By using a vacuum induction melting technique, a third element was added to the U-7Mo. Gamma phase stability of the quenched specimens was tested by high temperature annealing tests. X-ray diffraction showed that the addition of a small amount (~0.2 wt%) of Si improved the gamma stability of the U-7Mo significantly whereas Al worsened it. Other elements revealed no effects. To examine the diffusion behavior, diffusion couples were made by encapsulating U-7Mo-X plates with pure Al plates and hydraulically pressing the layers. After an annealing at 550°C, the reaction layer thicknesses were measured. Annealings of 4.5 gU/cm^3 U-7Mo-X/Al and U-7Mo/Al-Si dispersion fuels at 550°C and 580°C were carried out for 2 - 50 hrs to measure the growth rate. Reaction layer compositions of each diffusion couple were also measured by an electron probe microanalysis. The diffusion behavior of the U-7Mo was compared to that of U-7Mo-X alloys.

1. Introduction

In the reduced enrichment for research and test reactors (RERTR) program, uranium-molybdenum alloy fuel with high uranium density is being developed for high performance research reactors[1]. Although gamma phase U-Mo alloys have the best irradiation performance, U-Mo/Al dispersion fuels have shown an unacceptably large pore formation during an irradiation due to the unstable properties of an interaction layer (IL) between the U-Mo fuel particle and the Al matrix[2]. As the IL grows, the fuel temperature increases because its thermal conductivity is lower than matrix Al[3]. Moreover, since the IL has a lower density than the average of the

participating reactants, its growth causes a significant volume expansion of the fuel meat. It is necessary to develop a modified U-Mo alloy that is capable of either forming a more stable IL or reducing its growth. A method proposed by ANL is adding stabilizing elements to the U-Mo fuel and the Al matrix[4].

In this study, Si, Al, or Zr was added to U-7Mo alloy and Si was added to matrix Al. Gamma phase stability tests of the U-Mo-X alloys, diffusion couple tests between U-Mo-X and Al, and compatibility tests with U-Mo-X/Al and U-Mo/Al-Si dispersion fuels were performed.

2. Experimental Procedures

U-7Mo-X(=Si, Al, Zr) alloy was vacuum-induction melted in a zirconia crucible and casted into a rod for diffusion couple tests. Centrifugally atomized U-7Mo-X(=Si, Zr) alloy powder was fabricated for compatibility tests[5]. The average size of the U-7Mo-X powder ranged 200-300 ㎛. The U-7Mo-X powder and the aluminum alloys in a powder form (i.e. pure Al powders, Ai-0.4wt%Si, and Al-2.0wt%Si) were mixed in a V-mixer with a rotation speed of 90 rpm for 1 hr and hot-extruded at 400°C. The uranium loading density in the U-7Mo-X/Al(-Si) dispersion fuels was 4.5 gU/cm^{3}. The as-cast U-7Mo-X ingots were heat-treated in a vacuum at 950°C for 24 hrs and then quenched to stabilize the gamma uranium phase for the diffusion couple test. Gamma stabilized U-7Mo-X specimens were annealed at 500°C from 30 mins to 48 hrs to examine the stability of the gamma phase. U-7Mo-X vs. Al diffusion couples were also annealed at 550°C and 580°C from 2 hrs to 50 hrs in a vacuum atmosphere by using simple clamping equipment as shown in Fig. 1. The growth behavior of the ILs in U-7Mo-X/Al dispersion fuel was observed by annealing at 550°C and 580°C for up to 50 hours in a vacuum-sealed quartz tube. X-ray diffraction (XRD) techniques were used to compare the stability of the gamma phase in U-7Mo-X after annealing tests. The microstructures of the ILs in the diffusion-couple-test specimens and the annealed dispersion fuel samples were characterized by scanning electron microscopy (SEM). Concentration profiles of the ILs in the diffusion couples and in the annealed dispersion fuels were obtained by using a JEOL JXA8600 microprobe equipped with an energy dispersive spectrometer.

3. Results and Discussion

3-1. Gamma Phase Stability

As shown in the phase diagram of the uranium and molybdenum system in Fig.2[6], the gamma phase is not stable below about 600°C for a U-7Mo alloy. As a result, the gamma phase of U-7Mo alloy decomposes when annealed at temperature below 600°C. Annealing of U-7Mo or U-7Mo-X alloys at 500°C, as tested in this study, results in a transformation into a mixture of an alpha uranium phase and a gamma prime U_2Mo phase. Figure 3 compares the effects of Al and Si on the stability of the gamma phase of the U-7Mo-X ternary alloys. When 1-wt% Al is added to a U-7Mo alloy, the gamma phase decomposed earlier than a U-7Mo alloy and a U-7Mo-1Si alloy as shown in Fig. 3(a). Only the U-7Mo-1Al alloy was transformed to the alpha phase and a gamma prime phase after 1 hour at 500°C. Silicon, however, showed an excellent gamma stabilizing ability as shown in Fig. 3(b). Even after 24 hours of an annealing, U-7Mo-1Si

alloy did not show a typical diffraction pattern of a transformed uranium alloy when compared to U-7Mo and U-7Mo-1Al.

