PHASE STABILITY OF U-Mo-Ti ALLOYS AND INTERDIFFUSION BEHAVIORS OF U-Mo-Ti/Al-Si

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ABSTRACT

As a remedy for reducing reaction between U-Mo and Al in U-Mo/Al dispersion fuel, adding an alloying element such as Zr and Ti in U-Mo has been proposed at ANL. Although ANL's work showed the potential effectiveness of these elements based on thermodynamic and metallurgical analyses, the effect of a Ti addition in U-Mo remains unproven. The out-of-pile tests of U-Mo-Ti alloys, which focused on phase stability and interdiffusion behavior against Al, are meaningful to predict their efficacy during an irradiation. At the 2006 RERTR conference, we presented our work on the interdiffusion behaviors of U-Mo-Zr/Al-Si. In this paper, we will present the results for substituting U-Mo-Zr with U-Mo-Ti. Unlike U-Mo-Zr alloys, the gamma-heat-treated U-7Mo-xTi (x=1~3 wt%) exhibited a metastable γ-U phase, regardless of the Ti content. In these samples, however, a small amount of second-phase precipitates with a high Ti concentration was observed. The gamma phase stability of the U-Mo-Ti alloys at 500°C was similar to that of the U-Mo-Zr alloys. Interdiffusion test results between U-Mo-Ti alloys and Al-Si alloys will also be presented and a comparison with the previous results with U-Mo-Zr/Al-Si will also be included.

1. Introduction

U-Mo/Al dispersion fuel is being developed as a high-uranium-density fuel for high performance research reactors due to its excellent stability during an irradiation [1]. Although it meets all other fuel requirements, a further development of this fuel was delayed due to an unacceptable volume expansion caused by (U-Mo)-Al interaction layer (IL) formation and a subsequent gross pore formation at the interface between U-Mo and matrix Al [2]. However, the Si-modification of the Al matrix in U-Mo/Al dispersion fuel was recently proposed at ANL to

solve the gross pore formation problem [3,6]. Previous out-of-pile diffusion studies have shown that Si indeed accumulates in the IL between U-Mo and Al-Si [4,5]. This phenomenon was considered as the prerequisite for the Si additions to be effective. In-pile tests have also shown the positive effect of Si: the IL thickness was much thinner than that in the fuel plates using a pure Al matrix, and no porosity in the ILs was formed [6,7].

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 also suggested recently by ANL to further enhance the effect of the Si additions [3]. Among the above transition metals, our previous diffusion studies on the Zr-added U-Mo vs. Al-Si couples showed very promising results, in which a Zr addition to U-Mo was most effective in reducing the IL growth in combination with Si added to Al by forming the stabilized $U(Al,Si)_2$ compound in the ILs [8].

Ti, next to Zr, can also be one of potential candidates to stabilize the IL. There was a first out-of-pile diffusion study with a U-6Mo-1Ti/Al couple by CEA [9]. Their characterization of a diffusion couple, however, remains still unclear because it might have been masked by the decomposed phases formed in U-Mo-Ti during the diffusion annealing at 450°C-2h, where the temperature was much lower than the γ phase boundary. The RERTR irradiation test on alloy modifications by adding small amount of transition metals such as Zr and Ti in U-Mo will soon reveal their efficacies on fuel performance under irradiation condition [10].

In this study, we performed diffusion-couple tests between U-Mo-xTi and Al-ySi with various contents of Ti and Si. A comparison to the previous results with U-Mo-Zr/Al-Si was included to understand the nature of Ti alloying effect on diffusion behavior.

2. Experimental Procedures

Ternary alloys of U-7wt%Mo-xTi (x=1, 2, 3 wt%) were fabricated by using a vacuum-induction melting in a zirconia crucible. The as-cast U-7Mo-xTi ingots were then heat-treated in a vacuum at 950°C for 24 h and sequentially water-quenched to stabilize the γ-U phase. Stabilities of the γ-phase of the U-Mo-xTi alloys were compared by using an X-ray diffraction (XRD) after an annealing at 500°C from 10 min. to 48 h. The clamped U-7Mo-xTi vs. Al-ySi (y=0, 0.4, 2, 5 wt%) diffusion couples were annealed at 580 and 600°C from 3 to 5 h in a vacuum-sealed fused quartz tube. The test temperatures of 580 and 600°C were selected mainly because we wanted to investigate diffusion behaviors between U-Mo-Ti and Al-Si in the α+γ phase and close to the γ /α+γ phase boundary of U-Mo alloy [11]. At these high temperatures, the clamp pressure effect on diffusion couple tests becomes negligible due to a softening of Al.

Microstructures of the interaction layers (ILs) in the diffusion-couple-test specimens were examined with a scanning electron microscope (SEM). Concentration profiles of the ILs were measured with the electron probe micro-analysis (EPMA) method.

Table 1. Chemical composition of the U-Mo-Ti alloys. (wt.%)

	Chemical Analysis			Matrix(EPMA)			Precipitate(EPMA) (at.%)		
	U	Mo	Ti	U	Mo	Ti	U	Mo	Ti
U-7Mo-1Ti	91.54	6.58	0.91	92.96	6.38	0.66			
U-7Mo-2Ti	89.70	7.10	1.81	92.10	6.23	1.67	*10.54	56.85	32.62
							**17.54	15.18	67.28
U-7Mo-3Ti	88.87	7.31	3.25	91.83	6.08	2.09	+13.71	50.93	35.36
							++12.01	53.30	34.70

* round shaped ppt ** irregular shaped ppt on GB

\+ large ppt ++ small ppt on GB or in the grain

Table 2. Measured IL thicknesses of the U-Mo-Zr(Ti) vs. Al-Si diffusion couples.

