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FABRICATION OF COATED U-Mo POWDER AND THE EFFECT OF Si CONTENT ON THE INTERACTION LAYER GROWTH

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ABSTRACT

In order to retard the fuel-matrix interaction in U-Mo/Al dispersion fuel, Si-rich layer coating techniques on the surface of atomized U-Mo powder were studied. Coated U-Mo powders were fabricated by a high temperature diffusion reaction process using a Si powder bed. Si-rich layers were formed on the surface of U-Mo powder and their thickness was about 5~10 μm after Si pack annealing at 900°C for 1 hour under vacuum. Preformed thin oxide layers on the surface of as-atomized powder hindered uniform Si-rich layer formation. Interaction between Si-rich layer coated U-Mo and Al was evaluated by diffusion couple tests. Diffusion couple tests of U-7Mo vs. Al-Si were also performed with varying Si content. When the interaction behaviors of gamma phase U-7Mo and initially decomposed U-7Mo were compared, both U-7Mo alloys showed reduced interaction layer growth when Si is added to Al-Si and the Si content in the interaction layer was increased up to about 30 at%. However, gamma U-Mo has less interaction than decomposed U-Mo.

1. Introduction

Interaction between the U-Mo particle and the Al matrix is one of the challenging issues in the development of U-Mo/Al dispersion fuel. Silicon addition to the Al matrix has been a remedy to suppress the interaction[1]. Use of larger-than-usual size U-Mo powders can be an acceptable option to mitigate the interaction problem[2]. Irradiation tests with the Al-Si matrix resulted in much reduced interaction layer growth[3].
However, the Al-Si matrix may not be an ultimate solution and has some drawbacks. First, the concentration of Si in the interaction layer is not controllable. As the interaction grows, Si content in the interaction layer is diluted and the effects of Si addition diminished[4]. Second,

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too much Si in the Al matrix would be harmful to the subsequent reprocessing of spent fuel. Last, there are no clear figures for minimum necessary Si content for the U-Mo/Al dispersion fuel[5].

Si-rich layer can be formed during the fuel fabrication processes. Park et al. showed that Si-rich interaction layers were formed by pre-irradiation annealing at 580^{o}C[3]. The U-Mo/Al dispersion fuel sample fabricated by pre-irradiation annealing to form Si-rich layers is now under irradiation (KOMO-4) at HANARO.

Some critical questions are open in U-Mo/Al dispersion fuel development as follows:
- *How much Si should we add in the Al to suppress the interaction effectively?*
- *Is a pre-formed Si-rich interaction layer effective during irradiation?*
- *Do Si-rich interaction layers form on the decomposed U-Mo during pre-irradiation annealing?*
- *Is a Si-coated U-Mo powder fabricable? Is this method viable?*

During the pre-irradiation annealing aiming to form a Si-rich interaction layer, gamma phase U-Mo can be decomposed to alpha phase containing lamellar structures. It is reported that the interaction layer formation behavior of decomposed U-Mo is different from gamma phase U-Mo[6]. Diffusion couple tests using decomposed U-Mo and Al-Si were investigated in order to find whether the Si-rich interaction layer formation is affected by the decomposition of U-Mo during pre-irradiation annealing.

Si coatings on U-Mo particle surface can be an alternative approach to solve the interaction problems, because total Si amount in the U-Mo/Al dispersion fuel can be reduced, when Si is concentrated only on the surface of U-Mo particles. Advantages of the Si coating method include the higher Si content than that in the interaction layer forming with the Al-Si matrix.

There may be many ways to coat Si on the U-Mo particle. Generally coatings on a powder can be accomplished by solid state reaction, liquid phase reaction using molten salts, and gas phase deposition such as chemical vapor deposition or physical vapor deposition. In this study, a simple solid state diffusion method was tested to form Si-rich layers on the surface of atomized U-Mo powder.