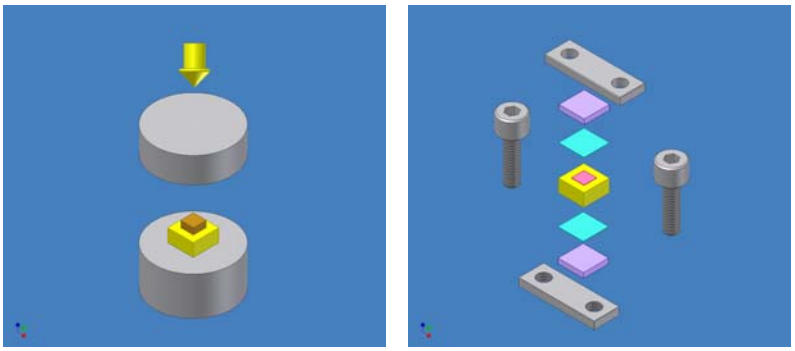


Fig. 1. Schematic illustration of the diffusion couple test equipment.

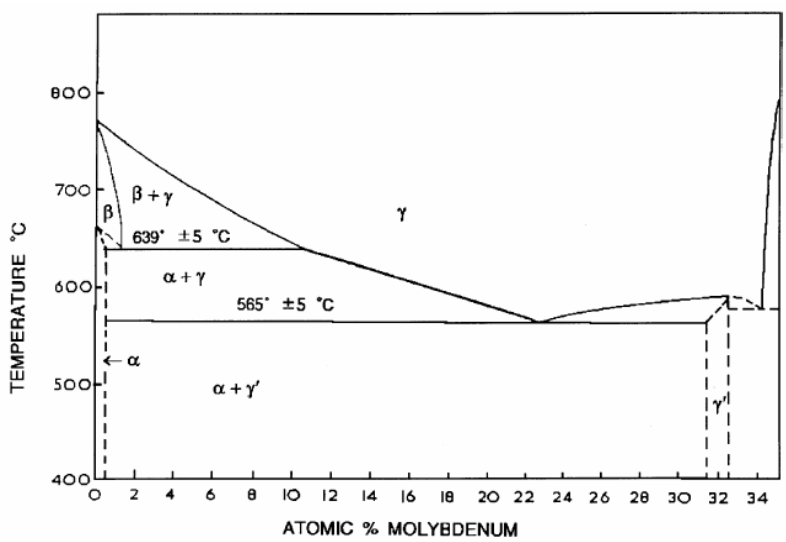
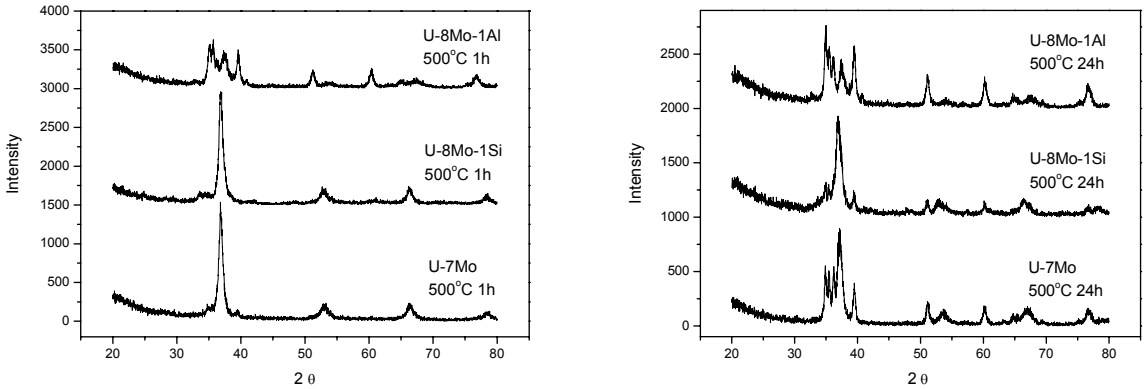


Fig. 2. Phase diagram of U-Mo system.



(a) (b)

Fig. 3. X-ray diffraction patterns showing the stability of the gamma phase in the U-7Mo, U-8Mo-1Al, and U-8Mo-1Si annealed at 500°C for (a) 1 hour and (b) 24 hours.

