

Effect of ternary alloying element addition on γ -U phase stability of U-14at.%Mo alloy at elevated temperature

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ABSTRACT

The phase stability of binary U-14at.%Mo, ternary U-10at.%Mo-4at.%X (X: V, Cr, Mn, Fe, Ni, Ru) and U-12at.%Mo-2at.%X (X: Ta, W) alloys at an elevated temperature has been characterized. The γ -U phase stability of the U-10at.%Mo-4at.%X (X: Ni, Fe) alloys of the ternary uranium alloys is similar to or better than that of the binary U-14at.%Mo alloy. The possible reasons for the good phase stability of the ternary U-10at.%Mo-4 at . % X (: Ni , Fe) alloys are related to the small atomic radii of Ni and Fe atoms, and the large alloying enthalpy.

1. Introduction

The conversion from high enriched uranium (HEU) to low enriched uranium (LEU) for use in research reactor fuel requires a large increase of uranium per unit volume to compensate for the reduction in enrichment, and further necessitates the use of higher

uranium density fuels. The relatively high density compound U_3Si_2 with a uranium density of 11.6 g-U cm^{-3} was found to possess a very stable irradiation behavior; however, the fabricability limit, not achieving a fuel volume loading greater than 55% in a commercially viable process, does not allow fuel element loadings higher than 6 g-U cm^{-3} [1-5]. Therefore, fuel dispersants with very-high uranium density, $> 15 \text{ g-U cm}^{-3}$, must be used. Uranium alloys including small amounts of alloying elements can be considered as fuel dispersants. Although pure uranium is a notoriously poor performer under irradiation, a series of alloys which maintain the metastable γ -phase have shown a good irradiation performance in bulk form under fast reactor conditions. U-Mo system could be a promising candidate [6].

Hence, in the renewed fuel development for research and test reactors, attention has shifted to very-high-density uranium alloys, as several high performance reactors still require the U-loadings of upto $8\sim 9 \text{ g-U cm}^{-3}$. 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 [7]. It has recently been reported that U-22at.%Mo alloy, prepared by centrifugal atomization, has the metastable isotropic γ -U phase supersaturated with substitutional molybdenum and the good gamma phase stability after isothermal annealing at elevated temperatures [8]. In addition, the U-22at.%Mo powder dispersed in aluminum did not show significant dimensional changes after annealing at elevated temperatures, and interdiffusion between U-22at.%Mo and aluminum was found to be minimal [9]. In this study, the eight ternary uranium alloys have been fabricated to examine the effect of minor ternary element addition of transition elements on the gamma phase stability of binary U-14at.%Mo alloy at elevated temperature. The ternary alloying elements (V, Cr, Mn, Fe, Ni, Ru, Ta and W) have been substituted for the Mo element with total alloy contents of 14 atomic percent. The γ -U phase metastability of binary U-Mo alloy and U-Mo-X (X: minor ternary element) alloys has been examined after isothermal annealing at 500°C .

2. Experimental procedure

U-14at.%Mo, U-10at.%Mo-4at.%X(X: V, Cr, Mn, Fe, Ni, Ru) and U-12at.%Mo-2at.%X(X: Ta, W) alloys were induction-melted in Y₂O₃ st. ZrO₂ crucibles at 1700°C, using depleted uranium lumps with 99.9 % purity and alloying elements with 99.9% purity. Most of the U-14at.%Mo alloy and ternary U-Mo-X alloys were cooled in a vacuum induction-melting furnace.

The frozen rods were heat-treated in a vacuum quartz tube at 900 °C for 100 hours to ensure chemical homogeneity, followed by water quenching. The uranium alloy specimens were annealed for incremental times at 500°C. The annealed samples were polished using 0.3 μm diamond paste, and examined by scanning electron microscope (SEM) to characterize the microstructure of the uranium alloys. X-ray diffraction analysis (XRD) using Cu K_α radiation was used to determine the phases of the alloy samples.