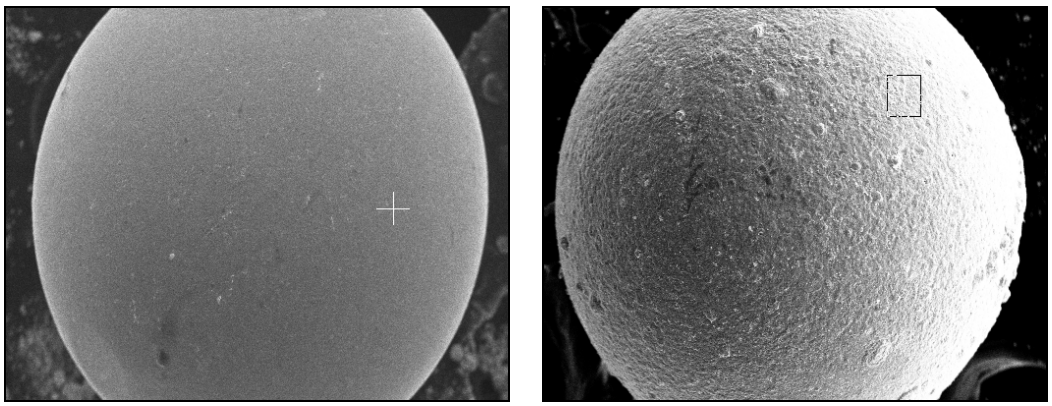
2. Experimental Procedures

Centrifugally atomized U-7wt%Mo powder with 200~300 μm in diameter was used for Si-rich coatings and induction melted U-7wt%Mo plate was used for diffusion couple tests. Pure Si powder (99%, -325 mesh) was used for a solid state diffusion coating in a Si powder bed after heat treatment at 500~900^{o}C under argon, argon-hydrogen or vacuum. Effects of small amount(~10wt% of Si powder) of additives such as NH_4Cl and Al on the coating layer formation were also investigated. Interaction layer formation between Si-rich layer coated U-Mo plate and Al plate was evaluated by diffusion couple tests. Si-rich layer coated U-7wt%Mo plate was fabricated by vacuum heat treatment at 900^{o}C for 1 hour under vacuum.
Diffusion couple tests of decomposed U-7Mo vs. Al-Si were also performed with varying Si content up to 5 wt%. Decomposed U-7Mo plates were fabricated by heat treatment at 500^{o}C for 48 hours. Gamma phase U-7wt%Mo plates were fabricated by heat treatment at 950^{o}C for 24

hours. Diffusion couple tests were conducted in a muffle furnace with annealing temperatures of 560~600^{o}C. Cross-sectional microstructures of the diffusion couple specimens were observed by using scanning electron microscopy (SEM). The elemental composition of the interaction layers were measured by using energy dispersive X-ray spectroscopy (EDS) and standardless quantitative data were obtained by the ZAF correction algorithm of the EDAX Genesis X-ray microanalysis software.

3. Results and Discussion

An as-atomized U-7Mo powder and a Si pack annealed powder were compared as shown in Fig. 1. Since centrifugally atomized powders were passivated under an Ar gas atmosphere in the atomization chamber in order to prevent spontaneous ignition of the fine powder, its surface is coated with a thin oxide layer as its compositions are listed in Table 1. After a Si pack annealing test at 900^{o}C for 1 hour under vacuum, morphological changes were observed in the surface of the atomized U-7Mo powder as shown in Fig. 1(b). When the surface compositions were measured by EDS, oxide-like compositions were detected as in Table 1. It means the initial surface oxide was not removed by the Si pack annealing. The oxide could not be removed by a heat treatment in a flowing pure argon gas or by the addition of hydrogen gas in the argon gas.



(a) (b)

Fig. 1. A scanning electron micrograph of (a) an as-atomized U-7wt%Mo powder and (b) a Si pack annealed U-7wt%Mo powder at 900^{o}C for 1 hour under vacuum.

Table 1. Surface layer compositions measured by EDS for samples shown in Fig. 1.