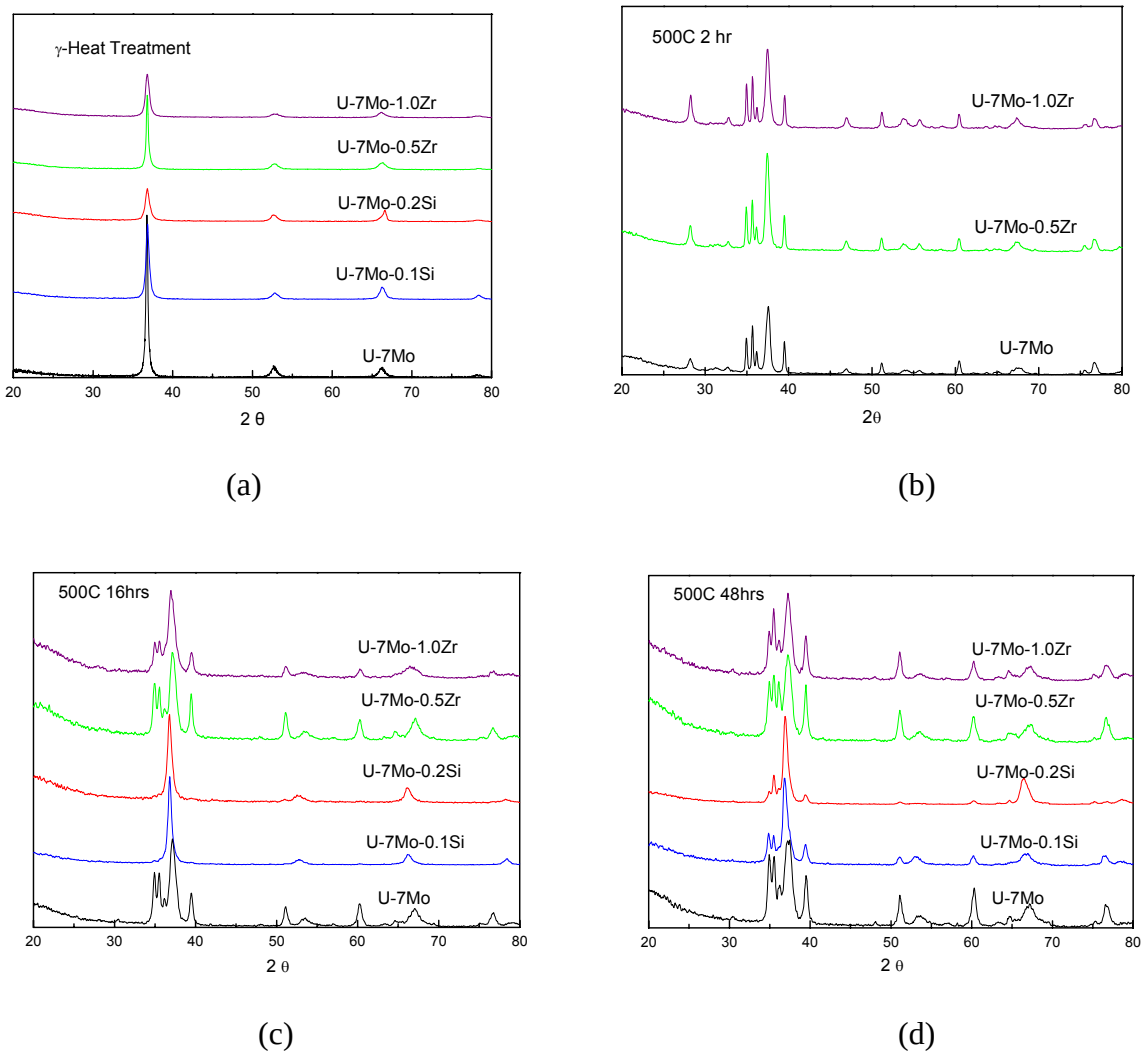


Fig. 4. X-ray diffraction patterns showing the stability of the gamma phase of U-7Mo-X(X=Si,Zr).

Since gamma phase uranium has a superior irradiational behavior, an addition of a ternary element which stabilizes the gamma phase is recommended. Moreover, Al which has been used as a matrix material for the dispersion fuel, may degrade the gamma stability during irradiation. Another reason for adding a ternary element is stabilizing the ILs of the U-Mo/Al dispersion fuel so as not to subject it to an unacceptable pore formation during irradiation. Based on a thermodynamic analysis, Zr was selected as a candidate element for the ternary U-Mo-X alloys. Si was also selected again as a candidate, but the amount was restricted down to 0.1 - 0.2 wt% due to the solubility limit of Si in Uranium alloys. Figure 4 shows the transformation behavior of the Si and Zr added U-Mo-X ternary alloy annealed at 500°C. Contrary to the literature data that Zr has been known to reduce the time for a transformation of U-7Mo from a gamma to an alpha phase, U-7Mo and U-7Mo-Zr showed similar decomposition behaviors in this study[7]. Si added ternary alloy showed retarded transformation behavior when compared to U-7Mo. It has been

reported that Si also stabilizes UAl_3 up to 600°C and the transformation of UAl_3 into UAl_4 is suppressed when 0.1 wt% of Si is added into a U-Al alloy[8].