3. Experimental results

The X-ray diffraction patterns of the U-14at.%Mo, U-10at.%Mo-4at.%X (X: V, Cr, Mn, Fe, Ni, Ru) and U-12at.%Mo-2at.%X (X: Ta, W) alloys quenched after isothermal annealing at 900°C for 100 hours (Fig. 1) showed that most peaks of uranium alloys were found to be the isotopic-metastable γ -U (bcc) phase, irrespective of the alloy sorts. X-ray diffraction patterns of the ternary U-10at.%Mo-4at.%X (X: V, Ru) and the ternary U-12at.%Mo-2at.%Ta alloys after isothermal annealing at 500°C for 0.5 hour showed that a considerable amount of γ -U phase was already decomposed into α -U phase and U₂Mo phase (Fig. 2). However, X-ray diffraction patterns of the binary U-14at.%Mo, the ternary U-10at.%Mo-4at.%X (X: Cr, Ru), and the ternary U-12at.%Mo-2at.%W alloy after isothermal annealing at 500°C for 4 hours showed that some γ -U phase was decomposed into α -U phase and U₂Mo phase (Fig. 3). However, X-ray diffraction patterns of the ternary U-10at.%Mo-4at.%X (X: Ni, Fe) alloys after isothermal annealing at 500°C for 4 hours showed that a slight amount of γ -U phase was decomposed into α -U phase, without the formation of U₂Mo phase (Fig. 4). The major

phases of the ternary U-10at.%Mo-4at.%X (X: Ni, Fe) alloys was still γ -U phase. After isothermal annealing at 500°C for 7 hours, X-ray diffraction patterns of the ternary U-10at.%Mo-4at.%X (X: Ni, Fe) alloys showed that some γ -U phase was decomposed into α -U phase and U₂Mo phase.

Scanning electron micrograph of the binary U-14at.%Mo alloy after isothermal annealing at 500°C for 4 hours showed that many fine precipitates, presumably U₂Mo, were already formed in places, irrespective of grain and grain boundary (Fig. 5). Scanning electron micrographs of the ternary U-10at.%Mo-4at.%X (X: Cr, Ru) and ternary U-12at.%Mo-2at.%W alloy after isothermal annealing at 500°C for 4 hours showed that γ -U phase was already transformed into a finely decomposed structure having a fabric morphology (Fig. 6). Microstructures of U-10at.%Mo-4at.%X (X: Ni, Fe) alloys were next to the granules with some decomposed precipitates around the grain boundary (Fig. 7).

4. Discussion

By quenching from γ -U phase region at 900°C, the U-14at.%Mo, U-10at.%Mo-4at.%X (X: V, Cr, Mn, Fe, Ni, Ru) and U-12at.%Mo-2at.%X (X: Ta, W) alloys retain an isotropic gamma phase as a metastable state. However, the γ -U phase of the uranium alloys annealed below the eutectoid temperature (560°C) has a tendency to be decomposed as the thermodynamically stable lamellar structure including γ -U phase and U₂Mo phase [6]. Hence, a considerable amount of γ -U phase of the ternary U-10at.%Mo-4at.%X (X: V, Ru, Mn) and U-12at.%Mo-2at.%Ta alloys was easily decomposed into α -U phase and U₂Mo phase after isothermal annealing for 0.5 hour. In addition, some γ -U phase of the binary U-14at.%Mo, the ternary U-10at.%Mo-4at.%X (X: Cr, Ru) and U-12at.%Mo-2at.%W alloys was decomposed into α -U phase and U₂Mo phase after isothermal annealing at 500 °C for 4 hours.