Alloy Composition	**Temp. / Time**	**Interaction Layer Thickness (μm)**			
		Al	**Al-0.4Si**	**Al-2Si**	**Al-5Si**
U-7Mo	**580 °C / 5 hr**	**135**		**25**	**35**
	600 °C / 3 hr	**240**	**29**	**65**	**63**
U-7Mo-2Zr	**580 °C / 5 hr**	**60**		**30**	**35**
	600 °C / 3 hr	**240**		**45**	**38**
U-7Mo-4Zr	**580 °C / 5 hr**	**35**		**30**	**32**
	600 °C / 3 hr	**80**		**25**	**20**
U-7Mo-1Ti	**580 °C / 5 hr**	**78**		**18**	**22**
	600 °C / 3 hr	**240**	**16**	**26**	**25**
U-7Mo-2Ti	**580 °C / 5 hr**	**40**		**20**	**20**
	600 °C / 3 hr	**51**	**16**	**25**	**23**
U-7Mo-3Ti	**580 °C / 5 hr**	**210**		**18**	**24**
	600 °C / 3 hr	**260**	**29**	**41**	**52**

3. Results and Discussion

3-1. Gamma Phase Stability

Although all the XRD measurements of the γ-heat-treated U-7Mo-xTi alloys showed a metastable isotropic γ-U (cubic) phase, observations of the microstructures of the γ-heat-treated U-7Mo-xTi alloys revealed that the precipitates with high Mo and Ti concentrations, mostly identified as $(U,Mo)_2Ti$ phase, are visible, along the grain boundaries or in the grains and its precipitation density became more dense as the Ti concentration increased to 3 wt% (see Fig. 1 and Table 1). From the microstructures and EPMA results of the γ-heat-treated U-7Mo-xTi alloys, the apparent solubility of Ti in ternary U-7Mo-xTi alloy seems to have a limit of ~1 wt%. However, as shown in Fig. 2, the γ-heat-treated U-7Mo-xTi alloys started to decompose to a mixture of the α-U and the γ′-U_2Mo phases even after an annealing at 500°C for 30 min., which is similar to the phase stability of U-7Mo-xZr alloys [8]. The SEM images of the decomposed γ-

phase after an annealing test (48 h) are shown in Fig. 3. The decomposed phases in the U-7Mo-xTi alloy began to develop preferentially at the grain boundaries as well as the phase boundaries.

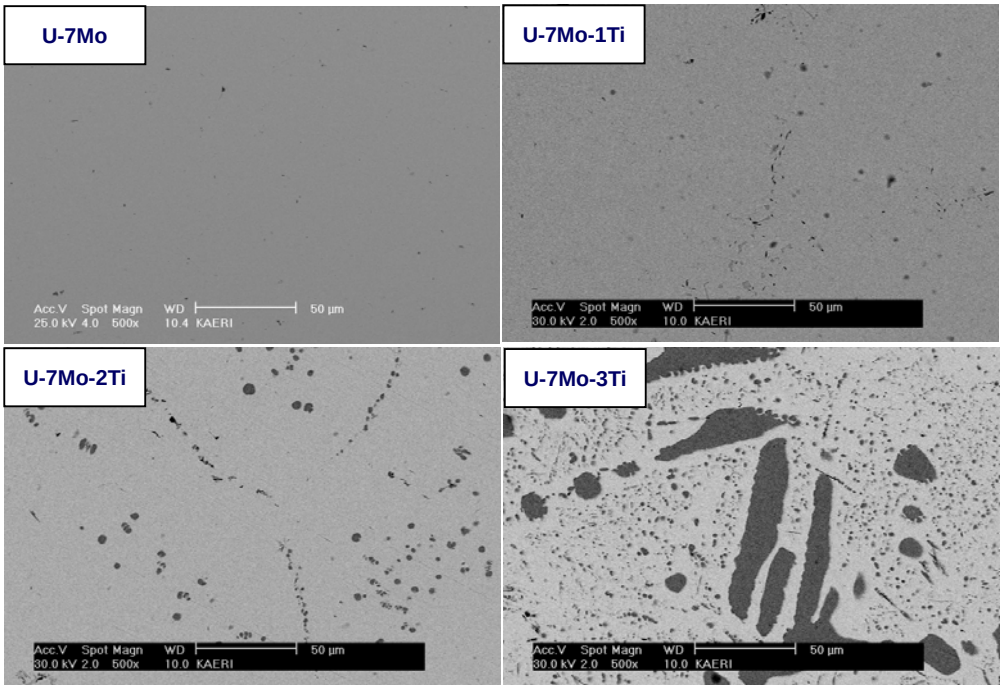


Fig. 1. Microstructures of the U-7Mo-xTi(x = 0, 1, 2, 3 wt%) alloys after a gamma heat treatment at 950°C 24h.

