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Thermal Compatibility of High Density U-Mo Powder Fuels Prepared by Centrifugal Atomization

Ki Hwan Kim, Hyun Suk Ahn, Se Jung Chang, Young Mo Ko,
Don Bae Lee, Chang Kyu Kim and Il Hyun Kuk
Korea Atomic Energy Research Institute

Abstract

Samples of extruded dispersions of 24 vol.% spherical U-2wt%Mo and U-10wt.%Mo powders in an aluminum matrix were annealed for over 2,000 hours at 400℃. No significant dimensional changes occurred in the U-10wt.%Mo/aluminum dispersions. The U-2wt.%Mo/aluminum dispersion, however, increased in volume by 26% after 2,000 hours at 400℃. This large volume change is mainly due to the formation of voids and cracks resulting from nearly complete interdiffusion of U-Mo and aluminum. Interdiffusion between U-10wt.%Mo and aluminum was found to be minimal. The different diffusion behavior is primarily due to the fact that U-2wt.%Mo decomposes from an as-atomized metastable γ-phase (bcc) solid solution into the equilibrium γ-U and U_2Mo two-phase structure during the experiment, whereas U-10wt.%Mo retains the metastable γ-phase structure after the 2,000 hours anneal and thereby displays superior thermal compatibility with aluminum compared to U-2wt.%Mo. In addition, the molybdenium supersaturated in U-10wt.%Mo particles inhibits the diffusion of aluminum atoms along the grain boundary into the particle. Also, the dissolution of only a few Mo atoms in UAl_3 retards the formation of the intermediate phase, as Mo atoms need to migrate from new intermetallic compounds to unreacted islands.

I. Introduction

High density γ-U phase alloy has begun to be developed in the renewed fuel program of the Reduced Enrichment for Research and Test Reactors (RERTR) [1]. It has been reported that high density atomized U-Mo powders prepared by rapid solidification have the metastable isotropic γ-U phase supersaturated with substitutional molybdenium, and with good γ-U phase stability, especially in U-10wt.%Mo alloy fuel [2]. If the alloy has good thermal compatibility with aluminum matrix, and this metastable gamma phase can be maintained during irradiation, U-Mo alloy would be a prime candidate for dispersion fuel for research and test reactors.

An atomized U-Mo particle can be considered as a number of polycrystalline metastable γ-U grains supersaturated with Mo [2]. In an attempt to evaluate the required properties of uranium-aluminum which can be regarded as a model system for the U-Mo - Al composites, a number of investigations have been performed on the interdiffusion or the interfacial reaction between uranium and aluminum [3-5]. It has been reported that in

uranium-aluminum system the isolated "islands" of unreacted uranium originated from nonplanar layer growth are present in the intermediate phase layer as a result of interfacial breakdown [6-8]. Adda et al. and Buddery et al. report the presence of only UAl_3 in the intermediate phase region, while Castleman and Bland have observed both the UAl_2 and UAl_3 phases, but no UAl_4 [3-4, 7, 9]. Subramanyam et al. [6] attribute the occurrence of the UAl_2 in the multiphase region to the thermal decomposition of UAl_3 phase at high temperature during slow cooling, while Castleman [9] has regarded the formation of the UAl_2 in that region as a consequence of on-going reaction between the isolated islands of uranium and the surrounding UAl_3.

Based upon the proceeding investigations in the uranium- aluminum system [3-9], the present work considers the dimensional changes, the interface damage and the formation of uranium-aluminide phases resulting from the sluggish reaction system of the atomized U-Mo powder versus the aluminum matrix. The fuel rods are made by extruding the blended powders with atomized U-Mo and aluminum. The characteristics related to the thermal compatibility of U-2wt.%Mo and U-10wt.%Mo alloy fuels at 400℃ are examined.

II. Experimental Procedure

Depleted uranium lumps (99.9 pct pure) and molybdenium buttons (99.7 pct pure) were used for the preparation of the U-Mo powders by rotating-disk centrifugal atomization. Dispersion fuel samples were prepared by extrusion of blended U-Mo powder and aluminum powders at a working temperature 400℃. U-2wt.%Mo and U-10wt.%Mo alloy fuel samples (25 mm long) were annealed at 400℃ for various times. After each anealing interval, the dimensional changes of the specimens were measured.

The samples were polished to 3 ㎛ diamond paste and were examined by scanning electron microscope (SEM) to characterize the morphology and the microstructure of fuel meat. Electron-probe micro-analysis (EPMA), energy dispersive spectrometry X-ray analysis (EDX), and X-ray diffraction analysis (XRD) using Cu K_α radiation, were also used to determine the chemical composition and the phase.

