ELSEVIER

Journal of Nuclear Materials 250 (1997) 79–82

journal of nuclear materials

Letter to the Editors

Thermal compatibility studies of unirradiated U–Mo alloys dispersed in aluminum

Don Bae Lee *, Ki Hwan Kim, Chang Kyu Kim

Research Reactor Fuel Development Project, Korea Atomic Energy Research Institute, PO Box 105, Yusung-ku, 150 Dukjin-dong, Taejon 305-353, South Korea

Received 28 April 1997; accepted 2 July 1997

Abstract

The thermal compatibility of centrifugally atomized U–Mo alloys with aluminium has been studied. The results of the investigations show that the U–2 wt% Mo/aluminum dispersions increase in volume by 26% at 400°C after 2000 h. This large volume change is mainly due to the formation of voids and cracks resulting from nearly complete interdiffusion of U–Mo and aluminum. No significant dimensional changes occur in the U–10 wt% Mo/aluminum dispersions. Interdiffusion between U–10 wt% Mo and aluminum is found to be minimal. The different diffusion behavior is primarily due to the fact that U–10 wt% Mo particles are much more supersaturated with substitutional molybdenum than U–2 wt% Mo particles. The aluminum diffuses into the U–2 wt% Mo particles relatively rapidly along grain boundary with nearly pure uranium, forming UAl_3 almost fully throughout the 2000 h anneal, whereas the molybdenum supersaturated in the U–10 wt% Mo particles inhibits the diffusion of aluminum atoms. U–10 wt% Mo displays superior thermal compatibility with aluminum compared to U–2 wt% Mo.

1. Introduction

In the renewed fuel development program of the Reduced Enrichment for Research and Test Reactors (RERTR) Program the development of a high density γ-U phase alloy has been undertaken [1]. As well, it has been reported that high-density atomized U–Mo powders prepared by rapid solidification consist of the metastable isotropic γ-U phase and possess good phase stability, especially in U–10 wt% Mo alloy fuel [2]. There was a considerable amount of volume increase in U alloys dispersed in aluminum resulting from the formation of the uranium aluminide and usually accompanied by an interdiffusion or an interfacial reaction between the dispersant and aluminum, at the operation temperature of the research reactor, even in the absence of a neutron flux [3]. Some characteristics, such as swelling of the dispersant–aluminum composites, detrimentally affect the performance of nuclear fuel materials. If the alloy has good thermal compatibility with the aluminum matrix and the metastable gamma phase can be maintained during irradiation, U–Mo alloy would be a prime candidate for dispersion fuel for research and test reactors.

Atomized U–Mo particles can be considered as 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 interfacial reaction between uranium and aluminum [4–6]. It has been reported that, in the uranium–aluminum system, the isolated 'islands' of unreacted uranium originated from non-planar intermediate phase layer growth [7–9]. Based upon the preceding investigations in the uranium–aluminum system [4–9], the present work considers the dimensional changes and the formation of uranium aluminide phases resulting from the reaction system between the U–Mo dispersant and aluminum matrix. For this purpose U–Mo alloy pow-

* Corresponding author. Tel.: +82-42 868 2318/2308; fax: +82-42 868 8346; e-mail: dblee nanum.kaeri.re.kr.

0022-3115/97/$17.00
PII S0022-3115(97)00252-3

ders with very-high densities, $\geq 15 \times 10^{-3}$ kg U/m^3, were prepared by rotating-disk centrifugal atomization. The fuel rods are made by extruding the blended powders with atomized U–Mo and aluminum. The characteristics relating to the thermal compatibility of U–2 wt% Mo and U–10 wt% Mo alloy fuels have been examined.

2. Experimental

Depleted uranium rods (99.9% pure) and molybdenum buttons (99.7% pure) were used for the preparation of the U–Mo powders, by rotating-disk centrifugal atomization. Dispersion fuel samples were prepared by extruding the blended powders with atomized U–Mo and Al at 400°C. U–2 wt% Mo and U–10 wt% Mo alloy fuel samples (25 mm long) were annealed at 400°C for various times. After each annealing interval, the dimensional changes of the specimens were measured.

The samples were polished to a 3 μm diamond paste, and then etched with reagent (nitric acid:acetic acid = 1:1) then examined by scanning electron microscopy (SEM) in order to characterize the morphology and the microstructure of the 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 content of the samples.