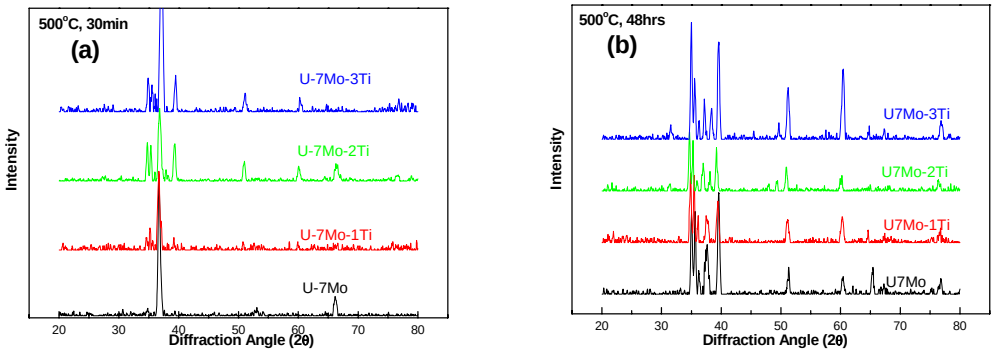


Fig. 2. X-ray diffraction patterns showing the transformation of the γ-phase in the U-7Mo-xTi annealed at 500°C (a) for 10 min. and (b) for 48 h.

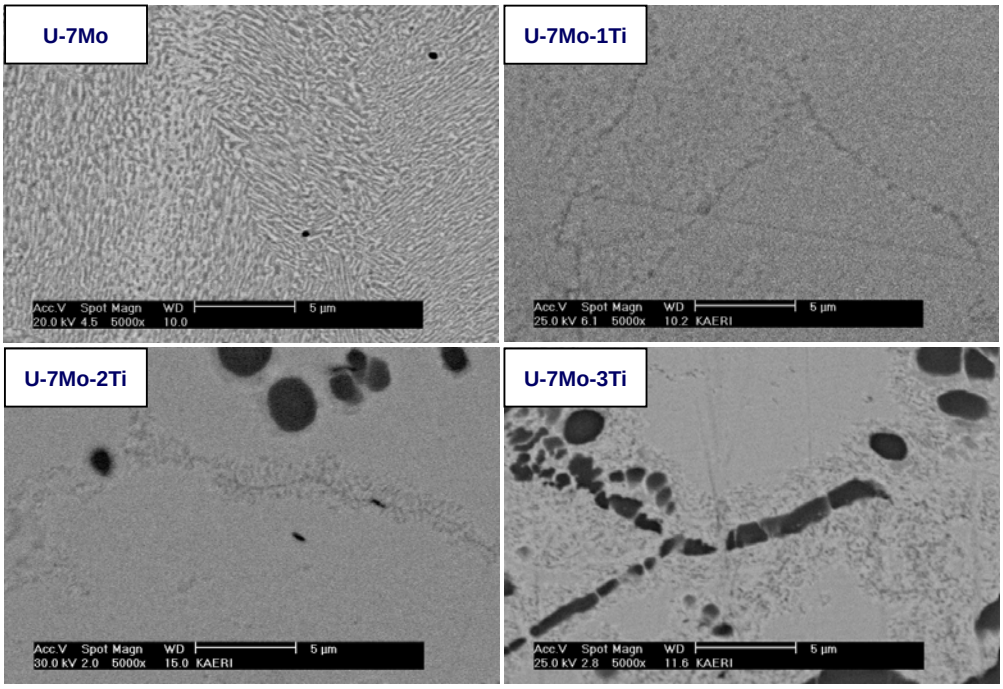


Fig. 3. Microstructures of the U-7Mo-xTi(x = 0, 1, 2, 3 wt%) alloys after a heat treatment (500°C 48h).

3-2. Microstructural Analysis and Growth of the Interaction Layers

The IL thickness data for the U-7Mo-xTi vs. Al-ySi diffusion couples annealed at 580°C-5h and 600°C-3h are summarized in Table 2 and compared with the previous result of U-7Mo-Zr/Al-Si [8]. The microstructures of IL for the U-7Mo-xTi vs. Al-ySi diffusion couples are also presented in Figs. 4-6. A Ti addition until 2 wt% in U-7Mo-xTi/Al decreased the IL thickness significantly with a similar effect as Zr does in U-7Mo-xZr/Al, in which the formation of a multi-phase structure in the IL is also visible. In Fig.4, the IL thickness at 580°C-5h was 135, 78, 40 μm for 0, 1, and 2 wt% Ti, respectively. However, the U-7Mo-3Ti/Al couple results in a extensive growth of the IL thickness (210 μm) due to the presence of dense precipitates in the gamma phase matrix.

The diffusion couple U-7Mo-xTi vs. Al-2Si shows a much thinner IL than the diffusion couple U-7Mo-xZr vs. Al-Si, as shown in Fig. 5 and Table 2. Moreover, the effect of Si for the diffusion couples of U-7Mo-1Ti vs. Al-ySi, see Fig. 6, on the reduction of the IL growth rate appears to be negligible. It is certain that the effectiveness of Ti addition in U-7Mo for suppressing IL growth appears to saturate at 1 wt%. Therefore, like Zr when added in U-Mo, Ti demonstrated to be another strong agent to suppress IL growth in combination with Si added to Al.

