PHASE STABILITY OF HIGH-DENSITY Al - U-10wt.%Mo FUEL WITH CENTRIFUGALLY ATOMIZED POWDER AT ELEVATED TEMPERATURE

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ABSTRACT

The phase stability of atomized U-10wt.%Mo powder and the thermal compatibility of dispersed fuel meats at elevated temperature were characterized. Atomized U-10wt.%Mo powder generally had a good γ-U phase stability during annealing at elevated temperatures. It is thought that the stability was related to supersaturation of substitutional molybdenum atoms in the metastable γ -U solid solution of atomized U-10wt.%Mo powder. The penetration mechanisms of the atomized U-10wt.%Mo particles at 500°C were classified as (a) through phase interface, leaving a kernel-like unreacted island, (b) through cell boundaries, showing several unreacted islands and more reacted regions. It is supposed that such islands originated from the decomposition of γ -U solid solution. The intermediate layer thickness and volume increase of the dispersion U-10wt.%Mo fuel specimens were almost the same as those of U_3Si_2 fuel, independent of annealing time.

1. Introduction

The conversion from high enriched uranium (HEU) to low enriched uranium (LEU) for use in research reactor fuel requires a large increase in the fissile uranium per unit volume to compensate for the reduction in enrichment. U_3Si_2 is found to possess very stable irradiation behavior, but the difficulties in rolling fuel meat do not allow loading higher than 6 g-U cm^{-3} [1-5]. Hence, in the renewed fuel development for research and test reactors, attention has shifted to high density uranium alloys. Early irradiation experiments with uranium alloys showed the promise of acceptable irradiation behavior if these alloys could be maintained in their cubic γ-U crystal structure [6]. It has been reported that high density atomized U-Mo powder prepared by rapid solidification has the metastable isotropic γ-U phase supersaturated with substitutional molybdenum, especially in U-10wt.%Mo alloy [7]. If the centrifugally atomized U-Mo powder can retain this gamma phase during fuel element fabrication and irradiation, and if it is compatible with aluminum matrix, the uranium alloy would be a prime candidate for dispersion fuel for research reactors.

In this study U-10wt.%Mo alloy powder which has high density above 15 g-U cm^{-3} was prepared by rotating-disk centrifugal atomization. The fuel rods were made by extruding the blended powders with atomized U-Mo and aluminum. The γ-U phase stability of atomized U-10wt.%Mo powder and the thermal compatibility of atomized U-10wt.%Mo-Al fuel meats during annealing at elevated temperatures have been examined.

2. Experimental Procedure

Depleted uranium lumps with 99.9 % purity and molybdenum buttons with 99.7 % purity were induction-melted in a graphite crucible coated with a high-temperature-resistant ceramic. The molten U-10wt.%Mo alloy was fed through an orifice onto a rotating graphite disk in an argon atmosphere. In order to obtain the desired size distribution and shape, the atomization parameters were adjusted [8]. The atomized powder was collected in a container at the bottom of the funnel-shaped chamber. Dispersion fuel rods were prepared by extruding the blended powders of U-10wt.%Mo and aluminum at a working temperature of 400°C. Atomized powder and compatibility specimen containing 45 vol.% of U-Mo particles were annealed for an incremental times at 400°C and 500°C. After each annealing interval, the dimensional changes of the specimens were measured.

The samples were polished to 0.3 μm diamond paste, and examined by a scanning electron microscope (SEM) to characterize the microstructure of the atomized particles and the fuel meats. 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 of the samples.