3. Results and discussion

Table 1 shows the dimensional changes of the Al–24 vol.% U–2 wt% Mo and U–10 wt% Mo alloy fuel samples annealed at 400°C for various times. Both U–2 wt% Mo and U–10 wt% Mo samples decrease in volume by a small amount during the first 100 h of heat treatment. This minor shrinkage may be due to some consolidation of the as-fabricated pores. However, after 1000 h a clear difference is observed between the two fuel compositions. After annealing at 400°C for 2000 h the U–2 wt% Mo sample shows a large volume increase, up to 26%. The volume of U–10 wt% Mo sample, on the other hand, remains the same except for a temporary decrease after the 1000 h anneal. Such a large volume increase is not exceptional in dispersion fuel compatibility tests. It is attributed to extensive interdiffusion of fuel and aluminum matrix, which apparently is accompanied by the formation of a large amount of porosity involving generation of pores and cracks filled with desorbed gases. The complete interdiffusion of U–Mo and aluminum in the samples would amount to a volume increase of only 2.5%, far short of the observed change in volume. Metallographic examinations of U–2 wt% Mo fuel sample annealed for 2000 h (Fig. 1) indeed confirm the existence of pores and cracks as the predominant cause of large volume increase in this sample. It is thought that aluminum atoms related to the diffusion into U–2 wt% Mo particles leave vacancies which develop further into voids. An interdiffusion or an interfacial reaction between the dispersant and aluminum results in the formation of uranium aluminide with low density around the particle periphery as the reaction proceeds with time. The growth of the intermediate phase of the U–Mo particles causes a tensile stress zone around the peripheral boundary as the volume of the uranium aluminide increases. The higher tensile constraints are imposed upon the brittle uranium aluminide layer with the growth of the intermediate phase. Eventually, cracks appear around the particle periphery at the moment that the tensile stress exceeds the mechanical strength of the brittle uranium aluminide [10,11].

Table 1
Dimensional changes of Al–24 vol.% U–Mo fuel samples after annealing at 400°C for various times (unit: %)

Time (h)	U–2 Mo alloy			U–10 Mo alloy		
	$\Delta\ell$	Δd	ΔV	$\Delta\ell$	Δd	ΔV
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	+26.0	−0.12	−0.11	−0.34

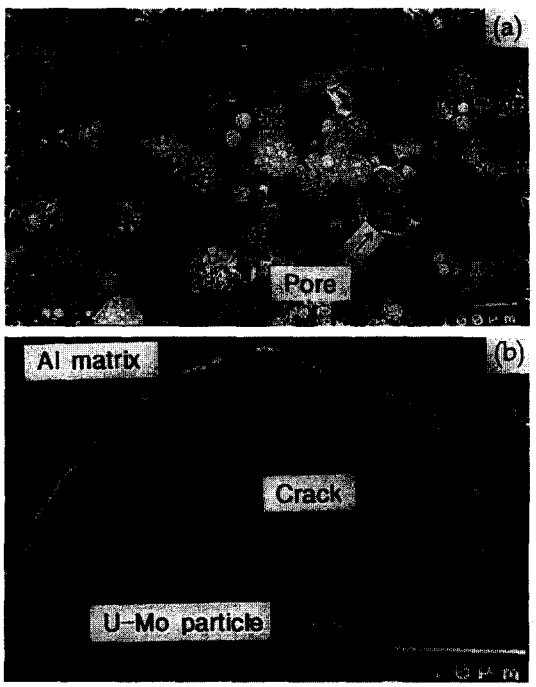

Fig. 1. Scanning electron micrographs of U–2 wt% Mo fuel sample after annealing at 400°C for 2000 h; (a) ×75, (b) ×2000.

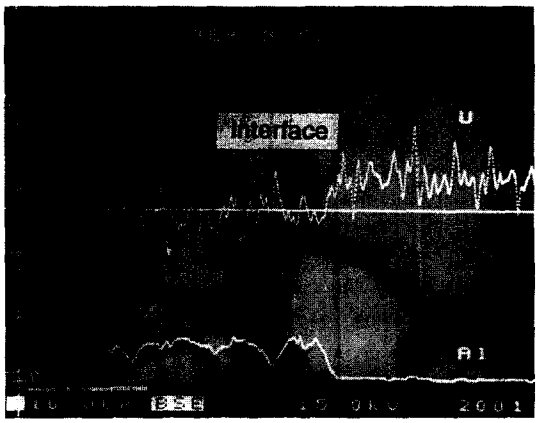

Fig. 2. Electron-probe micro-analysis traces on Al–24 vol.% U–2 wt% Mo fuel sample annealed at 400°C for 2000 h.