Scanning electron micrographs of the decomposed gamma phase after an annealing are shown in Fig. 5. In the U-Mo-Si alloy, the gamma phase surrounding the Si rich precipitates at the grain boundaries was transformed into a lamella structure primarily because Si forms precipitates with Mo and a Mo-depleted zone was formed. The decomposed boundaries can act as a penetration path for an interaction with the Al matrix in a dispersion fuel. The decomposed microstructure of the U-Mo-Zr alloy was similar to that of a U-Mo alloy as shown in Fig. 5(b).

3-2. Microstructural Analysis

Microstructures of the ILs between the U-Mo-X fuel and the Al matrix after diffusion tests at 550°C and 580°C were examined by using SEM. Most of the ILs grow inhomogeneously at 550°C due to a decomposition of the gamma phase in the U-Mo-X alloys. To analyze the interdiffusion behavior of the gamma phase, the results were compared with those from the tests at 580°C. Figure 6 shows the ILs between the U-Mo-X alloys and the Al matrix after annealing at 580°C for 2 hrs. The U-7Mo vs. Al diffusion couple test results are presented in Fig. 6. The ILs are not uniform, there thickness in the same specimen measures from 65 μm to 80 μm. The variation of the thickness of the ILs is attributed to an inhomogeneous contact pressure and surface oxidation. The U-7Mo-0.2Si vs. Al diffusion couple and the U-7Mo-0.5Zr diffusion couple have ILs of a similar thickness range when compared to the U-7Mo vs. Al diffusion couple. The minor alloying of a ternary element such as Si and Zr does not seem to change the growth kinetics of IL between the U-Mo-X and the Al.

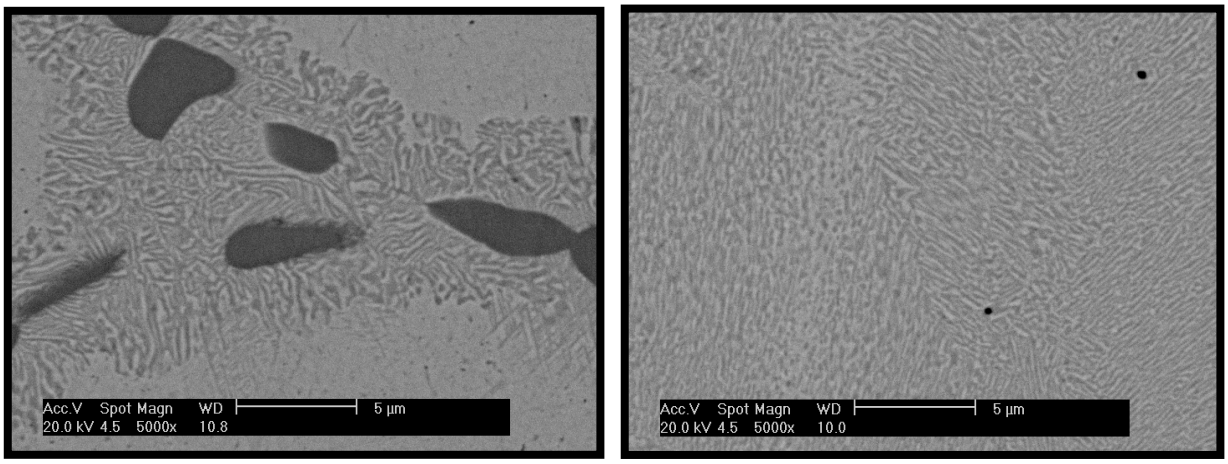
Interaction behavior of the U-Mo-X/Al(-Si) dispersion fuel at 550°C and 580°C was observed as shown in Fig. 7 and Fig. 8. When annealed at 550°C for 50 hrs, U-7Mo alloy, U-7Mo-0.2Si alloy and U-7Mo-1Zr alloy showed similar interaction behavior as shown in Fig. 7(a)-(c). In the U-7Mo/Al-2Si dispersion fuel, however, an irregular IL was frequently observed as shown in Fig. 7(d). The Al-Si matrix is more likely to penetrate into the U-Mo fuel because Si has a higher affinity for with U than Al does. All of the dispersion fuel annealed at 580°C for 10 hrs showed similar IL morphologies. In some areas of the fuel/matrix interface, there are highly grown regions when compared to the rest of the interface area. This area may be associated with a local decomposition of the gamma phase or an especially clean interface due to a peeling of an oxidation film on the U-Mo-X fuel particles during the extrusion.

3-3.Compositional Analysis

Chemical composition of the ILs in the diffusion couples and the dispersion fuels annealed at 580°C for 2 hrs and 10 hrs, and 550°C 5 hrs and 25 hrs were measured by using an electron probe micro-analysis. Fig. 9 shows the composition profiles silicon for the U-Mo-X vs. Al diffusion couples. In this analysis, especially the amount of Si cannot be measured precisely due to an overlap of Si peak with that of Al. Ryu *et al*.[9] observed two or three layers of interaction phases consisting of UAl_3 and UAl_4 type intermetallic phases showing 78-82 at% of Al. In the current study, none of the test samples showed the multilayers reported in Ref. 9. The Mo/U and Zr/U ratio in the U-7Mo-1Zr vs. Al diffusion couple were not changed in the U-7Mo-1Zr and in the IL. Compositional of Al in the IL in U-7Mo-1Zr vs. Al diffusion couple annealed at 550°C for 2 hrs increased from 82 to 87 at% towards Al.