III. Results and discussion

Table 1 shows the dimensional changes of the Al-24vol.% U-2wt.%Mo and U-10wt.%Mo alloy fuel samples annealed at 400℃ for various times. U-Mo fuel sample in the as-fabricated condition contains a small amount of porosity. About 5% densification is resulted from the sintering of fuel meats occurred during the initial period of heat-treatment. U-2wt.%Mo fuel sample shows a large volume increase up to 26% after annealing at 400℃ for 2,000 hours. The volume of the U-10wt.%Mo sample, on the other hand, remains the same, except for a temporary decrease after the 1,000 hour anneal.

Scanning electron micrographs of U-2wt.%Mo fuel meat after annealing at 400℃ for 2,000 hours (Fig. 1) illustrate some changes in structure related to the great penetration of Al atoms, especially prominent formations of pores in the particles, cracks around the particles.

It is thought that aluminum atoms related to the diffusion into U-2wt.%Mo particle leave vacancies which develop further into voids resulting in a great swelling. In this study, cracks are observed to be formed as a result of the constraints imposed upon the brittle intermediate phase layer by the geometry of the specimen configuration. Backscattered electron images of U-2wt.%Mo sample after annealing at 400℃ for 2,000 hours are illustrated in Fig. 2. Fuel particles, illustrated in Fig. 2-(a), are composed mainly of large islands, unreacted regions located in the center part, and small islands, penetrated regions directed toward the center part. It is shown that the new phase has developed in the peripherical boundary of the U-Mo particle, but has not developed much in the center part of the particle. It implies that the new phase begins to be formed from the circumferential rim due to the diffusion routes penetrated along the unstable paths such as the original grain boundaries of the uranium solid solution. Fuel particles, illustrated in Fig. 2-(b), are composed mainly of small islands, penetrated regions directed toward the center of U-2wt.%Mo powder. It is shown that the penetration of aluminum atoms in the initial step occurs mainly at the circumferential part of U-Mo particle, but in the final step the formation of intermediate phases develops toward the center of the particle. The original uranium grains have gradually been reduced to small islands, from large islands surrounded by the new phase in the matrix of U-Mo particles. All regions of fuel particles are filled with U-Al compounds. Eventually, the reactions cause an overall volume increase, that is, a thermally-induced swelling in the dispersion fuel due to lower density of uranium-aluminide phases and formation of voids.

Area scan analyses of U-2wt.%Mo sample with energy dispersive X-ray spectroscopy after annealing at 400℃ for 2,000 hours are illustrated in Table 2. The analysis results indicate that large islands and small islands are composed of 92at.% U, 7at.% Mo, 1at.% Al, and 68at.% U, 3at.% Mo, 28at.% Al, respectively. Large islands are gradually reduced to small ones due to the formation of intermediate phase around the interface between matrix and large island as Al atoms diffuse along grain boundary into the particle. In the same time Mo atoms diffuse into unreacted uranium regions, that is, large islands from new intermetallic compounds. In addition, the analysis results show that matrix consists of 76at.% Al, 22at.% U and 0.9at.% Mo. It is supposed that uranium-aluminide, mainly UAl_3, is formed in the matrix of particle and dissolve only a few molybdenium atoms. Fig. 3 shows the X-ray diffraction patterns for U-2wt.%Mo fuel meat after heat-treatment at 400℃ for 2,000 hours. U-2wt.%Mo fuel meat consists of Al, UAl_3, γ-U, α-U and U_2Mo phase. It is worth noticing that the uranium-aluminide, mainly UAl_3, is formed in the U-Mo particles due to the diffusion of Al atoms. It is also determined with energy dispersive X-ray spectroscopy that the matrix region of the particle consists mainly of UAl_3 which is heterogeneously formed along the grain boundary of uranium solid solution.

Scan electron image and micro-probe micro-analysis trace with backscattered electron images carried out on this annealed U-10wt.%Mo sample for 2,000 hours (Fig. 4) indicates some formation of reaction layer in the interface between U-Mo particle and Al matrix. Electron-probe micro-analysis trace and scan electron image carried out on this U-10wt.%Mo sample annealed at 400℃ for 2,000 hours illustrate that the SEM images of U-10wt.Mo powder still reveal some Mo segregation or cored microstructure, and some separated phases