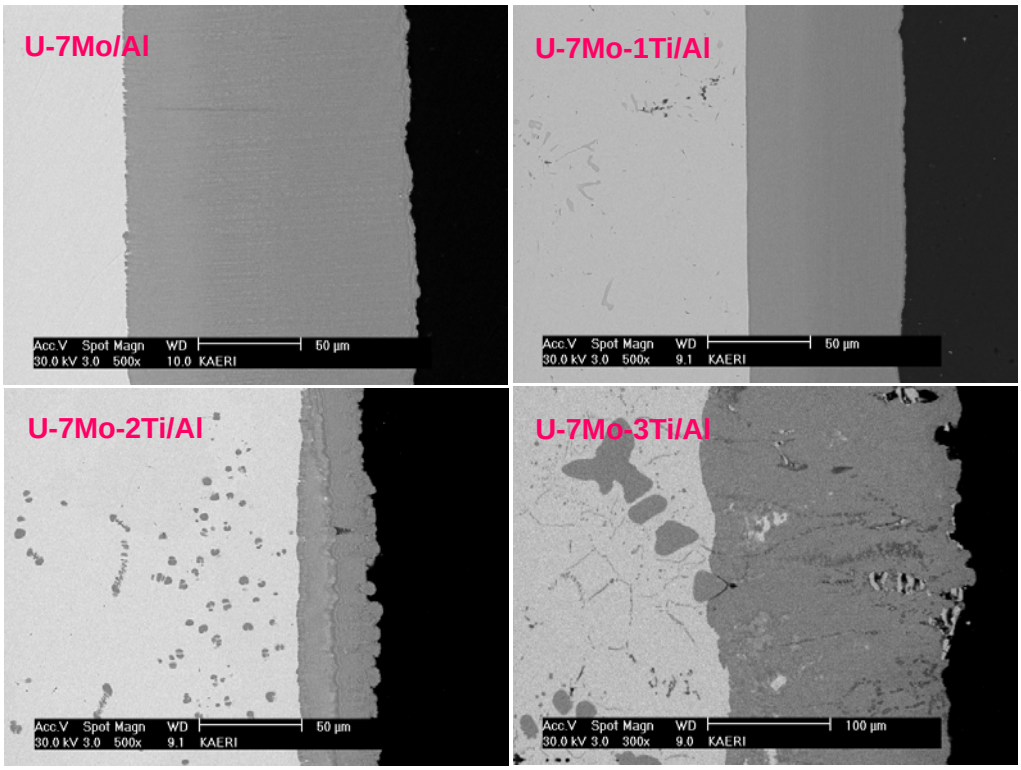


Fig. 4. SEM images of the ILs in the U-7Mo-xTi/Al (x=0, 1, 2, 3 wt%) diffusion couples after an annealing at 580°C 5 h.

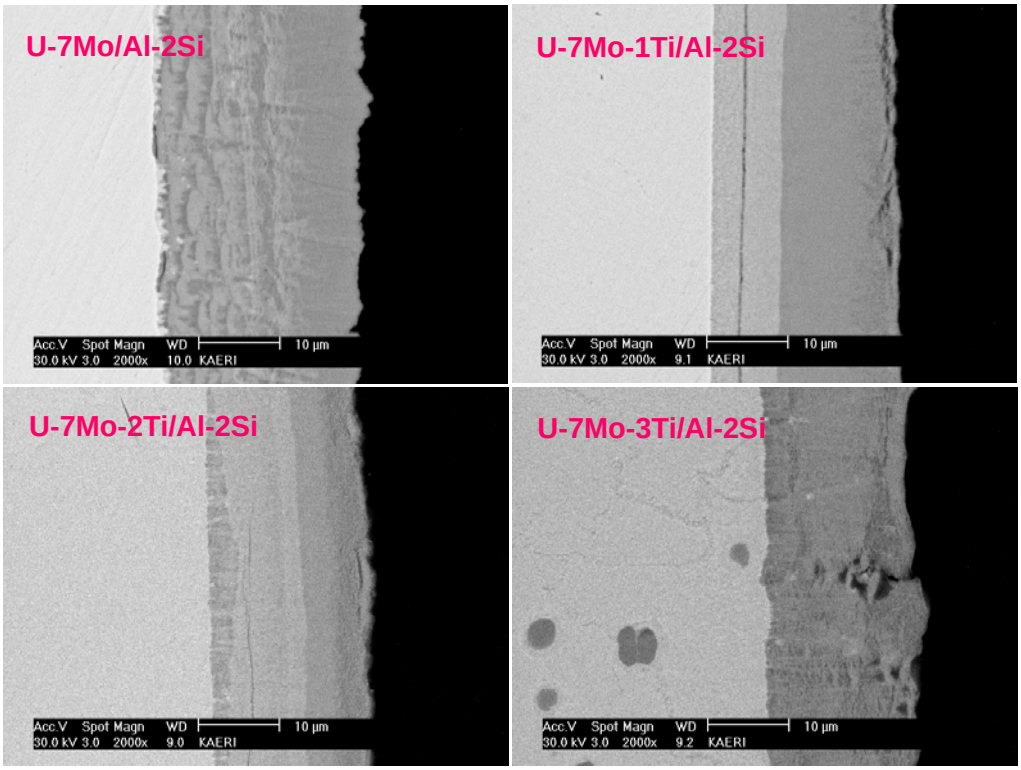


Fig. 5. SEM images of the ILs in the U-7Mo-xTi/Al-2Si (x=0, 1, 2, 3 wt%) diffusion couples after an annealing at 580°C 5 h.

