

An Investigation on the Fuel/Matrix Reaction Behaviors of U-Mo/Al Dispersion Fuels Prepared with Centrifugal Atomization

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ABSTRACT

The out-pile examinations of atomized U-Mo dispersion fuels after reaction between U-Mo and the Al matrix at elevated temperature were carried out in order to investigate heat generation, reaction kinetics and thermal compatibility. The heat generation of the dispersion fuels during the thermal cycle from room temperature to 700°C was measured employing differential scanning calorimetry (DSC). Growth rates of the reaction layer were fitted theoretically using spherical diffusion model. The effect of volume fraction and powdering method on the thermal compatibility of atomized U-Mo dispersion fuels was also examined.

1. Introduction

U-Mo fuel dispersant and Al matrix react to form intermetallic compounds when the U-Mo/Al dispersion fuel is annealed at high temperature. The reaction layer between U-Mo and the Al matrix induces the volume expansion and degradation of the thermal properties of U-Mo/Al dispersion fuels. It is important to investigate the growth behavior of the reaction layer and the variation of reaction heat. Compatibility refers to the effect of varied environments on dissimilar materials in contact with each other [1]. In dispersion fuels this manifests itself in dimensional and geometric changes that occur as a result of interdiffusion or other chemical reactions between the fuel dispersant and aluminum matrix [2-3]. The volume expansion produced by thermal annealing is thus a measure of the thermal stability of the dispersion fuels, and it is regarded as an indicator of expected in-reactor swelling performance [4].

It has also been shown that heating a uranium and aluminum couple in a vacuum at temperatures greater than 200°C causes pore formation [5-9]. Recently, a similar pore-forming reaction has been reported between uranium-silicide and aluminum [1]. As the reaction appears to be diffusion-controlled, it is exponentially dependent on temperature. In the case of U-Mo alloy, the reaction products of U-Mo and aluminum are $(U,Mo)Al_x$ ($2 \leq x \leq 4$), which is less dense than the combined reactants. The diffusivity of Al in U-Mo alloy is more rapid than that of U in Al. This may result in the so-called Kirkendall effect and the possible formation of pores in the Al matrix [10]. These pores have been proposed as contributing to the volume expansion of Al - (U-Mo) dispersion fuel.

U-Mo dispersion fuel for research reactors has been prepared by rolling or extruding the blended

powders of U-Mo and aluminum [11-12]. U-Mo particles are conventionally supplied by the mechanical comminution of as-cast U-Mo. In order to simplify the preparation process and improve the properties, a rotating-disk centrifugal atomization method has been used [13]. It is known that this process, in which the powder is prepared by a centrifugal force, has the advantages that the powder has a rapidly solidified γ -U microstructure, a relatively narrow particle size distribution, and a spherical shape [14-15].

In this study, high temperature annealing and differential scanning calorimetry of U-Mo/Al dispersion fuels are carried out to analyze the reaction behaviors of U-Mo/Al dispersion fuels. The activation energy of the reaction layer and the variation of reaction heat with the volume fraction of atomized U-Mo fuels were measured. In addition, the effect of the volume fraction and powdering method on the thermal compatibility of U-Mo alloys dispersed in Al was also examined. Because of the absence of radiation enhanced diffusion, the specimen was heated above the expected reactor fuel operating temperature, in order to stimulate any measurable diffusion. Microstructural examinations of the fuel particles after thermal annealing were carried out to determine the nature of thermal swelling.

2. Experimental procedure

Depleted uranium lumps (99.9 % pure) and Mo buttons (99.7 % pure) were charged and induction-melted in high-temperature-resistant ceramic crucibles. The superheated molten U-Mo metal was fed through a small nozzle onto a rapidly rotating graphite disk on a vertical axis. Liquid alloy droplets were then spread from the disk by a centrifugal force and cooled in an argon atmosphere. The atomized powder was collected in a container at the bottom of the funnel-shaped chamber. Otherwise, the molten U-Mo metal was alloyed and cast into a graphite mold in a vacuum atmosphere. The as-cast ingot was heat-treated in a vacuum for 100 hrs at 900°C to ensure compositional homogeneity, and then quenched to form a meta-stable gamma phase. The ingot was then machined into coarse chips and milled in a shatter box in an argon atmosphere using a hardened steel mill to obtain the appropriate particle size.