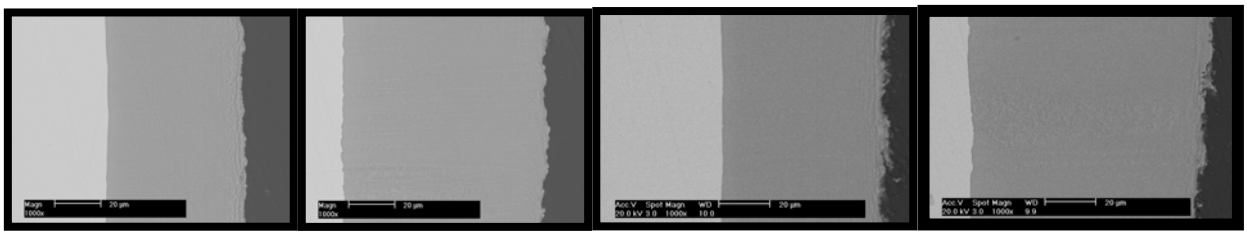
Compositional profiles of the IL in the U-7Mo/Al, U-7Mo-0.2Si/Al, U-7Mo-1Zr/Al and U-7Mo/Al-2Si dispersion fuels annealed at 580°C for 10 hrs were plotted in Fig. 10. U-7Mo/Al, U-7Mo-0.2Si/Al and U-7Mo-1Zr/Al dispersion fuels showed similar compositional profiles to the diffusion couple. The composition of Al was measured as 77-82 at%, whereas the U-7Mo/Al and U-7Mo-0.2Si/Al dispersion fuels showed a flat composition profile in the IL. The U-7Mo-1Zr/Al dispersion fuel showed a compositional gradient of Al in the IL from 77 to 82 at% towards Al as shown in Fig. 10(c). Fig.10(d) shows a steeper compositional gradient observed in the IL of the U-7Mo/Al-2Si dispersion fuel from 68 to 87 at%.

Figure 11 shows the compositional profiles of the IL in the U-7Mo-1Zr/Al and U-7Mo/Al-2Si dispersion fuels annealed at 550°C for 25 hrs. Zr/U ratio in the IL and in the fuel was virtually unchanged. Al content in the IL in U-7Mo-1Zr/Al dispersion fuel annealed at 550°C for 25 hrs increased from 78 to 81 at% towards Al. U-7Mo/Al-2Si dispersion fuel annealed at 550°C for 25 hrs shows higher Si content in the ILs than in the fuel and the matrix. This behavior has been predicted thermodynamically at ANL[4]. Contrary to the 550°C tests, U-7Mo/Al-2Si dispersion fuel annealed at 580°C for 10 hrs do not show Si accumulation in the IL. This temperature effect on Si diffusion requires a further study.



(a) (b)

Fig. 5. Scanning electron micrographs for (a) U-7Mo-0.1Si and (b) U-7Mo-1Zr annealed at 500°C for 48 hrs .



(a) (b) (c) (d)

Fig. 6. Scanning electron micrographs of ILs in (a) (b) U-7Mo vs. Al, (c) U-7Mo-0.2Si vs. Al, and (d) U-7Mo-0.5Zr vs. Al diffusion couples after annealing at 580°C for 2hrs.