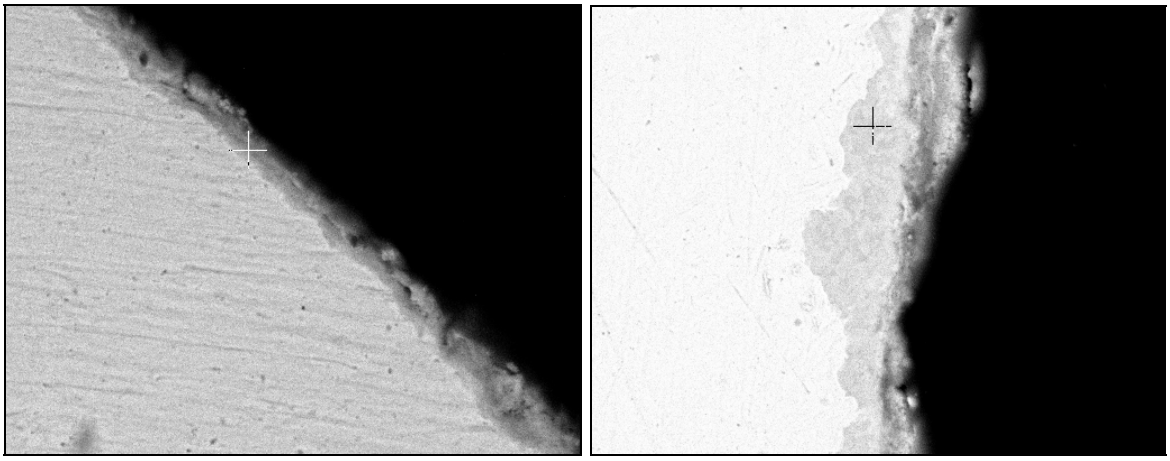
Element	As-atomized (at%)	Si Pack Annealed (at%)
O	78.1	75.7
Si	-	9.9
Mo	3.6	2.5
U	18.3	11.9

When the cross-sections of coated U-Mo powder were observed, reaction layers at the periphery region were formed as shown in Fig. 2. The effects of annealing temperature were investigated by varying the Si-pack annealing temperature from 500^{o}C to 900^{o}C. When the Si-pack annealing

temperature was 500°C or 700°C, a Si-rich layer did not form at the periphery region of atomized U-Mo powder. The interaction layer shown in Fig. 2(a) for the 700°C annealed sample was measured as an oxide layer. Its compositions are listed in Table 2.

Meanwhile, Si-rich layers were formed in the sample annealed at 900°C as shown in Fig. 2(b). The Si content was measured about 60 at% and the thickness of the layer is about 5~10 μm. It was found that an oxide layer remained at the outermost layer of the Si pack annealed U-Mo powder. There exists some agreement between the EDS results for the outermost layer of a Si pack annealed U-Mo powder as listed in Table 1 and Table 2.

It is considered that the Si atoms diffuse through the oxide layer and formed Si-rich layers inside the oxide layer by a diffusion reaction with U-Mo, because small amount(~9 at%) of Si is measured in the oxide layer. The oxide layers would act as a diffusion barrier and hinders the uniform Si-rich coatings formation on the atomized U-Mo powder. In order to form a Si-rich layer through the oxide diffusion barrier, annealing temperatures much higher than 700°C is required.



(a) (b)

Fig. 2. A cross-sectional scanning electron micrograph of Si pack annealed U-7wt%Mo powder at (b) 700°C for 1 hour and (b) 900°C 1 hour under vacuum.

Table 2. Reaction layer compositions measured by EDS for samples shown in Fig. 2.