Dispersion fuel rods having various volume fractions of U-Mo powders were prepared by extruding U-Mo and aluminum powders at a working temperature of 500°C in a vacuum sealed quartz tube. These extruded specimens were annealed for incremental times at 400~550°C up to for 1,000 hrs. The samples were polished to 0.3 μ m in diamond paste, and examined by a scanning electron microscope (SEM) to characterize the morphology and the microstructure of the fuels. Electron-probe micro-analysis (EPMA), energy dispersive spectrometry (EDS), X-ray diffraction analysis (XRD) using Cu K α radiation, were used to determine the chemical and phase composition of the samples. Reaction heat was measured by differential scanning calorimetry (DSC) from room temperature to 700°C at a heating rate of 10°C/min.

3. Results and Discussion

Annealing dispersion fuels at various temperatures with varying annealing time gives reaction layer growth rate at each temperature and activation energy for growth of the reaction layer. Fig. 1 shows the relationship between reaction layer thickness and annealing time at temperatures ranging from 500°C to

550°C. A spherical diffusion model is used for fitting the reaction layer growth rate on spherical particles and is described as follows [16] :

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

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 :

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

When reaction layer thickness is small ($h \ll 1$), Eq.(2) gives well known parabolic relationship for planar diffusion model. The reaction layer thickness - annealing time relationship gives the growth rate which is obtained from Fig. 1 and the activation energy of diffusion for growth of the reaction layer as shown in Fig. 2. The activation energy obtained from the spherical diffusion model is 316 kJ/mol and the activation energy obtained from this study is thought to be that for the diffusion of Al atoms in reaction layers. It was higher than that of U_3Si dispersion fuel, 220 kJ/mol.

It is required to know the initiation temperature and reaction heat of spontaneous reaction between U-Mo particles and the Al matrix. Differential scanning calorimetry (DSC) of Al-(U-6wt.%Mo) dispersion fuels exhibits the variation of reaction heat with varying the volume fraction of U-6Mo fuels from 10vol.% to 50vol.%. Fig. 3 represents the variation of DSC peaks from the reaction between U-6Mo fuels and the Al matrix around 645°C. When the volume fraction of U-6Mo was 10%, an endothermic peak from melting of the Al matrix and an exothermic peak from 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. 4. The SEM micrographs after the DSC experiment exhibit that the content of unreacted U-6Mo fuel increased with the increasing volume fraction of U-6Mo fuel from 30vol.% to 50vol.% as shown in Fig. 5.

The volume increases versus annealing time for Al-30vol.%(U-10wt.%Mo) dispersion samples annealed at 500°C are shown in Fig. 6. Most of the swelling in the 500°C samples occurred within 100 hrs, so the swelling appeared to reach a plateau gradually with time. Al-30vol.%(U-10wt.%Mo) fuel samples with comminuted powder show a large volume increase (up to 28%) compared with those prepared with atomized powder (15%) after annealing at 500°C for 500 hrs.

Scanning electron images of the 30 vol.% fuel samples with the comminuted powder after annealing at 500°C for 20 hrs and 300 hrs are shown in Fig. 7. Metallographic examinations of the comminuted fuel samples after annealing at 500°C for 20 hrs showed that the extent of the reaction product formation reached approximately half of the particle cross-section, and led to a considerable

volume change (15%) (Fig. 7). Very small particles exhibited complete reaction. The coarse comminuted particles showed two aspects of aluminum penetration. Most particles had several irregular unreacted islands (bright-grey) with cracks, presumably formed during the comminution process. However, some particles were composed of a considerable amount of reacted areas around their circumference and generally had a "kernel-like" structure with an unreacted center. As the annealing time increased, the unreacted U-10wt.%Mo regions were gradually reduced. Fuel samples annealed for 300 hrs are composed of reacted particles with small unreacted center. Electron-probe micro-analysis of the 30 vol.% comminuted fuel samples showed that the reacted zone of fuel particles was converted to the (U,Mo)Al₃ compound. The reaction caused an overall volume increase of 25% of the dispersion sample.