3. Experimental Results

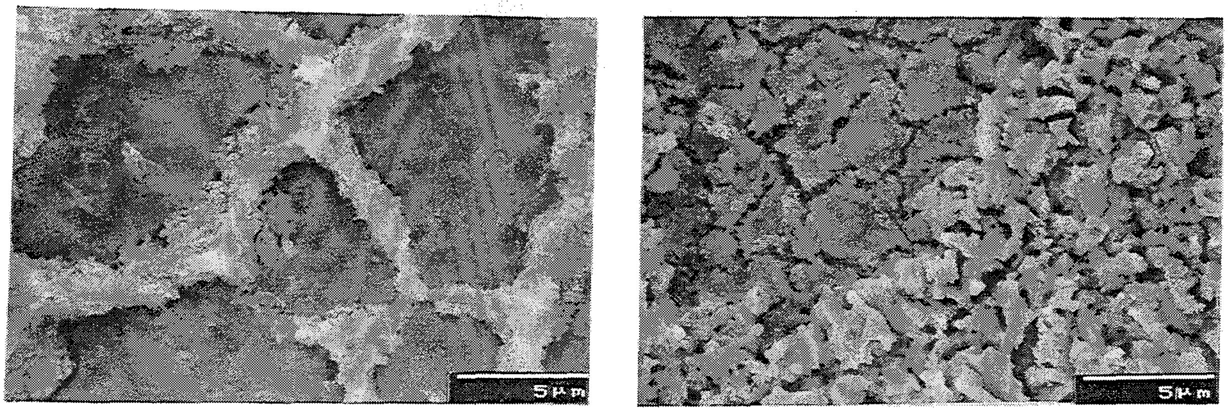

Fig. 1. Back-scattered scanning electron images of the annealed fuel samples after annealing; (a) 400°C, (b) 500°C.

The γ-U phase of U-10wt.%Mo powder annealed at 400°C untill 100 hours remained as it were [7]. However, the micrograph of the U-10wt.%Mo powder after 350 hours showed fine γ-U cell structure with decomposed α-U and γ'-U_2Mo phases around the cell boundary (Fig. 1-(a)). The X-ray diffraction pattern of the atomized U-10wt.%Mo powder showed that the major phase of U-Mo powder after 350 hours was γ-U phase. Some γ-U phases were decomposed as coarse α-U and γ'-U_2Mo phase after annealing. The micrograph of U-10wt.%Mo powder annealed at 500°C after 24 hours showed fine γ-U cell structure with fibric structure of decomposed phases. Most γ-U cells of atomized U-10wt.%Mo powder after annealing for 500 hours were already decomposed as coarse α-U and γ'-U_2Mo phase (Fig. 1-(b)). The X-ray diffraction pattern of the atomized U-10wt.%Mo powder showed that half of the γ-U phase of U-10wt.%Mo powder after 100 hours remained as it were; however the greater part of the γ-U phases of U-10wt.%Mo powder after 500 hours was decomposed as the α-U phase and the γ'-U_2Mo phase, including some γ-U phase. Fig. 2 shows the dimensional changes of the Al - 45vol.% U-10wt.%Mo fuel samples at 500°C for various times. Half of the swelling in the fuel samples at 500°C occurred within 10 hours, so the swelling appeared to reach a plateau gradually with annealing time. The intermediate phase layer formed around the interface between U-10wt.%Mo fuel and aluminum matrix increased in proportion to square root with annealing time. The volume change of the dispersion fuel specimens was less than that of Al - U_3Si_2 dispersion fuel specimens for the same time, independent of annealing time. Even after annealing for 500 hours the Al - U-10wt.%Mo dispersion fuel samples did not show a large volume increase, up to 34%.

Back-scattered scanning electron images of the fuel samples after annealing at 500°C for 200 hours are

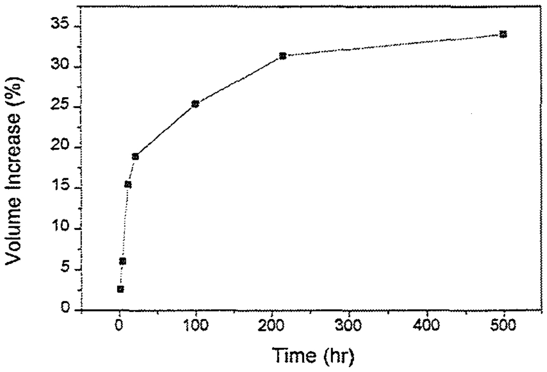

Fig. 2. The dimensional increase of the Al - 45vol.% U-10wt.%Mo fuel samples at 500°C for various times.