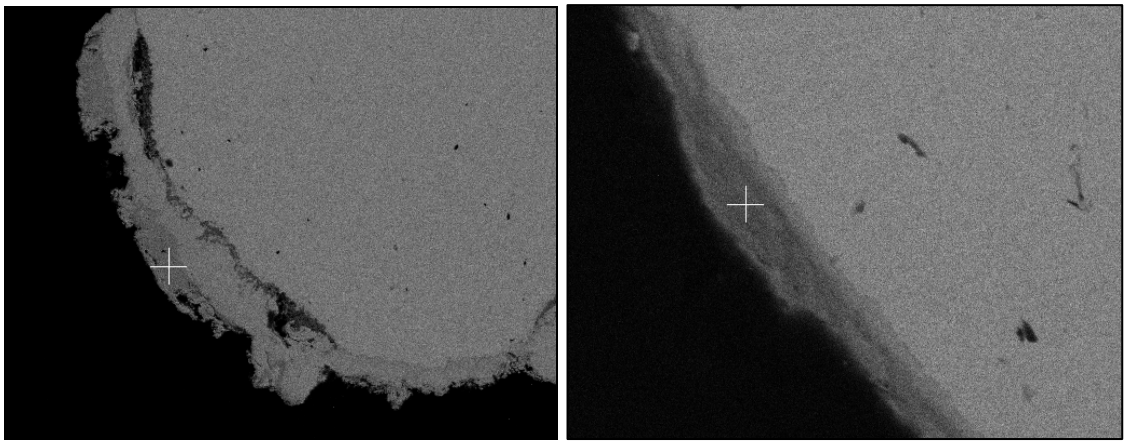
Element	**Si Pack 700°C (at%)**	**Si Pack 900°C Inner Layer (at%)**	**Si Pack 900°C Outer Layer (at%)**
O	85.1	-	69.4
Si	-	59.0	09.5
Mo	02.5	08.9	02.3
U	12.4	32.1	18.8

In order to find beneficial additives to Si powder for uniform coatings on the atomized U-Mo powder, NH_4Cl and Al were chosen as promising additive candidates. NH_4Cl was chosen because Si powder and ammonium chloride react to form $SiCl_4$ which is a gaseous phase at a high

temperature and it will react with U-Mo. Al was chosen expecting that the diffusion of silicon would be enhanced if uranium aluminides form.

However, surface morphology after vacuum heat treatment in the Si powder bed with ammonium chloride powders was very irregular as shown in Fig. 3(a). The thickness of the reaction layer is thicker (>10μm) and the layer consisted of two distinctively-colored layers. Si content in the outer layer was about 70 at% and 53 at% of Si was measured in the inner layer. When Al powders are added to Si powder, only oxide layer was formed after Si pack annealing at 900^{o}C as shown in Fig. 3(b).

Addition of the additives chosen in this study was not effective in forming uniform Si-rich coatings on atomized U-Mo powders. Gas phase reaction of $SiCl_4$ with U-Mo resulted in thick non-uniform coating layers. Addition of Al powder to Si powder was not successful because Al powders have surface oxide layers already and the oxide can react with U-Mo powder. Therefore, vacuum annealing in a pure Si powder bed was chosen as a standard Si pack annealing process for further experiments.



(a) (b)

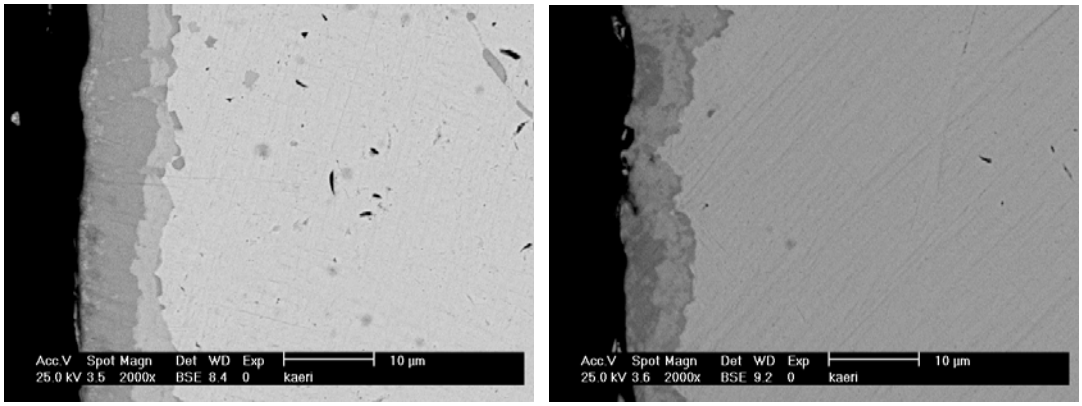
Fig. 3. A cross-sectional scanning electron micrograph of Si pack annealed U-7wt%Mo powder at 900^{o}C 1 hour under vacuum (a) in a Si pack with NH_4Cl and (b) in a Si pack with Al.

