Reaction Layer Growth and Reaction Heat of U-Mo/Al Dispersion Fuels

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Abstract

The growth behavior of reaction layers and heat generation during the reaction between U-Mo fuel powder and the Al matrix in U-Mo/Al dispersion fuels were investigated. Annealing of 10vol.% U-10Mo/Al dispersion fuels at temperatures from $500^{\circ}C$ to $550^{\circ}C$ was carried out for 10 min. to 100 hrs to measure the growth rate and activation energy of diffusion in the reaction layer. The heat generation of U-Mo/Al dispersion fuels with 10 50vol.% of U-Mo fuel during the thermal cycle from room temperature to $700^{\circ}C$ was measured employing differential scanning calorimetry. Exothermic heat from the reaction between U-Mo fuel and the Al matrix is the largest when the volume fraction of U-Mo fuel is about 30vol%. The unreacted fraction of U-Mo fuel increases as the volume fraction of U-Mo fuel increases from 30vol% to 50vol%, while an endothermic reaction is also generated due to the melting of the Al matrix when the volume fraction of U-Mo fuel is less than 30%.

1. Introduction

The spent fuel acceptance program of research reactor fuels will not be available for the fuels irradiated after May 12, 2006[1]. The replacement program of current uranium silicide fuels to reprocessable U-Mo fuels will be implemented to research reactor fuels. The RERTR program has worked out a new program to develop, demonstrate, and qualify U-Mo fuels with a uranium density of 5-6 gU/cc[2]. U-Mo fuel powder can be produced by the atomizing technology developed by KAERI[3]. However, U-Mo fuel and the Al matrix react to form intermetallic compounds when the U-Mo/Al dispersion fuel is annealed at high temperatures. The reaction layer between U-Mo and the Al matrix induces the volume expansion and degradation of thermal properties of U-Mo/Al dispersion fuels[4]. It is important to investigate the growth behavior of the reaction layer and the variation of reaction heat.

In this study, high temperature annealing and differential scanning calorimetry of U-Mo/Al dispersion fuels are carried out to analyze the reaction behavior of U-Mo/Al dispersion fuels. The growth rate with temperature, activation energy of diffusion in the reaction layer, and variation of reaction heat with the volume fraction of atomized U-Mo fuels were measured.

2. Experimental Procedures

U-(6,10wt%)Mo alloy was melted using a lump of depleted uranium(99.9%) and Mo(99.7%) by vacuum induction melting in a zirconia crucible, and then centrifugally atomized to U-(6,10wt%) alloy powders. U-Mo powders 75-90   in diameter and Al powders 20   in diameter were mixed in a V-mixer with a rotation speed of 90rpm for 1 hour and hot extruded at 400°C with an extrusion ration of 38:1. The volume fraction of U-Mo fuels varies by 10, 30, 40 and 50vol%. The microstructure of U-Mo/Al dispersion fuels were characterized by using scanning electron microscopy (SEM), and energy dispersive spectrometry(EDS) and X-ray diffraction were used to identify the composition of the reaction layers. The reaction behavior between U-Mo fuel particles and the Al matrix was observed by annealing of 10vol% U-10Mo/Al dispersion fuels at 550-550°C up to 100 hours in a vacuum sealed quartz tube. Reaction heat was measured by differential scanning calorimetry(DSC) from room temperature to 700°C at a heating rate of 10°C/min. The microstructure of U-Mo/Dispersion fuels after the reaction was measured by scanning electron microscopy.