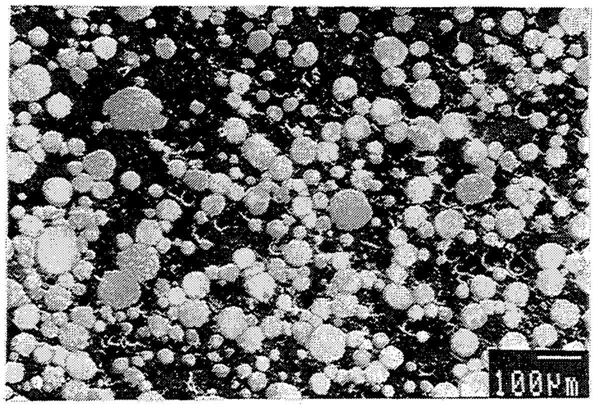

Fig. 3. Back-scattered scanning electron images of the fuel samples after annealing at 500°C for 200 hours.

shown in Fig. 3. The region of the fuel samples imaged in Fig. 2 may be divided into two general areas: (a) islands with white, (b) dark-grey regions. Metallographic examinations of the samples showed that most particles exhibited an irregular interface and a rim of an intermediate phase in the circumferential region. Fine particles had several unreacted islands (white), and reacted intermetallic compounds (dark-grey) as a matrix in the U-10wt.%Mo particles. The fuel meats showed two aspects of the penetration with aluminum atoms. The particles were composed of a considerable amount of reacted areas around the circumferential part and generally had a "kernel-like" structure with an unreacted island, and several unreacted islands. The penetration degree of most atomized particles with a kernel-like structure did not reach a half of particle cross-section despite of long annealing at elevated temperature. The area scan analyses of the U-10wt.%Mo samples annealed for 200 hours, by using energy dispersive X-ray spectroscopy (EDX), indicated that white regions were composed of 81 at.%U, 17 at.%Mo and 2 at.% Al, whereas dark-grey regions consisted of 20at.%U, 4 at.%Mo and 75 at.%Al, that is, $(U,Mo)Al_3$. Uranium-aluminide with a small amount molybdenum, mainly UAl_3 was formed in the U-Mo particles due to the diffusion of Al atoms. Electron probe micro-analysis (EPMA) traces of the fuel sample also confirmed that there was some formation of intermediate phase regions between U-Mo particle and Al matrix. The atomized U-10wt.%Mo particle had more unreacted regions, compared with the atomized U_3Si_2 particle. It led to a volume change of 31% which was less by 8% than that of the atomized U_3Si_2 fuel samples (Fig. 1) [9].

4. Discussion

By rapid solidification in terms of centrifugal atomization from the melt, the centrifugally atomized powder retained a gamma phase as metastable state. However, the γ-U phase of U-10wt.%Mo alloy annealed below the eutectoid temperature (560°C) had a tendency to be decomposed as the thermodynamically stable lamellar structure including α-U and γ'-U_2Mo phases [10]. A scanning electron micrograph carried out on the U-10wt.%Mo powder annealed at 400℃ untill 100 hours, illustrated that U-10wt.%Mo powder revealed a fine grain structure below 3 ㎛ in size with microsegregation of molybdenum atoms [7]. These results were resulted from supersaturation of Mo in the metastable γ -U solid solution of U-10wt.%Mo alloy. Large content of substitutional Mo atoms with low diffusivity caused the migration of U atoms difficulty, and inhibited the decomposition and the coarsening of γ -U. This confirmed that the γ - U phase of atomized U-10wt.%Mo powder could be retained at 400℃ for an extended time, presumably because the diffusion-controlled transformation is retarded at increased Mo content. Fine laminae were nucleated primarily at γ-U cell boundary at 400°C (Fig. 1). γ-U in the cells is decomposed as α-U and γ-U with high Mo content than γ'-U_2Mo phase as would be expected for normal eutectoid reaction [11-12]. Then transformation occurred continuously involving the formation of ordered intermediate phase (γ'). However, the decomposition of γ-U at 500°C took place primarily by the cellular mechanism [13].