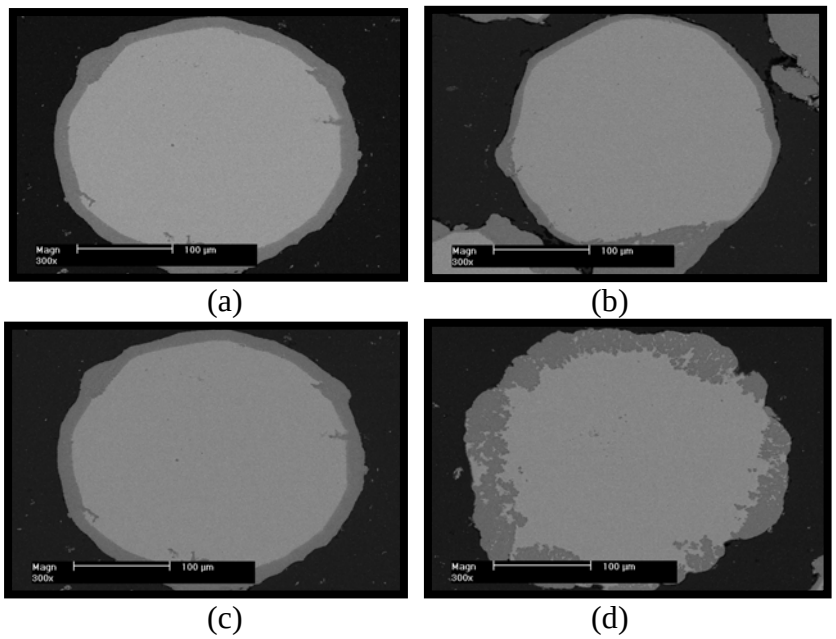


Fig. 7. Scanning electron micrographs of ILs in (a) U-7Mo/Al, (b) U-7Mo-0.2Si/Al, (c) U-7Mo-1Zr/Al and (d) U-7Mo/Al-2Si dispersion fuels after annealing at 550°C 50 hrs.

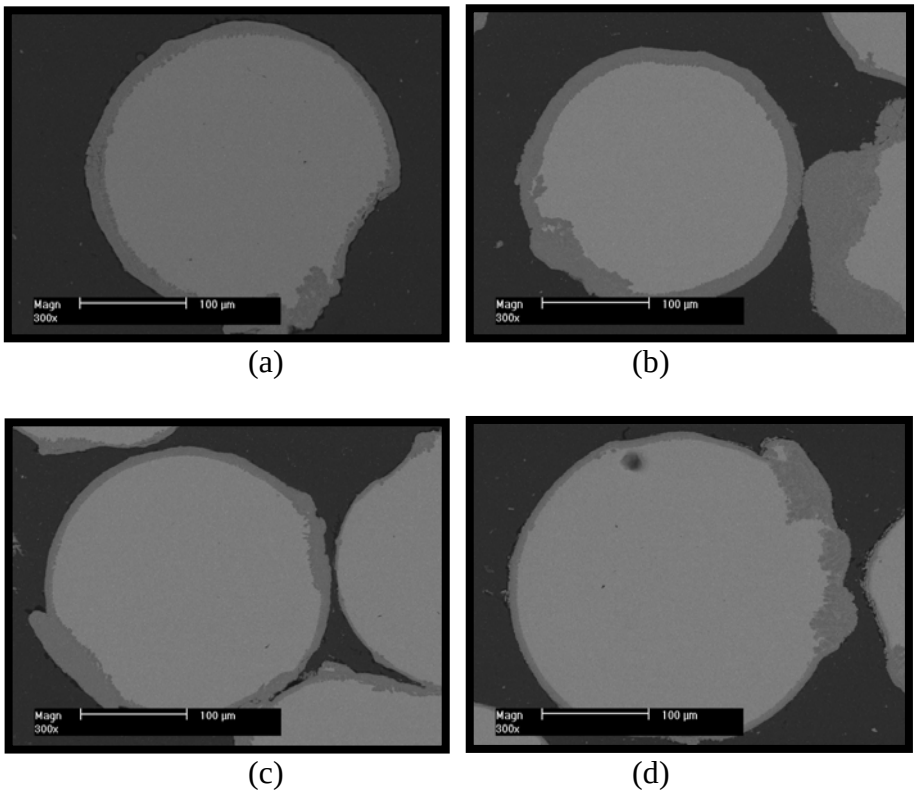


Fig. 8. Scanning electron micrographs of ILs in (a) U-7Mo/Al, (b) U-7Mo-0.2Si/Al, (c) U-7Mo-1Zr/Al and (d) U-7Mo/Al-2Si dispersion fuels after annealing at 580°C 10 hrs.