Electron-probe micro-analysis (EPMA) traces on the annealed sample for 2000 h (Fig. 2) confirm formation of an intermediate phase layer in the interface between the U–Mo particle and the Al matrix. The composition profile shown in the probe trace illustrates a slow decrease of Al around the interface, a considerable penetration of Al atoms through the interface and some Al penetration in the unreacted large island, which is regarded as the evidence of a large volume change (26%) in the sample annealed for 2000 h. The results of an area scan analysis of the U–2 wt% Mo sample annealed for 2000 h by using energy dispersive X-ray spectroscopy (EDX) are shown in Table 2. The analysis results indicate that large islands are composed of 92 at.% U, 7 at.% Mo and 1 at.% Al, whereas small islands consist of 68 at.% U, 3 at.% Mo and 28 at.% Al. In addition, the EDX analysis results show that the matrix consists of 76 at.% Al, 22 at.% U and 0.9 at.% Mo. The X-ray diffraction pattern shows that the U–2 wt% Mo fuel sample after heat treatment for 2000 h consists of UAl_3, α-U, U_2Mo, γ-U and Al phase (Fig. 3). It is worthwhile to mention that the uranium–aluminide with a small amount of molybdenum, mainly UAl_3, is formed in the U–Mo particles due to the diffusion of Al atoms. EPMA analysis indicates substantial aluminum penetration into the fuel particles. Interdiffusion appears to be characterized by aluminum diffusion along the U–Mo grain boundaries. Diffusion of aluminum in uranium is relatively

Table 2
Area scan analysis of U–2 wt% Mo fuel sample with energy dispersive X-ray spectroscopy after annealing at 400°C for 2000 h

Locations	Composition (at.%)		
	uranium	molybdenum	aluminum
Fuel matrix	22	< 1	76
Small islands	68	3	28
Large islands	92	6	1

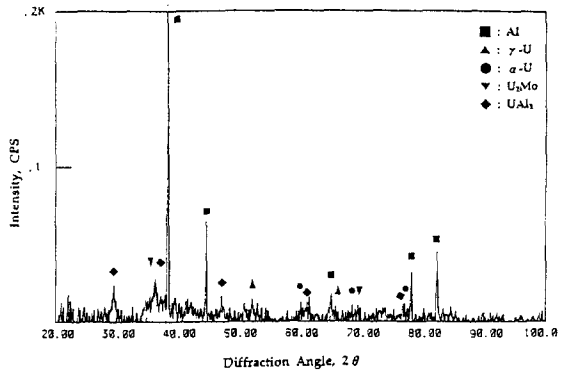

Fig. 3. X-ray diffraction patterns for U–2 wt% Mo fuel sample after heat treatment at 400°C for 2000 h.

rapid and, particularly in U–2 wt% Mo, the grain boundary areas consist of nearly pure uranium. This grain boundary penetration by aluminum results in significant swelling of the dispersion samples. The interdiffusion of aluminum and uranium normally results in the formation of UAl_3, which is also the case here. Proceeding from the particle perimeter, relatively large islands of unreacted fuel are enveloped by UAl_3. These larger islands are then consumed by the further growth of the UAl_3 phase which then becomes the fuel matrix, thus leaving small islands dispersed throughout the new UAl_3 phase.

EPMA traces with backscattered electron images on the annealed Al–24 vol.% U–10 wt% Mo sample for 2000 h (Fig. 4) indicate a relatively slow decrease around the interface and some diffusion of Al atoms through the interface. The area scan analysis using EDX also shows that some aluminum atoms (about 3 at.%) have penetrated into U–10 wt% Mo particles. Al atoms are present in the grain boundary (2 at.%) more than in the grain (2 at.%). It is thought that such concentration distribution is associated with some penetrations of Al atoms along the grain boundaries in U–10 wt% Mo particles, like U–2 wt% Mo

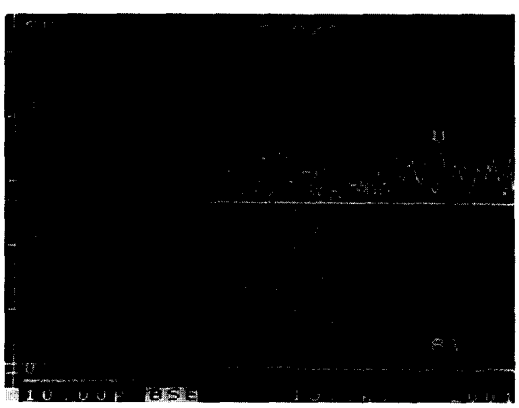

Fig. 4. Electron-probe micro-analysis traces on U–10 wt% Mo fuel sample annealed at 400°C for 2000 h.