As the aluminum reacts with the fuel, the fuel's volume increases due to the difference between densities of the original particle and reaction product, and due to the pores produced by the Kirkendall effect [14]. The volume of the U-10wt.%Mo dispersion fuel sample annealed at 400℃, remained the same even after 2000 hours anneal, without formation of intermediate phase layer [15]. However, the swelling of this U-10wt.%Mo fuel sample after annealing at 500℃ for 200 hours showed a larger amount up to 31%, with formation of (U,Mo)Al_3 of 8 μm in thickness. The increase in annealing temperature accelerated the penetration rate of aluminum atoms in the fuel particles. The U-10wt.%Mo dispersion fuel samples did not show a smaller volume increase, compared with that of U_3Si_2 dispersion fuel specimens. The possible reason can be supposed as follows. It is thought that such results originated from larger atomic radius and lower diffusivity of supersaturated substitutional molybdenum atoms in the metastable γ -U solid solution, relative to those of silicon atoms. In addition, large content of Mo atoms caused the migration of U atoms difficulty and inhibited the great decomposition and coarsening of γ -U. Molybdenum atoms supersaturated in the grain boundary inhibited the diffusion of aluminum atoms which proceeds along the grain boundary into the U-10wt.%Mo particle. In the initial stage of annealing at 500℃, atomized U-10wt.%Mo particles showed a thin kernel-like intermediate phase layer around the perimeter, penetrated through a phase interface. However, after the middle stage of annealing at 500℃, atomized U-10wt.%Mo particles sometimes had several unreacted islands, showing more reacted regions. It is supposed that such several islands were related to the decomposition of γ -U solid solution. The phase decomposition led to lamellar structure of α-U and γ'-U_2Mo phases, providing large numbers of nucleation sites and growth routes due to greater interface area.

5. Conclusions

The phase stability of atomized U-10wt.%Mo powder and the thermal compatibility of dispersed fuel meats at elevated temperatures were characterized.

1) After annealing at 400°C for 350 hours atomized U-10wt.%Mo powder showed fine γ-U cell structure with decomposed α-U and γ'-U_2Mo phases only around the cell boundary. However, the greater part of γ-U phases of atomized U-10wt.%Mo powder annealed at 500°C for 500 hours was already decomposed as α-U and γ'-U_2Mo phases, with some retained γ-U phases. It is thought that the stability was related to supersaturation of substitutional molybdenum atoms in the metastable γ -U solid solution of atomized U-10wt.%Mo powder.
2) The intermediate phase, formed by interdiffusion between atomized U-Mo particle and aluminum matrix after annealing at 500°C, was (U,Mo)Al_3.
3) In the initial stage of an annealing at 500℃, atomized U-10wt.%Mo particles showed a thin kernel-like (U,Mo)Al_3 layer around the perimeter, penetrated through a phase interface. However, after the middle stage of annealing, atomized U-10wt.%Mo particles sometimes had several unreacted islands, showing more reacted regions. It is supposed that such several islands originated from the decomposition of γ - U solid solution.
4) The intermediate layer thickness and volume increase of the dispersion U-10wt.%Mo fuel specimens were almost the same as those of U_3Si_2 fuel, independent of annealing time. Even after annealing for 500 hours the Al - U-10wt.%Mo dispersion fuel samples did not show a large volume increase, up to 34%.

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