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Letter to the Editors

Neutron diffraction study of U–5.4 wt% Mo alloy

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Abstract

The structure of U–5.4 wt% Mo alloy prepared by the centrifugal atomization method and the decomposition of the alloy at elevated temperature were studied. The single uniform γ-phase was obtained after annealing the synthesized alloy at 700°C for 48 h. The homogenized alloy was annealed at 400°C and 500°C to search for an ordered phase and study the decomposition process. No ordered phase in U–5.4 wt% Mo alloy after annealing was observed. With the result from the Rietveld refinement of the neutron diffraction patterns it was concluded that the b parameter of the α-phase is contracted like metastable α'-phase and phase boundary of the α-phase region at 500°C lies near 2.6 at.% Mo. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

The development of high density U-alloys with an increased concentration of U is one of the key problems for developing high neutron flux research reactors with low enrichment uranium fuel. The U–Mo alloy system is one of the prospective candidates because a solid solution of Mo in γ-U has acceptable irradiation properties for reactor fuel [1]. According to the phase diagram of the U–Mo system (Fig. 1) [2], below 560°C, the γ-phase is metastable, while the equilibrium state corresponds to a mixture of α-U and γ'-phases (U_2Mo).

Therefore, the prospect of using a U–Mo alloy as reactor fuel is closely connected with the possibility of retaining a metastable γ-phase state in alloys at temperatures below 560°C during fuel element fabrication and irradiation. Kim et al. [3] showed that a U–10 wt% Mo alloy has rather good thermal stability and retains the γ-U phase after annealing at 400°C for 100 h.

The formation of a transient ordered state in phase separating alloys when both ordering and decomposition processes are going on simultaneously can considerably retard the process of decomposition [4,5]. From this point of view, the U–Mo alloys with a composition near U–5.4 wt% Mo (12.5 at.%) which corresponds to the stoichiometry U_7Mo or $U_{22}Mo_3$ are interesting. The superlattice U_7Mo is one of those which are predicted by the ordering theory [6] for bcc alloys in a disordered state. In addition, an ordered structure with tetragonal cell (γ^0-phase) was observed experimentally [7–9] in alloys containing 11.39–12.73 at.% Mo. The stoichiometry $U_{22}Mo_3$ was assigned to the ordered γ^0-phase in [7,8], though the stoichiometry corresponding to the superlattice was U_3Mo.

The phase boundary between α-phase and γ'-phase regions below 560°C which determines the terminal composition of the α- and γ'-phases forming as a result of γ-phase decomposition was not studied specially. Dwight [2] positioned them near 0.5 at.% Mo for the α-phase and 31 at.% for the γ'-phase (see Fig. 1).

The aim of this work was to find out whether the metastable superlattice is formed or not in U–5.4 wt% Mo alloy during decomposition at temperatures below 560°C. Another aim was to determine the phase boundary of the α- and γ'-phase regions using neutron diffraction. Neutron diffraction was chosen because the high X-ray absorption of uranium atoms causes intense localized heating. In addition, there are difficulties in preparing a proper powder sample for X-ray diffraction

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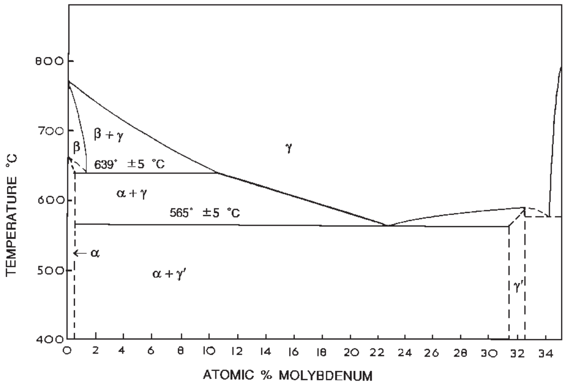

Fig. 1. U–Mo phase diagram.

because in the case of a highly absorbing material the diffraction pattern is greatly affected by the roughness of the sample surface.

2. Experiment

A U–5.4 wt% Mo (12.5 at.%) alloy was prepared by the centrifugal atomization method described in [3]. For heat treatment, every sample was sealed in an evacuated quartz ampoule and air-cooling was used after annealing. The powder neutron diffraction patterns from 5° to 155° were measured at room temperature using the 32-detector high-resolution powder diffractometer (HRPD) at KAERI. Monochromatic neutrons with a wavelength of 0.18339 nm were obtained from a Ge(3 3 1) monochromator with a 90° take-off angle. The sample was contained in a cylindrical vanadium can, 8 mm in diameter and 40 mm in height.