around the grain boundary [2]. Al exists more in the grain boundary (5at.%) than around in the grain (2at.%). It implies that such concentrations are associated with some penetrations of Al atoms along the grain boundaries in U-10wt.%Mo particles like U-2wt.%Mo particles. It is thought that these results are originated from the supersaturation of Mo in the metastble γ-U solid solution of U-10wt.%Mo alloy. Large content of substitutional Mo atoms with low diffusivity cause the migration of U atoms difficulty and inhibit the great decomposition and coarsening of γ-U. Eventually, the microstructure and the phase of the annealed U-10wt.%Mo specimen don't change greatly despite so long heat-treatment at 400℃. It is supposed that molybdenum atoms supersaturated in the grain boundary inhibit the diffusion of aluminum atoms which proceeds along the grain boundary into the U-10wt.%Mo particle. The annealed U-10wt.%Mo specimen has longer incubation time in the volume change relative to the annealed U-2wt.%Mo specimen. Hence, it is thought that the diffusion-controlled swelling resulted from Al penetration can be retarded greatly by heavy supersaturation with Mo atoms in the γ-U solid solution of the U-10wt.%Mo particle. Metallographic examinations of U-10wt.%Mo sample show that almost all particles exhibit a regular and a round interface, and few cracks at the peripherical boundary of U-Mo particle resulted from no reaction between U-Mo particle and aluminum matrix as the U-10wt.%Mo sample for 100 hours. In addition, this sample shows no structural changes related to thermally-induced swelling. Area scan analyses with energy dispersive X-ray spectroscopy also show that U-10wt.%Mo particles have some penetrated aluminum atoms (about 3at.%.), resulted in a slight volume increase in the sample.

Ⅳ. Conclusion

1) Dispersions of atomized U-Mo powders in aluminum, when annealed at 400℃, show very different behavior depending on the molybdenum content of the uranium-alloy. Samples containing 2wt.%Mo increased in volume by 26% after 2,000 hours, whereas the volume of samples containing 10wt.%Mo remained nearly constant.
2) The difference is believed to be caused by the decomposition of the U-2wt.%Mo alloy particles into the equilibrium γ-U/U_2Mo -phase microstructure. Extensive diffusion of aluminum into this γ-phase structure leads to the formation of porosity and volume increase of the dispersion. Alloys containing lower molybdenum fractions that allow decomposition to the equilibrium α-U/U_2Mo microstructure are incompatible with aluminum because of extensive interaction.
3) The U-10wt.%Mo alloy particles retain their as-solidified meta-stable γ-U structure, into which aluminum diffusion is minimal. In addition, the molybdenium supersaturated in U-10wt.%Mo particles inhibits the diffusion of aluminum atoms along the grain boundary into the particle. Also, the dissolution of only a few Mo atoms in UAl_3 retards the formation of the intermediate phase, as Mo atoms need to migrate from newly intermetallic compounds to unreacted islands. This indicates that, excluding unknown irradiation effects, U-10wt.%Mo would be compatible with an aluminum matrix in a dispersion fuel.

References

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(Unit: %)

Time (hr)	U-2Mo Alloy			U-10Mo Alloy		
	Δ ℓ	Δ d	Δ V	Δ ℓ	Δ d	Δ V
11	-0.15	-0.17	-0.49	-0.09	-0.18	-0.45
40	-0.03	-0.30	-0.63	-0.02	-0.06	-0.14
107	0	-0.23	-0.46	-0.14	-0.05	-0.24
350	+0.19	+0.06	+0.31	-0.07	0	-0.07
1000	+1.83	+0.39	+2.61	-1.04	-1.52	-4.08
2000	+4.28	+10.86	+26.00	-0.12	-0.11	-0.34

Table 1 Dimensional changes of Al-24vol.% U-Mo fuel meats after annealing at 400℃ during various times.

Locations	Composition(at.%)		
	U	Mo	Al
Matrix	22	0.9	76
Small Islands	68	3	28
Large Islands	92	7	1

Table 2 Area scan analyses of U-2wt.%Mo fuel meat with energy dispersive X-ray spectroscopy after annealing at 400℃ for 2,000 hours.

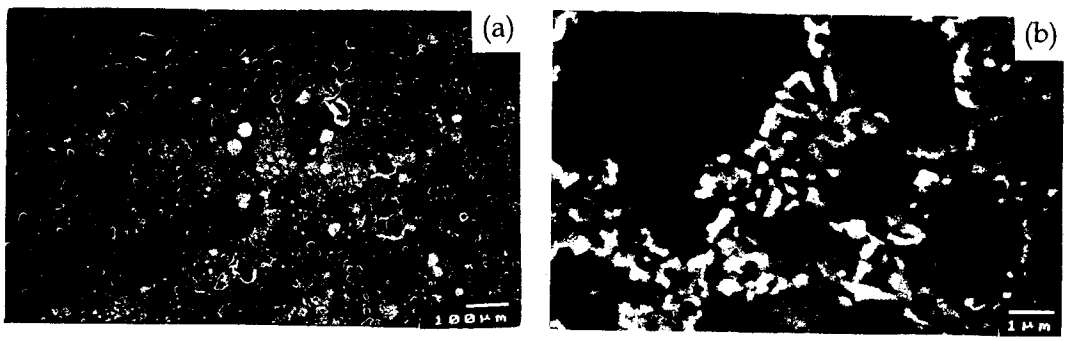

Fig. 1. Scanning electron micrographs of U-2wt.%Mo fuel meat after annealing at 400℃ for 2,000 hours; (a) x75, (b) x10000.