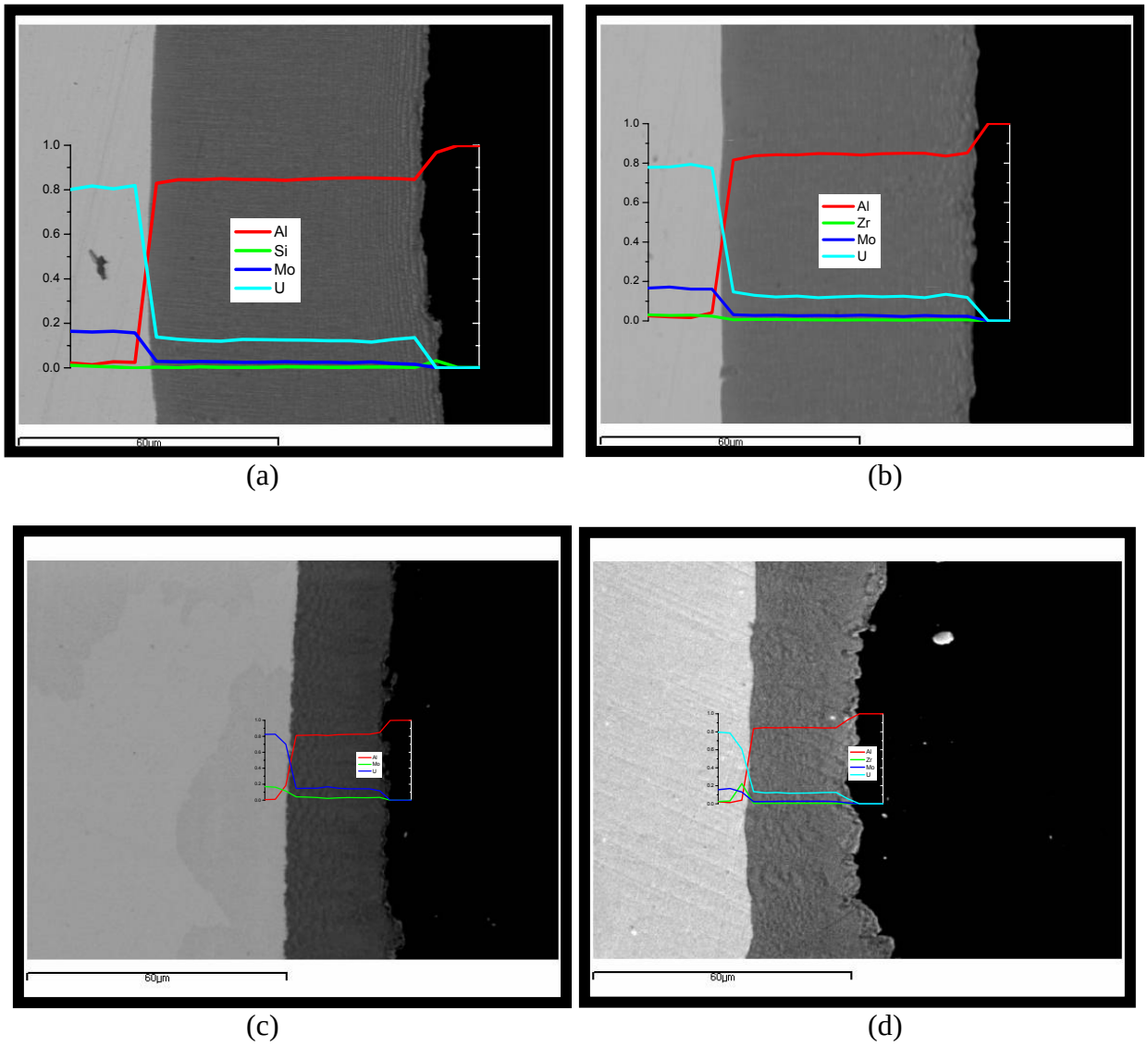
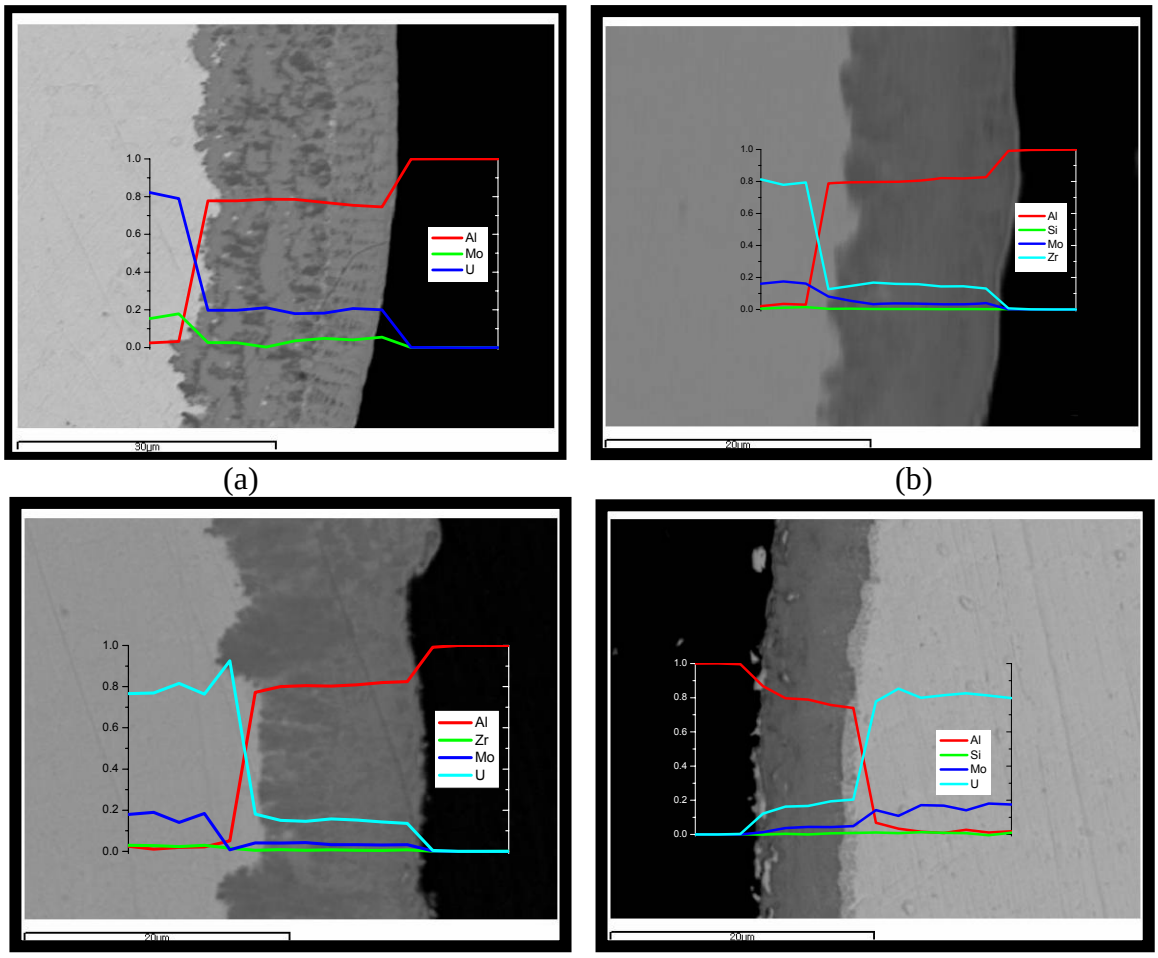