3. Results and Discussion

Fig. 1 shows the micrograph of 10vol% U-10Mo/Al dispersion fuel after annealing for 64 hours at 500°C. The bright region is atomized U-Mo alloy, the dark region is the Al matrix, and reaction layers formed between the U-Mo particles and the Al matrix. The reaction behavior of U-Mo/Al is categorized into surface reaction, internal reaction and full reaction. Internal reaction behavior results from the diffusion of Al atoms through the grain boundary of atomized U-Mo powders[5]
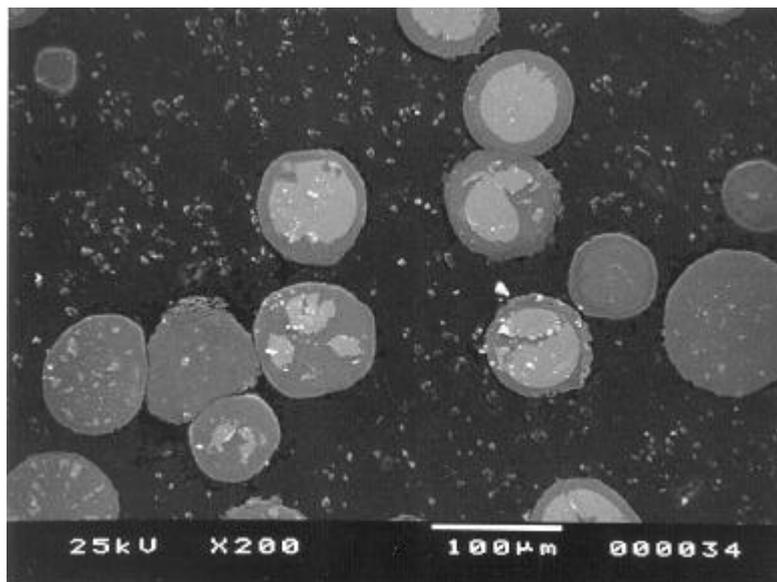

Fig. 1. Typical microstructure of 10vol.% U-10Mo/Al after annealing for 64 hrs at 500°C.

Energy dispersive spectroscopy was used to qualitatively identify the composition of the reaction layer between atomized U-Mo powders and the Al matrix. Fig. 2 exhibits that the reaction layer consists of two layers when annealed for more than 25 hours at 525°C, meanwhile 1 reaction layer was shown at 500°C. As listed in Table 1, the composition of the reaction layer at 500°C and internal layer at 525 and 550°C was measured as $(U,Mo)Al_3$ and the external layer at 525 and 550°C shows a composition of $(U,Mo)Al_{4.5}$. X-ray diffraction patterns of the reaction layer obtained by extraction of the Al matrix displays superposition of many peaks expected from UAl_3 as shown in Fig. 3. It is necessary to measure the exact composition of reaction layer by a neutron diffraction technique or transmission electron microscopy[6].
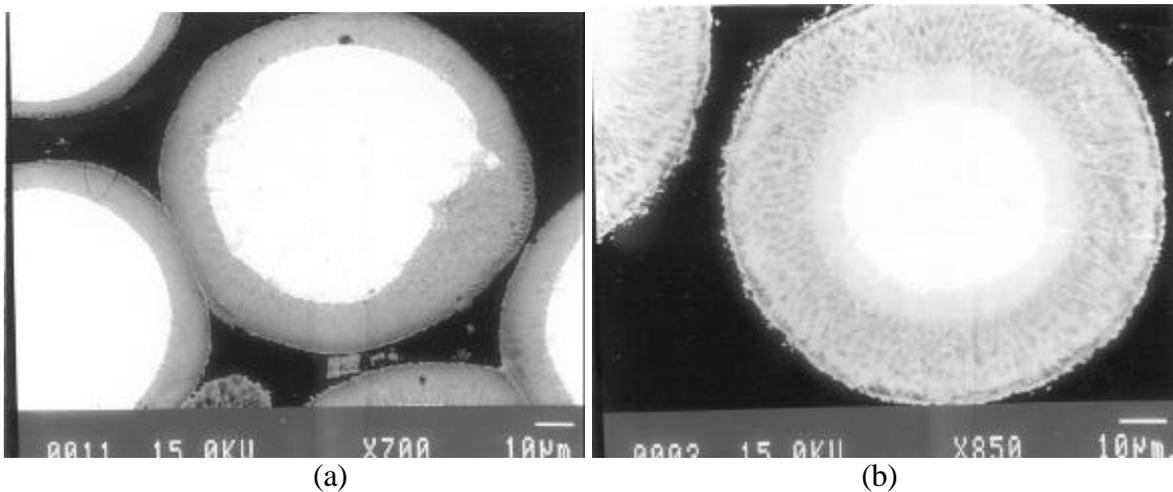