Fig. 5. Scanning electron image on U–10 wt% Mo fuel sample annealed at 400°C for 2000 h.

particles. It is regarded as the evidence of some dimensional changes (3.7%) after the 1000 h anneal in the U–10 wt% Mo/aluminum dispersions as shown Table 1. Metallographic examinations of the Al–24 vol.% U–10 wt% Mo sample show that almost all particles exhibit regular and round interface, and few cracks at the peripheral boundary of the U–Mo particle resulting from the absence of reaction between the U–Mo particle and aluminum matrix. On the other hand, scan electron image and EPMA traces on this U–10 wt% Mo sample annealed for 2000 h illustrate that the SEM image of U–10 wt% Mo powder still reveals some Mo segregation or cored microstructure, and some separated phases around the grain boundary (Fig. 5) [2]. Micrographs of the U–10 wt% Mo fuel sample annealed for 2000 h show that the fine cellular structure, less than 5 μm in size, still remains without great coarsening of uranium grains, despite very long annealing. It is thought that these results originated from the supersaturation of Mo in the metastable γ-U solid solution of U–10 wt% Mo alloy. Large content of substitutional Mo atoms with low diffusivity causes difficulty in the migration of U atoms and inhibits the greater decomposition and coarsening of γ-U (Fig. 5). Hence, the microstructure and the phase of the annealed U–10 wt% Mo sample have changed a little from its as-solidified cored structure, despite long heat treatment at 400°C. It is supposed that molybdenum atoms supersaturated in the grain boundary inhibit the diffusion of aluminum atoms which proceeds along the grain boundary of the U–10 wt% Mo particle. The annealed U–10 wt% Mo specimen has a longer incubation time for the volume change, compared with the annealed U–2 wt% Mo sample [12,13]. Hence, it is thought that the diffusion-controlled swelling resulting from Al penetration can be greatly retarded by heavy supersaturation with Mo atoms in the γ-U solid solution of the U–10 wt% Mo particle.

References

[1] J.L. Snelgrove et al., Proc. 19th Int. Meeting on Reduced Enrichment for Research and Test Reactors, Seoul, South Korea, 1996.
[2] K.H. Kim et al., Proc. 19th Int. Meeting on Reduced Enrichment for Research and Test Reactors, Seoul, South Korea, 1996.
[3] M.A. Feraday, M.T. Foo, R.D. Davidson, J.E. Wineger, Nucl. Technol. 58 (1982) 233.
[4] Y. Adda, M. Beyeler, A.A. Kirianenko, B. Pernot, Mem. Sci. Rev. Metall. 57 (1960) 423.
[5] J.H. Buddery, M.E. Clark, R.J. Pearce, J.J. Stebbs, J. Nucl. Mater. 13 (1964) 169.
[6] D. Subramanyam, M.R. Notis, J.I. Goldstein, Metall. Trans. 16A (1985) 589.
[7] R.J. Pearce, R.D. Giles, L.E. Tavender, J. Nucl. Mater. 24 (1967) 129.
[8] R.D. Bland, Electrochem. Tech. 6 (1968) 272.
[9] A.D. LeClaire, I.J. Bear, J. Nucl. Energy 2 (1956) 229.
[10] L.S. Castleman, J. Nucl. Mater. 3 (1961) 1.
[11] N.E. Daniel, E.L. Foster, R.F. Dickerson, Battelle Memorial Institute Report No. BMI-1389, 1959.
[12] R.C. Birther, C.W. Allen, L.E. Rehn, G.L. Hofman, J. Nucl. Mater. 152 (1988) 73.
[13] J.P. Durand, P. Laudamy, K. Richer, Proc. 18th Int. Meeting on Reduced Enrichment for Research and Test Reactors, Williamsburg, USA, 1994.