Scanning electron images of the 30 vol.% fuel samples with atomized powder after annealing at 500°C for 20 hrs and 300 hrs are shown in Fig. 8. Metallographic examinations of the samples after annealing at 500°C up to 300 hrs showed that most particles generally exhibited a regular and smooth interface. There was some discernable formation of an intermediate phase layer in atomized particles with some completely reacted particles. Thus, the atomized sample has reacted to a lesser degree overall compared to the comminuted particles, and the volume increase in the atomized fuel specimens was about half that of the comminuted fuel specimens (Fig. 7). After 300 hrs at 500°C the 30 vol.% U-10wt.%Mo fuel samples with atomized powder, were composed mainly of particles with smaller unreacted centers. Electron-probe micro-analysis of the 30 vol.% atomized fuel samples showed that the reacted zone of fuel particles were converted to the (U,Mo)Al₃ compound. The reaction caused an overall volume increase of 12% of the dispersion sample.

Samples with the comminuted powder showed a larger volume increase compared with those prepared with atomized powder. The possible reasons can be supposed as follows. The specific surface area of the spherical atomized powder, $5 \times 10^{-3} \text{ m}^2/\text{g}$, is about 50% smaller than that of the irregular comminuted powder, $9.2 \times 10^{-3} \text{ m}^2/\text{g}$, resulting in a correspondingly smaller diffusion interface, resulting in a smaller Al - (U-10wt.%Mo) interface area. Moreover, interdiffusion in the comminuted particles during thermal annealing can be divided into two paths; first, uniform diffusion, through the interacted phase, leaving a kernel-like island or several islands; secondly, through cracks or deformation zones. These cracks and deformation zones may play a role in accelerating the penetration of aluminum atoms. The comminuted powder particles have distinctive aluminum penetration paths in the form of cracks and deformation zones that originated from the comminution process, leaving no uniform reaction layer and several small unreacted islands. Samples in the atomized powder have somewhat different penetration paths. That is, in addition to uniform diffusion there appears to be diffusion along the many grain boundaries in the much finer grained material, leaving unreacted islands [17].

The effect on the volume change of Al-(5~45vol.%(U-7wt.%Mo) dispersion fuel samples annealed at 500°C is shown in Fig. 9. Most of the swelling in the 500°C samples occurred within 100 hrs. The amount of swelling was found to increase with increasing volume fraction of U-7wt.%Mo powder. The volume change of the Al-45vol.%(U-7Mo) dispersion fuel sample was about four times as much as that of the Al-5vol.%(U-7Mo) fuel sample fuel specimens after annealing at 500°C for 300 hrs. This difference in volume increase is somewhat smaller than the proportional volume fraction of the U-7Mo powder. Scanning electron images of the dispersion fuel samples after annealing at 500°C for 100 hrs are shown in Fig. 10. As the volume fraction decreased, the unreacted U-7Mo regions gradually increased. The 5vol.%(U-7wt.%Mo) dispersion fuel sample exhibited almost complete reaction. The extent of the reaction product formation of the 25vol.%(U-7Mo) dispersion fuel sample reached approximately half of the particle cross-section. The 45vol.%(U-7Mo) dispersion fuel sample had a small amount of reacted areas around their circumference.

4. Conclusions

- 1) The growth rate and the activation energy for diffusion in reaction layer were obtained by the spherical diffusion model.
- 2) The reaction heat measured by DSC shows that endothermic melting and exothermic reaction were 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.%.
- 3) U-Mo dispersion fuel samples with comminuted powder showed a larger volume increase compared with those including atomized powder after annealing.
- 4) The reasons were determined as follows.
 - i) The smaller surface area of atomized spherical powder in comparison to the irregular comminuted powder.
 - ii) U-Mo dispersion fuel samples with comminuted powder have exclusive penetration paths, that is, cracks and deformation zones originated from the mechanical comminution process, leaving no uniform reaction layer and several small unreacted islands.
- 5) The volume change of U-Mo dispersion fuel samples was found to increase with increasing volume fraction after annealing. The unreacted fraction of U-Mo fuel gradually increased, as the volume fraction of U-Mo fuel increased.

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