(a)   (b)

Fig. 2. Scanning electron micrographs showing the reaction layers in U-Mo powder annealed for 25 hrs at (a) 500°C and (b) 525°C.
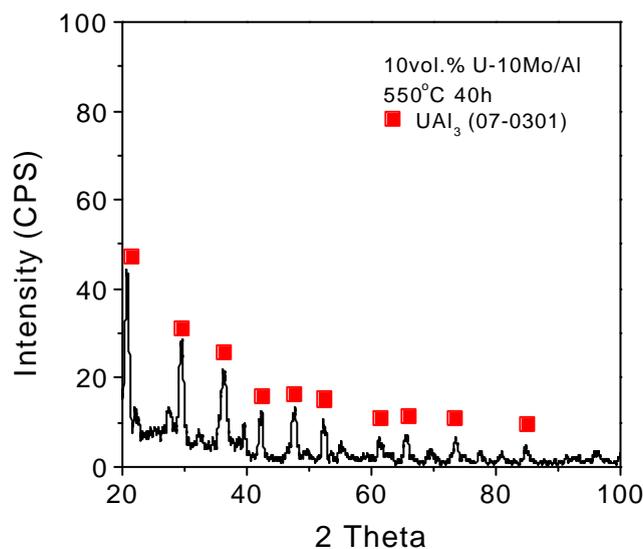

Fig. 3. XRD patterns of Al-extracted U-Mo powder annealed after 40 hrs at 550°C.

Table 1. Compositions of U, Mo, and Al in the reaction layer by energy dispersive spectroscopy.

composition (at.%)	500°C/25h	525°C/25h		550°C/25h	
		Internal	exterior	internal	exterior
U	19.5	20.5	11.2	18.0	13.8
Mo	4.1	3.8	3.7	4.9	2.9
Al	76.4	75.7	85.1	77.1	83.3

Fig. 4 shows the relationship between reaction layer thickness and annealing time and temperature. A spherical diffusion model is used for diffusion phenomena on spherical particles and is described as follows[7]:

$$\left[1 + 2\left(\frac{r_c}{r_o}\right)^3 - 3\left(\frac{r_c}{r_o}\right)^2\right] r_o^2 = kt \tag{1}$$

where r_c is the radius of unreacted powder, r_o is the initial radius of powder, k is the proportional constant, and t is annealing time. Eq.(1) is expressed as a function of reaction layer thickness, h $(= r_o - r_c)$ as follows :

$$h^2\left(1 - \frac{2h}{3r_o}\right) = kt \tag{2}$$

The reaction layer thickness-annealing time relationship gives the growth rate which is obtained from Fig. 4 and the activation energy of diffusion for growth of the reaction layer as shown in Fig. 5. The activation energy obtained from the spherical diffusion model is 316kJ/mol and the activation energy obtained from this study is thought to be that for the diffusion of Al atoms in the reaction layers.
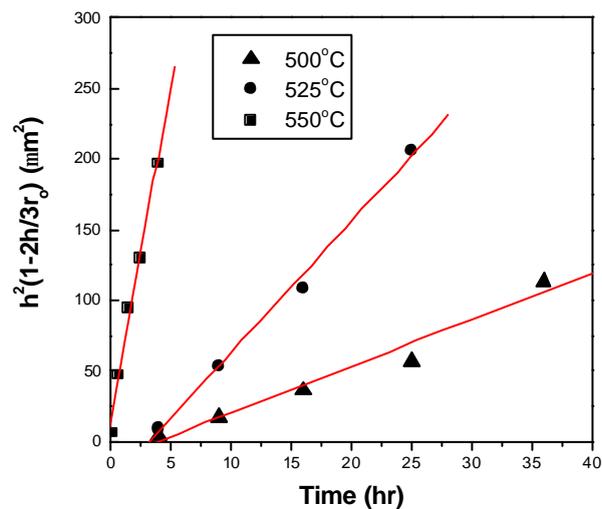