However, after isothermal annealing for 4 hours, a slight amount of γ -U phase of the ternary U-10at.%Mo-4at.%X (X: Ni, Fe) alloys was decomposed only into α -U phase, without the formation of U_2Mo . The primary decomposition of the γ -U phase of the ternary U-10at.%Mo-4at.%X (X: Ni, Fe) alloys after isothermal annealing at 500°C for 4 hours is initiated by the cellular reaction at the grain boundary by the cellular mechanism [10]. Below the eutectoid temperature, the cells consist initially of α -U and enriched γ -U rather than α -U and U_2Mo as would be expected for a normal eutectoid reaction [11, 12]. After 7 hours at 500 °C, the enriched γ -U phase in the lamellar structure gradually orders to form U_2Mo . The transformation occurs continuously involving the formation of ordered intermediate phase (U_2Mo) in Mo-enriched γ -U zone. Similar cellular structures also are produced by discontinuous precipitation in many age-hardening systems [13].

The possible reasons why the ternary U-10at.%Mo-4at.%X (X: Ni, Fe) alloys have a good γ -U metastability are supposed as follows. First, nickel and iron atoms have smaller atomic radii than uranium atom. The minor addition of Ni or Fe element in the U-Mo alloy causes the contraction of the metastable γ -U phase with body-centered-cubic lattice and retards the migration of uranium atoms. Consequently, the metastability of the γ -U phase in the α -U + U_2Mo phase field arises primarily from the contraction of the cubic lattice through the substitution of the small Ni or Fe atom, inhibits the decomposition of γ -U phase during isothermal annealing [13]. Second, R. Meidema [14] showed that Ni and Fe elements can contribute to an increase in chemical potential and an alloying enthalpy during uranium alloy formation. It leads to a relatively higher gamma phase stability and retards the decomposition of γ -U phase.

5. Conclusions

The phase stability of the binary U-14at.%Mo, the ternary U-10at.%Mo-4at.%X (X: V, Cr, Mn, Fe, Ni, Ru) and the ternary U-12at.%Mo-2at.%X (X: Ta, W) alloys at an elevated temperature was characterized.

- 1) The ternary U-10at.%Mo-4at.%X (X: V, Cr, Ru) and the ternary U-12at.%Mo-2at.%X (X: Ta, W) alloys do not have better γ -U phase stability at an elevated temperature than the binary U-14at.%Mo alloy.
- 2) The γ -U phase stability of the ternary U-10at.%Mo-4at.%X(X: Ni, Fe) alloys at elevated temperature is similar to or better than that of the binary U-14at.%Mo alloy.
- 3) It seems that the possible reason for the good phase stability of the ternary U-10at.%Mo-4at.%X(X: Ni, Fe) alloys are related to the small atomic radii of Fe and Mo atoms and, the large alloying enthalpy of the ternary alloys.

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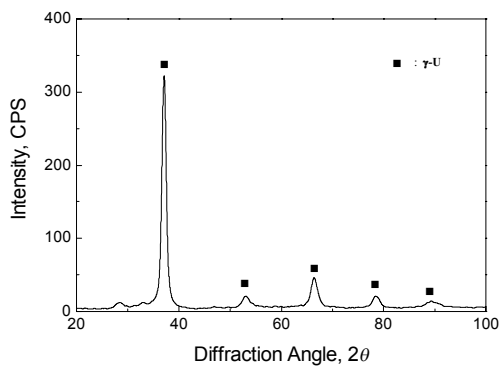


Fig. 1. The typical X-ray diffraction pattern of the U-14at.%Mo and the ternary U-Mo-X alloys quenched after annealing at 900°C for 100 hrs.

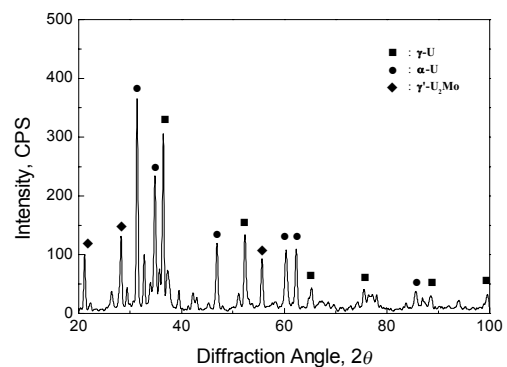


Fig. 2. The X-ray diffraction pattern of the U-10 at.%Mo-4at.%V alloy after annealing at 500°C for 0.5 hrs.