Table 3. Reaction layer compositions measured by EDS for samples shown in Fig. 3.

Element	**Si pack with NH_4Cl Outer Layer (at%)**	**Si pack with NH_4Cl Inner Layer (at%)**	**Si pack with Al (at%)**
O	-	-	67
Si	70.6	52.7	6
Al	-	-	8
Mo	-	-	5
U	29.4	47.3	14

Two types of U-7wt%Mo plates were prepared to evaluate the diffusion barrier performance of Si-rich coatings on U-Mo. One is a gamma phase U-Mo plate and the other is a decomposed U-Mo. Both U-Mo plates were coated with Si-rich layer of 5~10 μm in thickness by the Si pack annealing

at 900°C for 1 hour under vacuum as shown in Fig. 4. The compositions of Si-rich layer on either U-Mo plate were similar and the Si content was around 65 at%. When the layer was characterized by X-ray diffractometry, mixed peaks of various silicides were obtained and the results are under a detailed analyses for crystallographic indexing.



(a) (b)

Fig. 4. A cross-sectional scanning electron micrographs of (a) decomposed U-7wt%Mo plate and (b) gamma phase U-7wt%Mo plate after Si pack annealing at 900°C for 1 hour.

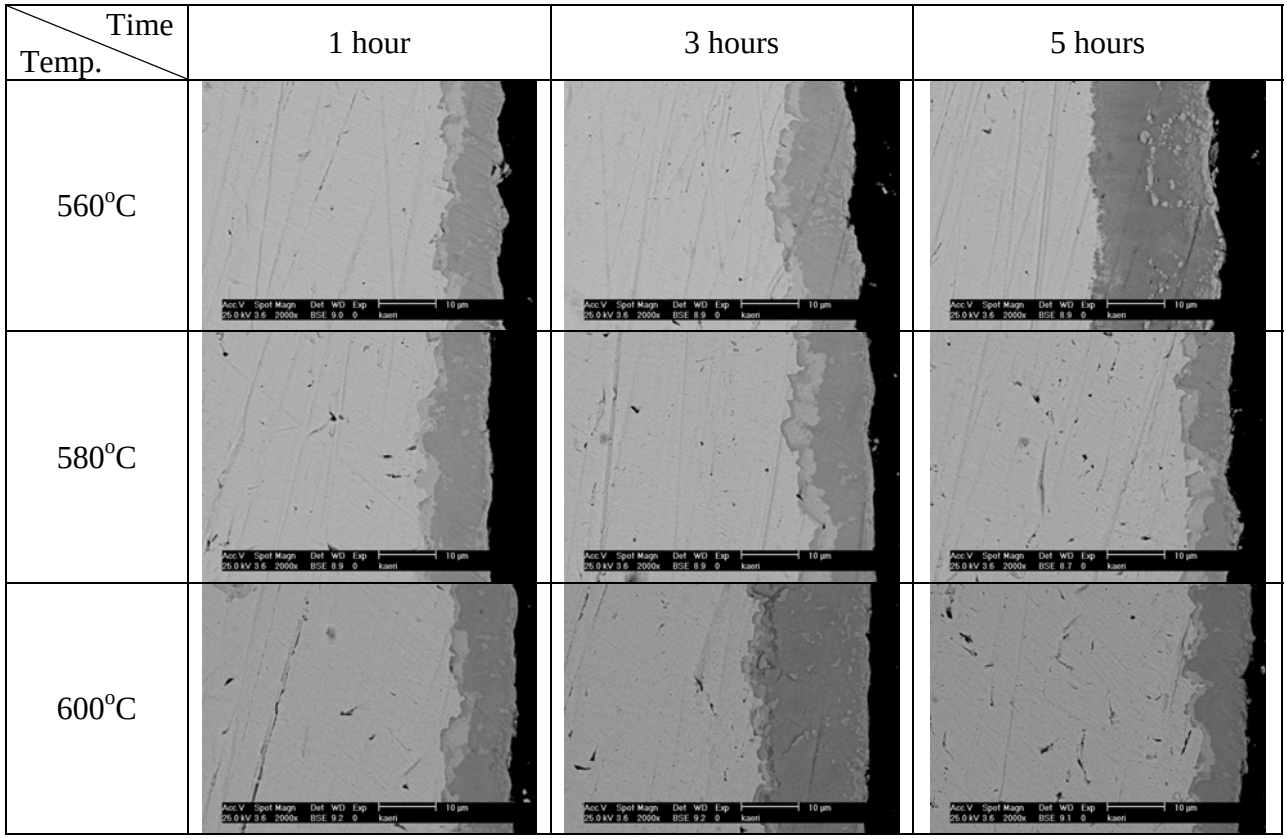


Fig. 5. Microstructures of Si-rich coatings after diffusion couple tests with Al.

Fig. 5 shows the results of diffusion couple tests between coated U-7Mo plates and Al plates. Most couples showed limited growth of the coating layers and thicknesses of coatings remained within 10~20 μm after annealing at 560~600°C up to 5 hours. This reveals the effectiveness of Si-rich