Fig. 4. Variation of the thickness parameter of the reaction layer obtained by the spherical diffusion model with increasing holding time at 500, 525, 550°C.
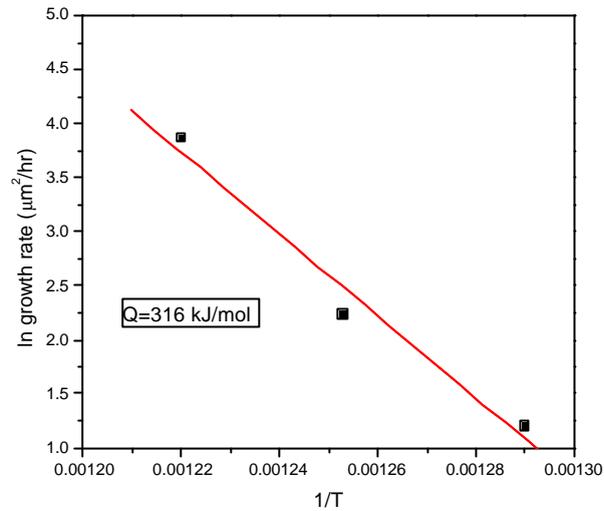
Fig. 5. Activation energy obtained by the spherical diffusion model.

Differential scanning calorimetry(DSC) of U-6Mo/Al dispersion fuel exhibits the variation of reaction heat with a varying volume fraction of U-6Mo fuels from 10vol% to 50vol%. Fig. 6 represents the variation of DSC peaks from reaction between U-6Mo fuels and the Al matrix around 645°C. When the volume fraction of U-6Mo was 10%, a endothermic peak from melting of the Al matrix and a exothermic peak from the reaction were superposed due to the limited U-Mo content in dispersion fuel resulting in residual Al. The exothermic reaction heat decreased as the volume fraction of U-Mo fuel increases from 30vol% to 50vol% due to the decrease in the counterpart of the reaction. Assuming the reaction compounds are $(U-Mo)Al_3$, the volume fraction for the complete reaction between U-6Mo and Al are calculated to be 29vol%. The maximum reaction heat was obtained at the volume fraction of U-6Mo is about 30vol% as shown in Fig. 7. The SEM micrographs after the DSC experiment exhibit that the content of unreacted U-6Mo fuel increased with the volume fraction of U-6Mo fuel as shown in Fig. 8.
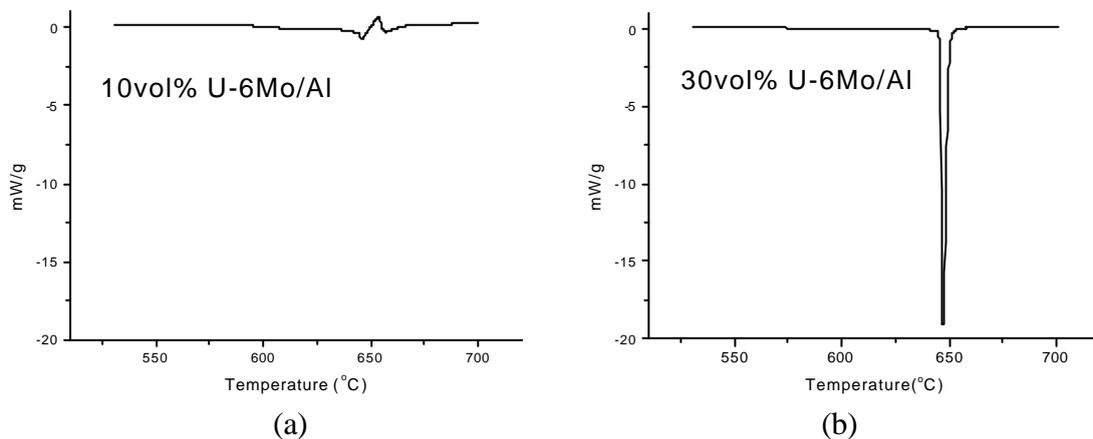