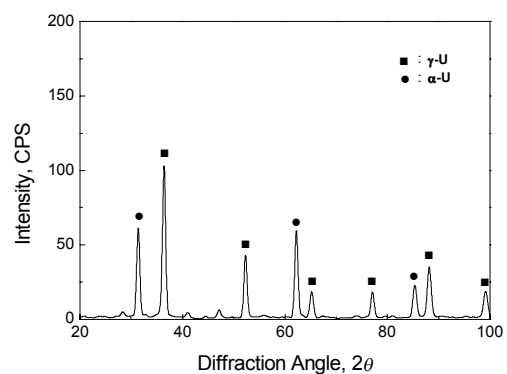
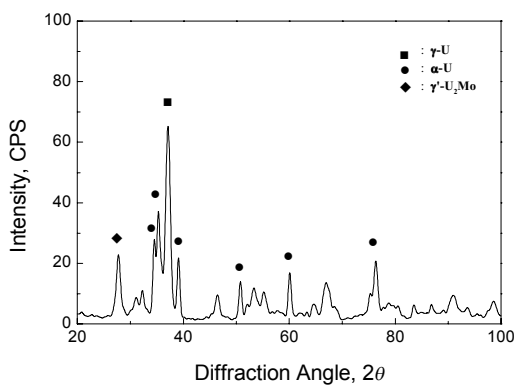


Fig. 3. The X-ray diffraction pattern of the U-14at.%Mo alloy quenched after annealing at 500°C for 4 hrs.

Fig. 4. The X-ray diffraction pattern of the U-10 at.%Mo-4at.%Ni alloy after annealing at 500°C for 4 hrs.

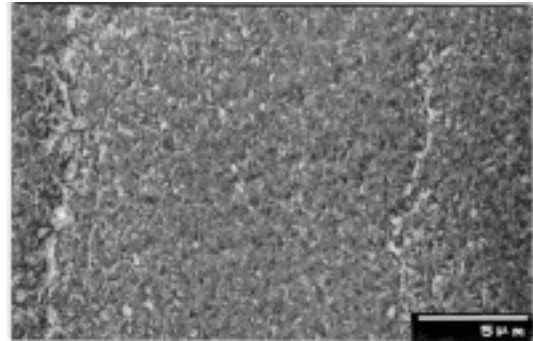
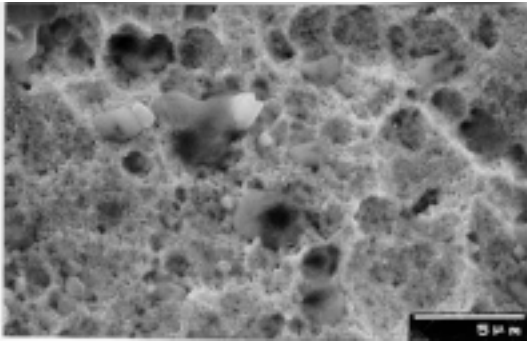


Fig. 5. The micrograph of the U-14at.%Mo alloy quenched after annealing at 500°C for 4 hrs.

Fig. 6. The micrograph of the U-10at.%Mo-4at.%Ru alloy after annealing at 500°C for 4 hrs.

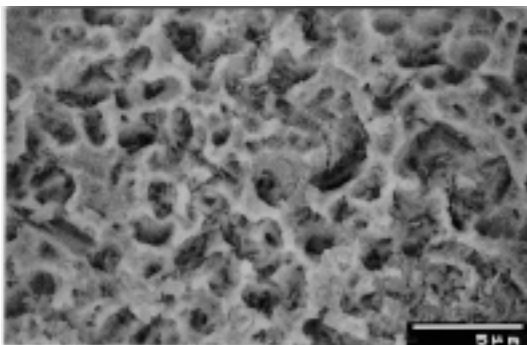


Fig. 7. The micrograph of the U-10at.%Mo-4at.%Fe alloy quenched after annealing at 500°C for 4 hrs.