coatings as a diffusion barrier in U-Mo/Al dispersion fuel, since several hundreds-micrometer-thick interaction layers were obtained in a diffusion couple of U-Mo vs. Al annealed at 600°C for 5 hours. Si content in the coatings was remained about 60 at% which is much higher than the Si-rich interaction layer in U-Mo vs. Al-Si diffusion couples, while 5 at% of Al was also detected in the Si-rich coatings after the diffusion couple tests. Annealing tests of dispersion fuel using coated U-Mo powders are necessary to confirm the viability of the Si-rich layer coating method.

Si-rich interaction layer formation behaviors of gamma U-Mo and decomposed U-Mo were compared as shown in Fig. 6. The two types of U-Mo alloys showed some similar features including the reduction of interaction layer thickness when Al-Si is coupled with U-Mo. However, the reduction of interaction thickness was not improved as Si content is increased from Al-2wt%Si to Al-5wt%Si. The maximum Si content in the interaction layer was about 30~35 at% in either case. Resultant thicknesses of the interaction layers differentiate the two U-Mo alloys. Thicker interaction layers were obtained in decomposed U-Mo at the same annealing condition, implying that the diffusion kinetics in the decomposed U-Mo is faster than in the gamma phase U-Mo.

The U-7wt%Mo alloy decomposes readily at pre-irradiation annealing temperatures ranging 500~600°C. Although Si-rich interaction layers form on the decomposed U-Mo according to this study, thicker interaction layer will be obtained if decomposition of U-Mo is not avoided. Eutectic melting of Al-Si should be taken into account when the pre-irradiation annealing temperature increased to temperature higher than 600°C, because the gamma phase stabilizing temperature for U-7wt%Mo becomes higher than eutectic melting temperature of Al-Si with high Si content.