(a)

(b)

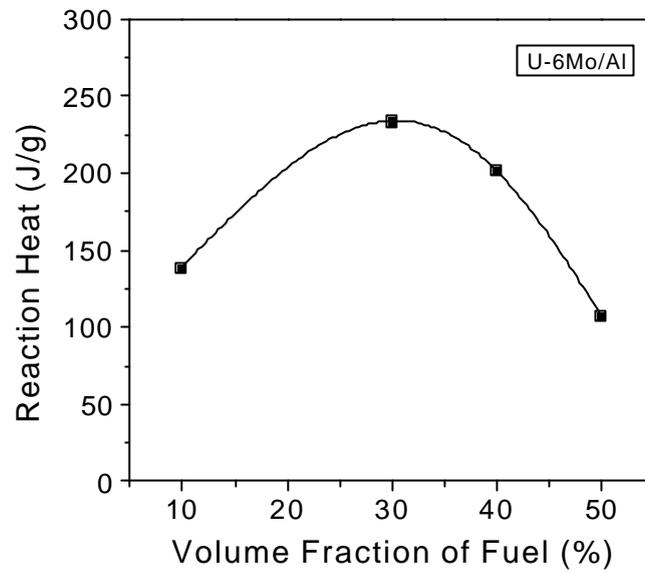Fig. 6. The DSC peak of U-6Mo/Al dispersion fuel on heating from room temperature to 700°C.

Fig. 7. Variation of reaction heat of U-6Mo/Al dispersion fuel on heating from room temperature to 700°C.
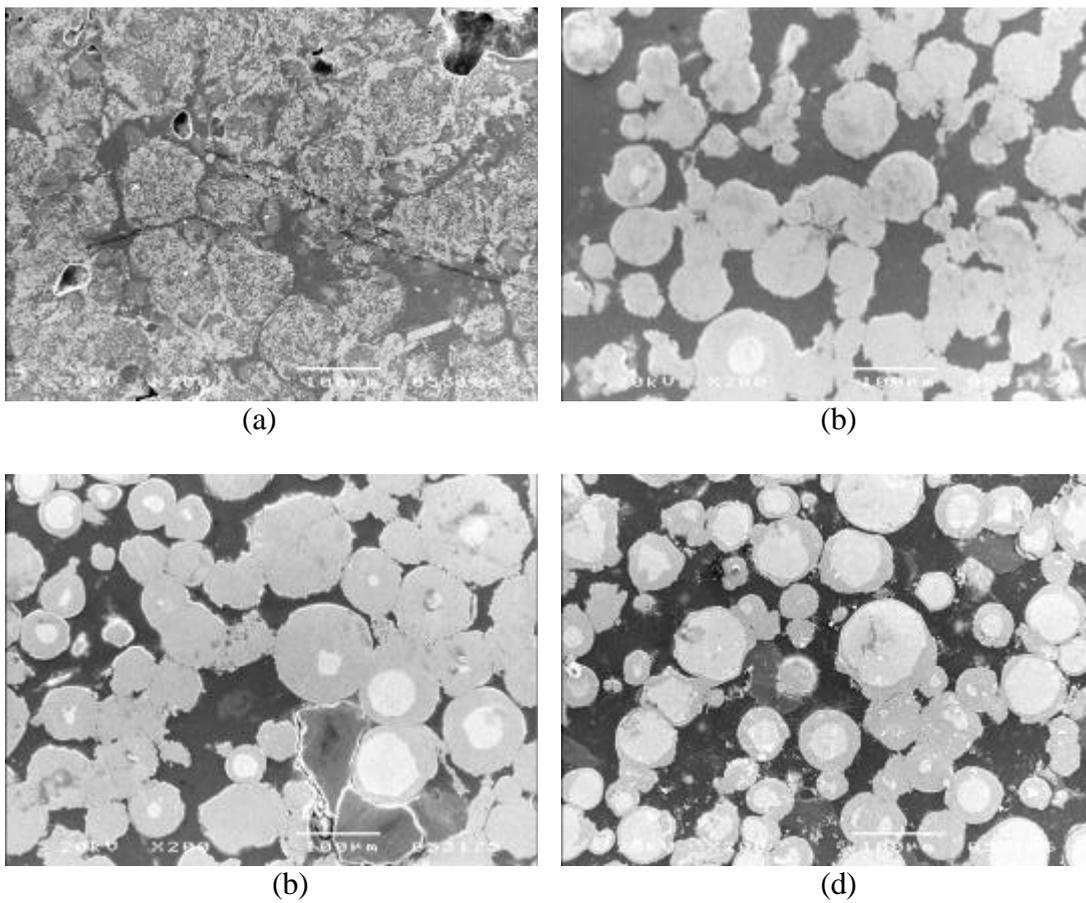