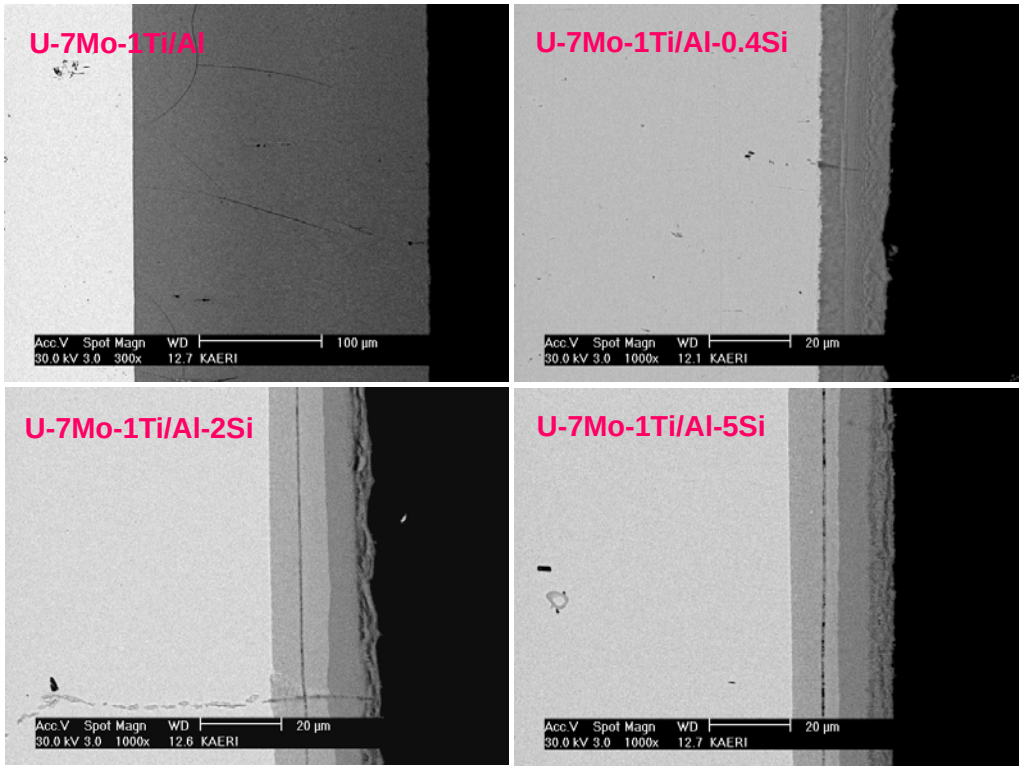


Fig. 6. SEM images of the ILs in the U-7Mo-1Ti/Al-ySi (y=0, 0.4, 2, 5 wt%) diffusion couples after an annealing at 600 ^{o}C 3h.

3-3. Compositional Analysis of IL

We measured the constituent concentrations in the ILs of the diffusion couples by using the EPMA method. In Figs. 7-9, the concentration distribution profiles are superimposed to the corresponding micrographs of the ILs. The U-7Mo-xTi (x=0, 1, 2, and 3) vs. Al diffusion couples annealed at 600°C for 3 h shown in Fig. 7 exhibited similar compositional profiles for the ILs as the U-7Mo-xZr vs. Al couple showed previously. The Al-to-(U+Mo) ratio increased from the U-Mo side to the Al side of the ILs, which has a chemical composition similar to UAl_4, whereas the Ti concentration remained constant, and negligible, throughout the ILs.

Preferential accumulation of Si in the interaction products of the U-Mo-Ti/Al-Si diffusion couples was observed, as demonstrated by the U-7Mo-xTi/Al-2Si couples (Fig. 8), in which the position of the peak Si accumulation in the IL moved to the U-Mo side as the Si content in the Al-Si increased. A high-Si accumulation (~60 at% Si) was also found in the layer on the U-Mo-Ti side, which was also observed in the U-Mo-Zr/Al-Si couple. However, it is noticeable that the composition of this layer was measured to be from $U(Al,Si)_2$ to U(Al,Si), while the composition in the U-Mo-Zr/Al-Si was $U(Al,Si)_2$ [8]. This indicates that Ti facilitates Si diffusion more efficiently to stabilize the ILs than Zr does. However, as shown in Fig. 8, in case of the U-7Mo-1Ti/Al-0.4Si diffusion couple, a weak Si accumulation was observed only at the Al-Si side, which implies that there seems to be a limitation of the minimum Si content in Al-Si in order to

establish a sufficient Si-diffusion.