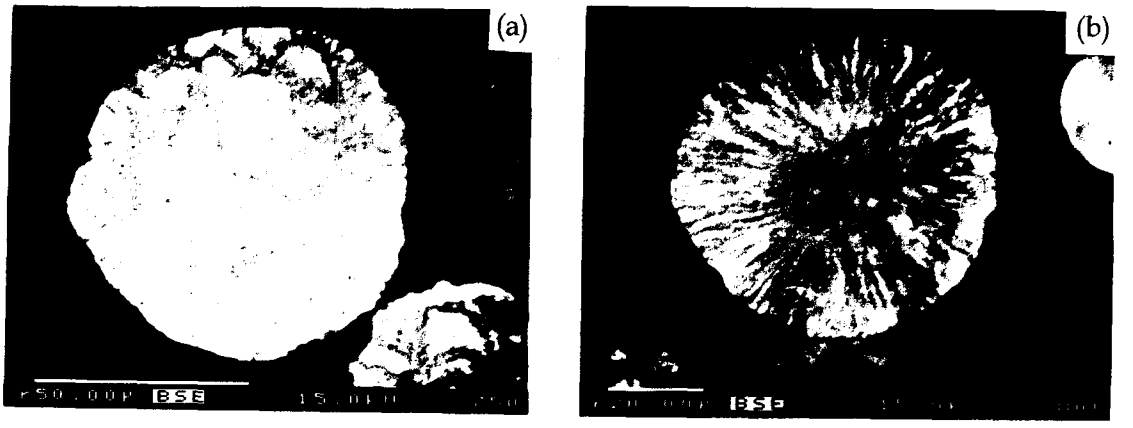

Fig. 2. Backscattered electron images of Al-24vol.% U-2wt.%Mo fuel meat after annealing at 400℃ for 2,000 hours; (a) large and small islands, (b) only small islands..

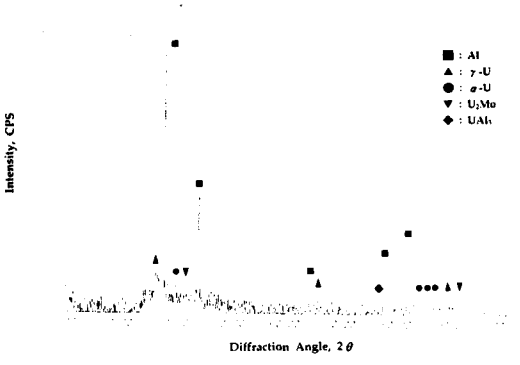

Fig. 3. X-ray diffraction patterns for U-2wt.%Mo fuel meat after heat-treatment at 400℃ for 2,000 hours.

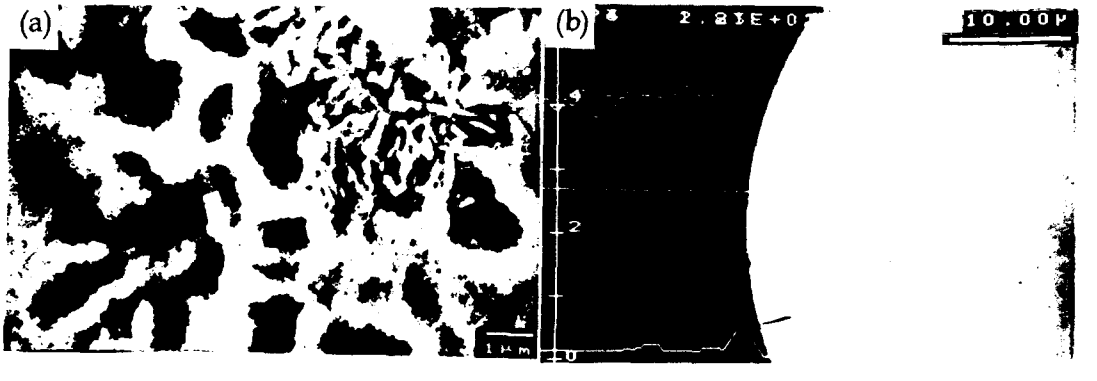

Fig. 4. Scan electron image (a) and micro-probe micro-analysis trace with backscattered electron image (b) of U-10wt.%Mo fuel sample annealed for 2,000 hours.