(a)

(b)

(b)

(d)

Fig. 8. Scanning electron micrographs of U-Mo/Al dispersion fuels after reaction during the DSC heating cycle from room temperature to 700°C.
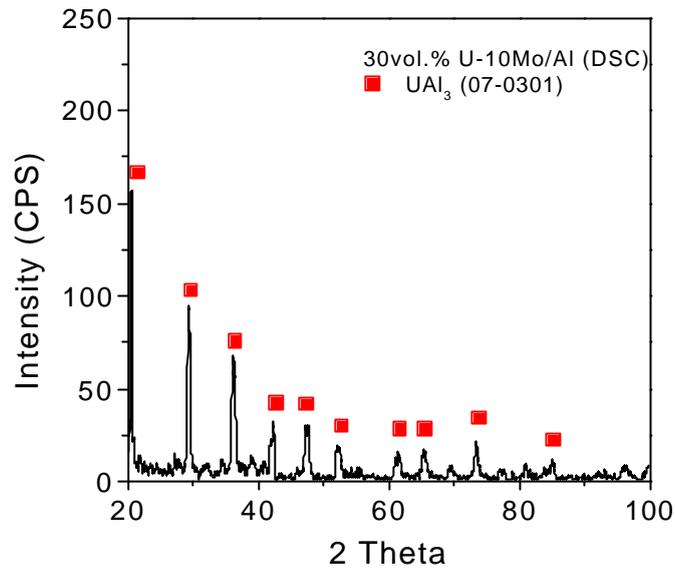
Fig. 9. XRD patterns of reacted U-Mo/Al dispersion fuels during DSC cycle from room temperature to 700°C.

Fig. 9 shows the X-ray diffraction patterns of reacted 30vol% U-10Mo/Al dispersion fuel after the DSC cycle from room temperature to 700°C. Most of the XRD peaks are consistent with the 2 theta value from the data for UAl_3. The XRD results mean that the predominant product after the reaction has the composition of $(U,Mo)Al_3$.

4. Conclusions

1. Annealing of U-Mo/Al dispersion fuel shows a single reaction layer of $(U,Mo)Al_x$ (x=3) at 500°C and double reaction layers of $(U,Mo)Al_x$ (x=3, 4.5) at 525, 550°C.

2. The growth rate and activation energy for diffusion in the reaction layer were obtained by the spherical diffusion model.

3. Reaction heat measured by DSC shows that endothermic melting and exothermic reaction was superposed when the volume fraction of U-Mo fuel was 10% and the reaction heat decreased as the volume fraction of U-Mo fuel increased from 30 to 50vol%

Acknowledgements

References

1. A.Travelli, Proc. of the 14th International Meeting on RERTR, Sao Pailo, Brazil, (1998).
2. G.L. Hofman, J. Nucl. Mater., 140 (1986) 256.
3. C.K. Kim, Proc. of the 14th International Meeting on RERTR, Jakarta, Indonesia, (1991).
4. S. Nazare, J. Nucl. Mater., 124 (1984) 14.
5. K.H. Kim et al., Nucl. Eng. Design, 178 (1997) 111.
6. B.S. Seong et al., J. Nucl. Mater., 277 (2000) 274.
7. J. Crank, The mathematics of diffusion, Claredon Press, Oxford (1975) p.89.