Figure 10 compares the diffusion paths in the ternary phase diagrams for the U-Mo-Ti(Zr) vs. Al-Si diffusion couples. Unlike the previous results of the U-Mo-Zr/Al-Si couple [8] shown in Figs. 10 (a)-(b), the U-Mo-Ti vs. Al-0.4Si couple formed an IL with the Al/(U+Mo) ratio of ~3 and the U-Mo-Ti vs. Al-Si(higher than 2 wt%) formed an IL with the Al/(U+Mo) ratio of 1~2. Although an addition of 1 wt% Ti to U-Mo is considered to be nearly equivalent to that of 2 wt% Zr due to a difference in their atomic weights, Ti, in addition to Zr, appeared to be another strong stabilizer for the ILs in combination with Si added to Al. Therefore this can also provide a positive sign for irradiation tests.

The atomic ratios of (Al+Si) to (U+Mo+Ti) are compared in Fig. 11 for all the test cases. In this figure, we see that, (i) Ti addition to U-Mo regardless of the Ti content, and without a Si addition to Al, does reduce the Al-to-(U+Mo) ratio of the interaction product below 4. (ii) The Si addition to Al with a small amount of Ti addition to U-Mo can reduce the ratio to below 3. (iii) Although Ti addition is 1 wt%, the U-7Mo-1Ti vs. Al-2Si diffusion couple showed that the interaction product formed near the U-Mo-Ti/IL interface had the Al/(U+Mo) ratio less than 2. When we compare the atomic ratios with the previous U-Mo-Zr/Al-Si data [8], it appears that Ti addition to U-7Mo is more effective in reducing the Al/(U+Mo) atomic ratio than Zr.

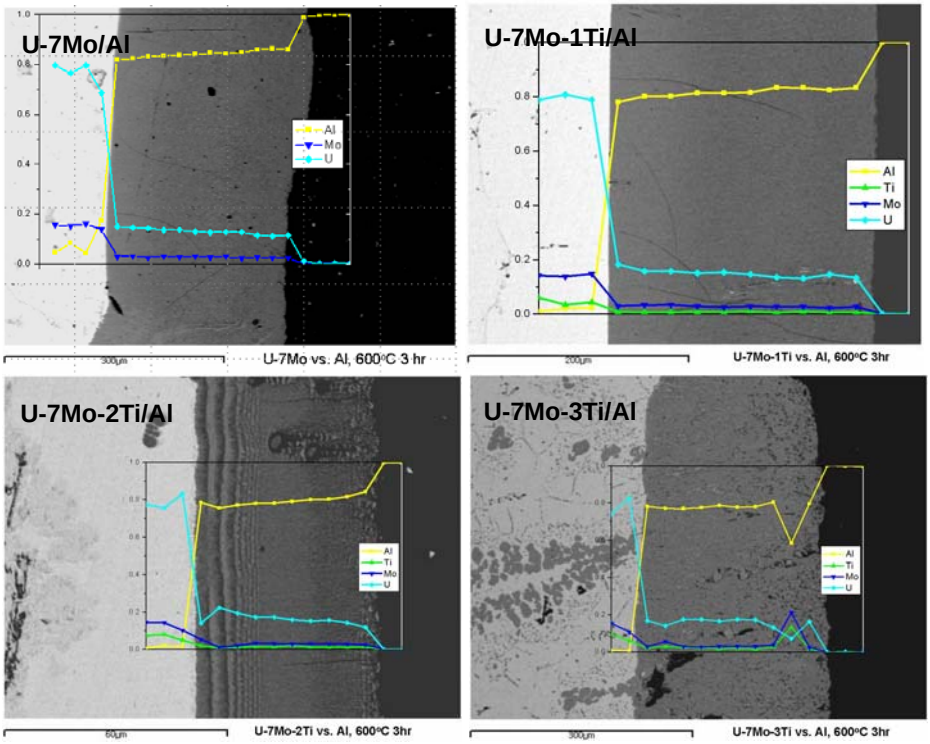


Fig. 7. Compositional profile of the IL in the U-7Mo-xTi/Al (x=0, 1, 2, 3 wt%) diffusion couples annealed at 600°C 3h.