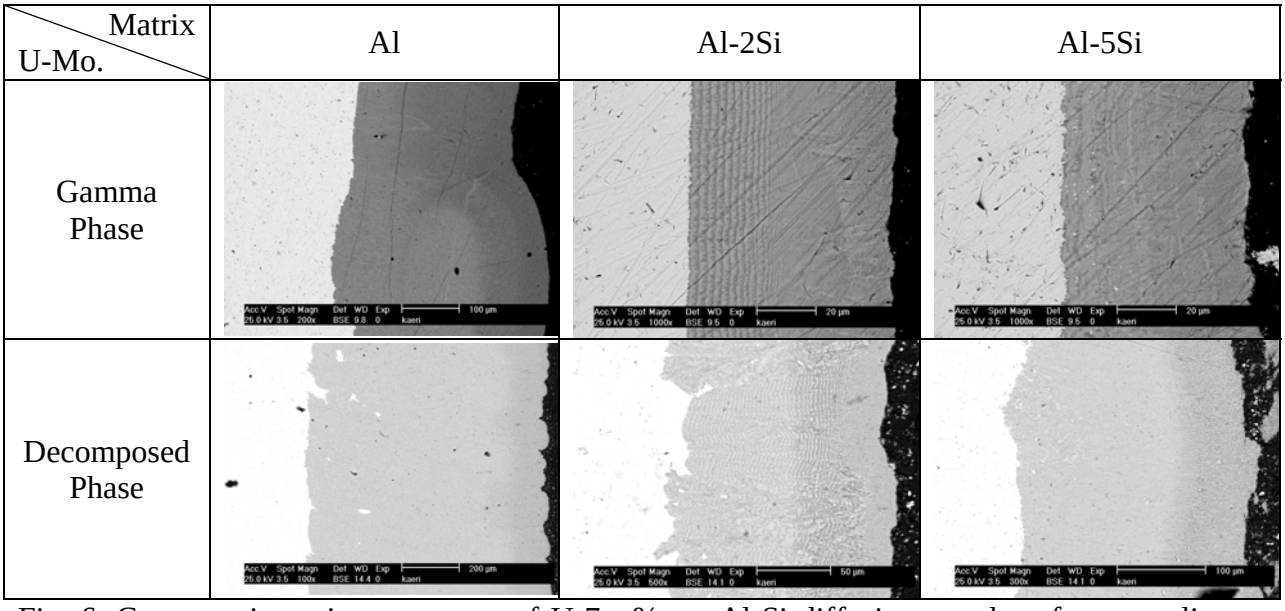


Fig. 6. Cross-section microstructures of U-7wt% vs. Al-Si diffusion couples after annealing at 600°C for 5 hours.

4. Conclusions

Si-rich layer coated U-Mo powders were fabricated by using a Si powder pack annealing method. Vacuum annealing at 900^{o}C resulted in Si-rich coatings on U-7wt%Mo powders, while surface oxide remained even after the Si pack annealing. Si-rich coatings were very effective in suppressing the interaction during diffusion couple tests between coated U-Mo plate and Al. When the interaction layer growth behaviors of gamma phase U-7Mo and decomposed U-7Mo were compared, the Si content in the interaction layer for each case was increased up to about 30 at% similarly, but gamma U-Mo has less interaction than decomposed U-Mo.

Acknowledgments
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References

[1] G.L. Hofman, M.R. Finlay, Y.S. Kim, "Post-Irradiation Analysis of Low Enriched U-Mo/Al Dispersion Fuel Miniplate Tests, RERTR 4 and 5," Proceedings of the 26th International Meeting on Reduced Enrichment for Research and Test Reactors, Vienna, Austria, Nov. 7–12, 2004.

[2] C.K. Kim, J.M. Park, H.J. Ryu, "Use of a Centrifugal Atomization Process in the Development of Research Reactor Fuel," Nuclear Engineering and Technology, Vol. 39, p. 617 (2007).

[3] J.M. Park, H.J. Ryu, Y.S. Lee, S.J. Oh, C.K. Kim, B.O. Yoo, Y.H. Jung, C.G. Seo, C.S. Lee and H.T. Chae, "PIE Results of the KOMO-3 Fuels and the Future Irradiation Plan," Proceedings of the 30th International Meeting on Reduced Enrichment for Research and Test Reactors, Washington D.C., U.S.A., Oct. 5-9, 2008.

[4] H.J. Ryu, J.M. Park, C.K. Kim, Y.S. Kim , "Analyses on the Interaction Products of U-Mo/Al-Si Dispersion Fuel for an Estimation of the Required Si Content," Proceedings of the 30th International Meeting on Reduced Enrichment for Research and Test Reactors, Washington D.C., U.S.A., Oct. 5-9, 2008.

[5] Y.S. Kim, H.J. Ryu, G.L. Hofman, S.L. Hayes, M.R. Finlay, D.M. Wachs, G.S. Chang, "Interaction Layer Growth Correlations for (U-Mo)/Al and Si-added (U-Mo)/Al Dispersion Fuels," Proceedings of the 28th International Meeting on Reduced Enrichment for Research and Test Reactors, Cape Town, South Africa, Oct. 29-Nov. 2, 2006.

[6] M. Mirandou, S. Arico, M. Rosenbusch, M. Ortiz, S. Balart, L. Gribaudo, "Characterization of the interaction layer grown by Interdiffusion between U–7wt%Mo and Al A356 alloy at 550 and 340^{o}C", J. Nuclear Materials, Vol. 384, p.268 (2009).