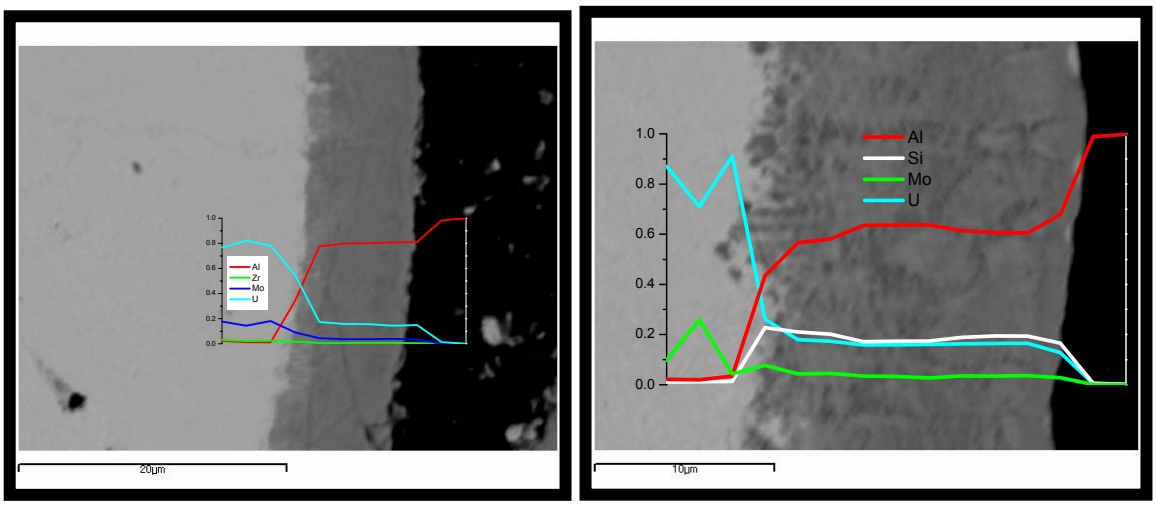
Fig. 9. Compositional profile of IL in (a) U-7Mo-0.2Si vs. Al and (b) U-7Mo-1Zr vs. Al diffusion couple annealed at 580°C for 2 hrs, and (c) U-7Mo vs. Al and (d) U-7Mo-1Zr vs. Al diffusion couple annealed at 550°C for 5 hrs.



(a) (b)

(c) (d)

Fig. 10. Compositional profile of IL in (a) U-7Mo/Al, (b) U-7Mo-0.2Si/Al, (c) U-7Mo-1Zr/Al and (d) U-7Mo/Al-2Si dispersion fuel annealed at 580°C for 10 hrs.



(a) (b)

Fig. 11. Compositional profile of IL in (a) U-7Mo-1Zr/Al and (b) U-7Mo/Al-2Si dispersion fuel annealed at 550°C for 25 hrs.

4. Conclusions

Gamma stability of U-Mo-X alloy was enhanced by the addition of Si, while Zr did not show any distinguishable effect. Diffusion Couple tests showed that the IL growth behaviors of the U-Mo-Si and U-Mo-Zr ternary alloys were similar when compared to the U-7Mo vs. Al diffusion couple test. Annealing tests of a dispersion fuel using U-Mo-Si and U-Mo-Zr alloy fuel showed a similar interaction behavior with a U-Mo/Al dispersion fuel. When Al-0.4Si or Al-2.0Si alloy is used as a matrix material, a penetration of the IL into a fuel particles became inhomogeneous. High Si content was measured in an IL of U-Mo/Al-Si dispersion fuel annealed at 550°C.

Acknowledgement

This study was supported as a National Nuclear Research Program by the Ministry of Science and Technology of Korea.

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