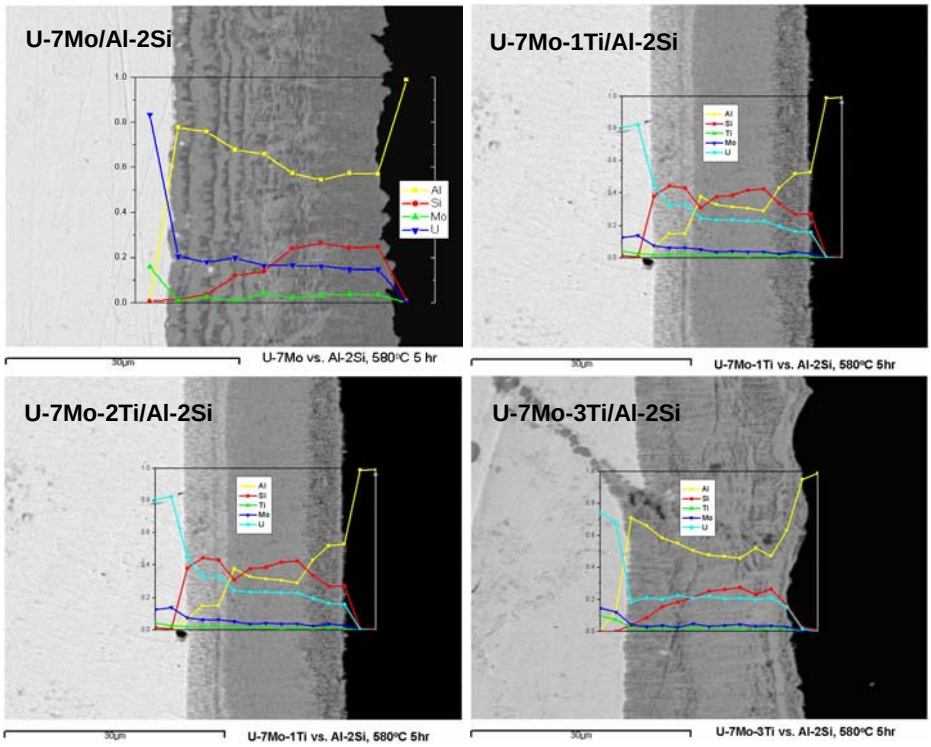


Fig. 8. Compositional profile of the IL in the U-7Mo-xTi/Al-2Si (x=0, 1, 2, 3 wt%) diffusion couples annealed at 580°C 5h.

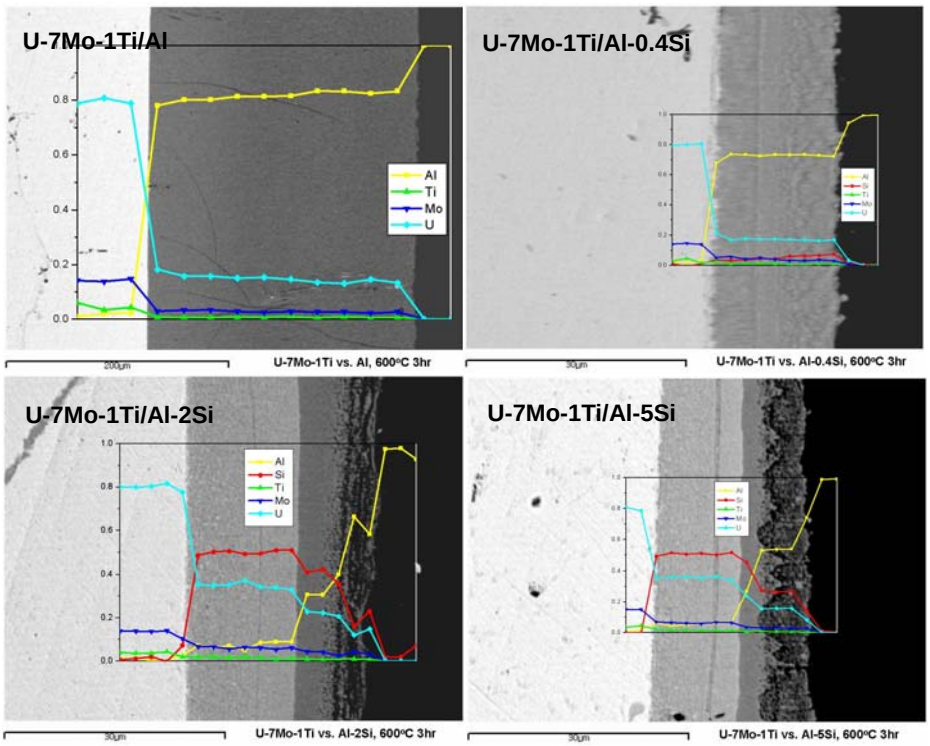
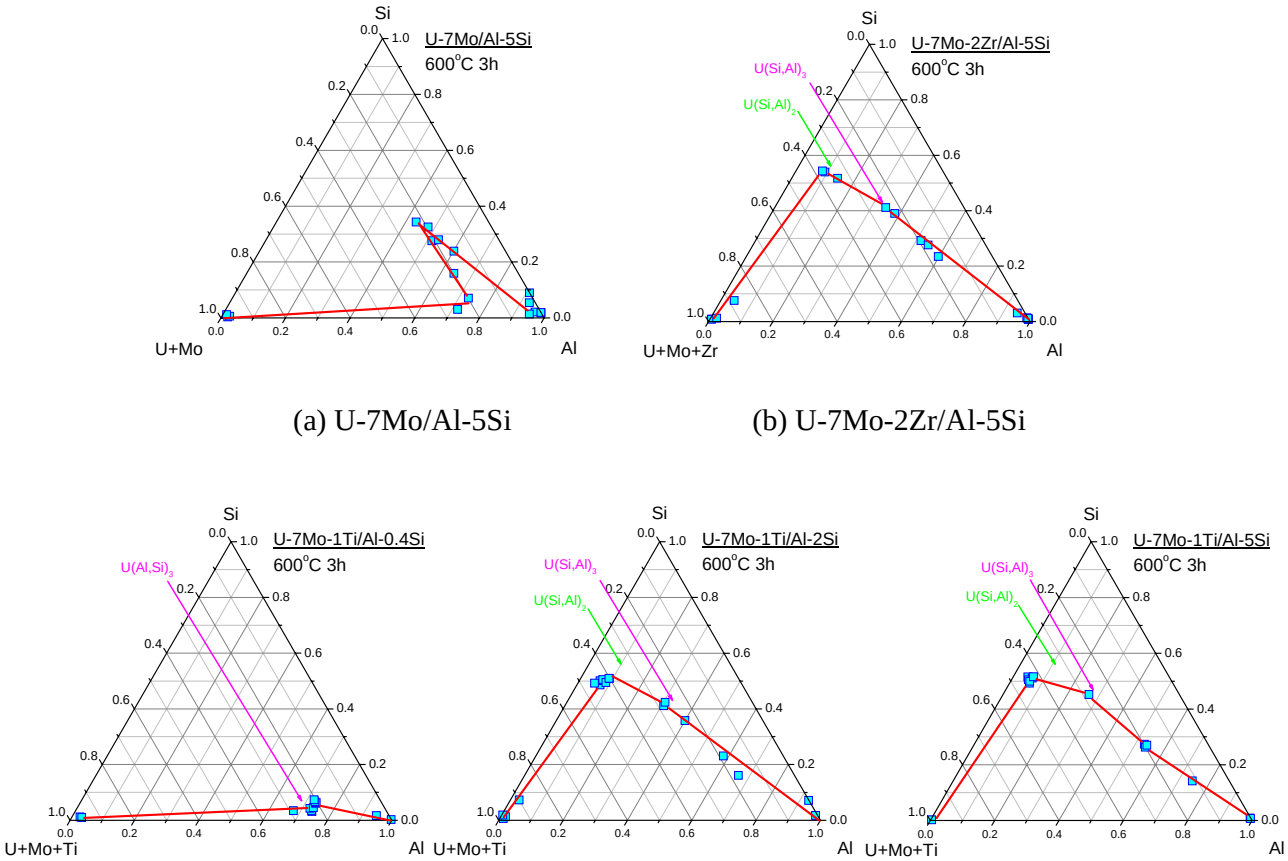


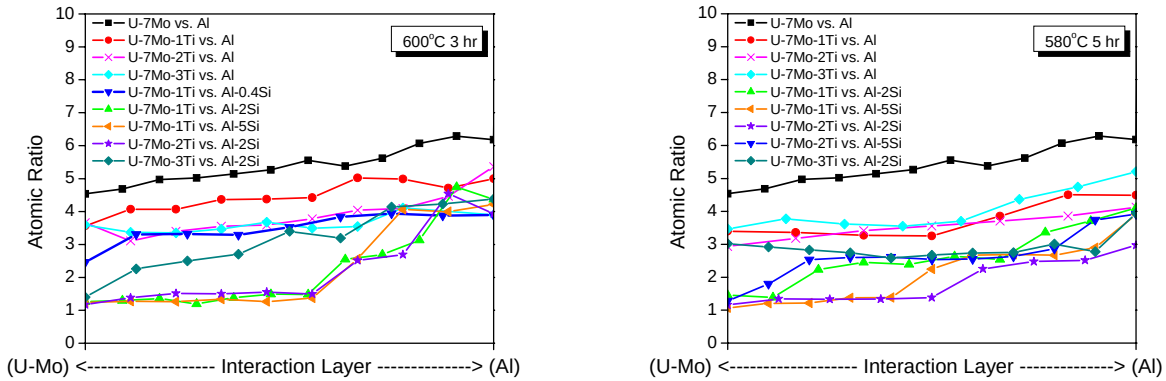
Fig. 9. Compositional profile of the IL in the U-7Mo-1Ti/Al-ySi (y=0, 0.4, 2, 5 wt%) diffusion couples annealed at 600°C 3h.



(a) U-7Mo/Al-5Si (b) U-7Mo-2Zr/Al-5Si

(c) U-7Mo-1Ti/Al-0.4Si (d) U-7Mo-1Ti/Al-2Si (e) U-7Mo-1Ti/Al-5Si

Fig. 10. Comparison of the diffusion paths for the inter-diffusion of (a) U-7Mo/Al-5Si, (b) U-7Mo-2Zri/Al-5Si, (c) U-7Mo-1Ti/Al-0.4Si, (d) U-7Mo-1Ti/Al-2Si and (e) U-7Mo-1Ti/Al-5Si diffusion couples annealed at 600°C 3 h.



(a) (b)

Fig. 11. Composition ratios of (Al+Si) to (U+Mo+Ti) in the interaction products of the U-7Mo-xTi vs. Al-ySi diffusion couples annealed at (a) 600°C 3 h and (b) 580°C 5 h.

4. Conclusions

From the experimental results and discussion, we can draw the following conclusions:

(1) Compared to U-Mo-Zr alloy, U-Mo-Ti alloy showed a similar γ-phase stability of the U-Mo alloy as the Ti content increased to 3 wt%. The apparent solubility of Ti in ternary U-7Mo-xTi alloy seems to have a limit of ~1 wt%.

(2) The U-Mo-Ti vs. Al-Si diffusion couple showed a much thinner IL than the U-Mo-Zr vs. Al-Si diffusion couple. The effectiveness of Ti addition in U-7Mo for suppressing IL growth appears to saturate at 1 wt%.

(3) Like Zr when added in U-Mo, Ti demonstrated to be another strong agent to suppress IL growth in combination with Si added to Al. Although Ti addition is 1 wt%, the U-7Mo-1Ti vs. Al-2Si diffusion couple showed that the interaction product formed near the U-Mo-Ti/IL interface had the Al/(U+Mo) ratio less than 2. Moreover, Ti addition to U-7Mo is more effective in reducing the Al/(U+Mo) atomic ratio than Zr.

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