3. Results

The neutron diffraction study of the as-synthesized alloy showed that it is not a single phase. Along with diffraction peaks corresponding to the γ-phase, very weak diffraction peaks corresponding to the uranium oxides UO and UO_2 were observed in the neutron diffraction pattern. Thus, the phase composition of the sample was the same as that of U–10 wt% Mo alloy prepared by the centrifugal atomization method [10]. Broadening of the diffraction peaks corresponding to the γ-phase was observed. The peak broadening can be caused by reasons such as particle size, strain, non-uniformity in the composition, etc. The grains in particles of the U–Mo alloy prepared by the centrifugal atomization method are too large (~2 μm) [3] to cause the peak broadening. Strain should exist in as-synthesized alloy because of the extremely rapid cooling by the centrifugal atomization method. However, we assume that the broadening is mainly caused by the non-uniformity in the composition, because it was distinctly observed in U–10 wt% Mo alloy [10]. The Rietveld refinement under the assumption of two γ-phases with different composition like U–10 wt% Mo [10] did not give good agreement. Therefore, we assume that the sample contained mixture of γ-phases with different composition.

In order to obtain a single γ-phase state, the as-synthesized sample was annealed at 700°C for different times and then cooled in air. The single γ-phase state was obtained only after annealing at 700°C for 48 h. As a result of annealing, part of the UO phase transformed to UO_2. The Rietveld refinement of a structural model consisting of the single phase γ-U solid solution (96.74%), UO (2.20%) and UO_2 (1.06%) converged to $\chi^2 = 3.7$. The lattice parameter of the γ-phase, $a = 0.3445$ nm, obtained from the Rietveld refinement, corresponds to 11.44 at.% Mo according to the Dwight equation [2]. No superlattice reflections were observed in the neutron diffraction pattern. After homogenizing treatment at 700°C for 48 h the samples were annealed at 400°C and 500°C for different times.

After annealing at 400°C for 10 h the γ-phase partially decomposed so that α (43.59%) and U_2Mo (32.88%) phases appeared in addition to γ (22.82%) and UO_2 (0.71%) phases. The UO phase completely transformed to the UO_2 phase. The process of decomposition had not been completed even after annealing at 400°C for 500 h: about 10.8% of γ-phase remained in the sample. No additional superlattice reflections were observed in neutron diffraction patterns after annealing at 400°C.

After annealing at 500°C for 500 h (Fig. 2) the process of decomposition was practically completed: about 2.48 wt% of γ-phase remained in the sample (Table 1).

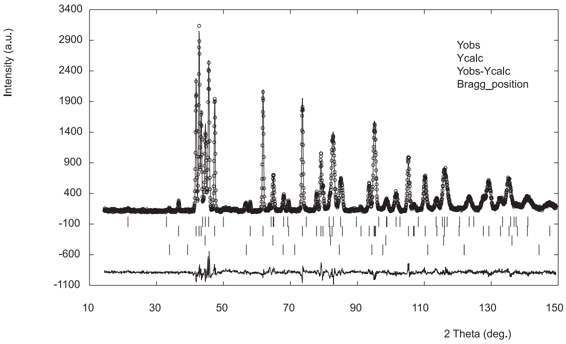

Fig. 2. Neutron diffraction pattern of U–5.4 wt% Mo alloy after annealing at 500°C for 500 h.

Table 1
Results of Rietveld refinements of the annealed (500°C–500 h) sample. (UO_2 phase is not included.)

Phase	Space group	Lattice parameter (nm)	Wt. fraction (%)	R-Bragg
α	Cmcm	$a = 0.286138(10)$ $b = 0.584113(18)$ $c = 0.496541(17)$	67.57	4.17
U_2Mo	I4/mmm	$a = 0.341911(16)$ $c = 0.984239(72)$	29.33	6.09
γ	Im3m	$a = 0.342392(463)$	2.48	12.3

No additional superlattice reflections were observed in the neutron diffraction patterns of samples annealed at 500°C.

Rietveld refinement showed that the *b* lattice parameter of α-phase forming during decomposition is contracted relative to the $b = 0.58695$ nm for pure α-U [11]. Tangri et al. [7] showed that the U–Mo alloys containing up to 11 at.% Mo, when water-quenched from the γ-phase region, form a metastable α′-phase which they defined as 'distorted alpha' with a contracted *b* lattice parameter. Using the dependence of the *b* parameter on Mo content studied by Tangri et al. [7], the Mo content in α-phase forming during the decomposition was determined. 2.6 at.% Mo in α-phase after annealing at 500°C for 500 h (2.2 at.% Mo for 400°C–500 h) was obtained. Mo content (30.5 at.%) in the U_2Mo phase in an alloy decomposed after annealing at 500°C for 500 h was calculated using the quantitative phase composition determined by Rietveld refinement (Table 1). The value 30.5 at.% is in good agreement with the phase boundary of the U_2Mo phase region given by Dwight [2] (see Fig. 1).

4. Discussion and conclusion

Formation of a transient ordered phase during decomposition is caused by the difference in kinetics for process of ordering and decomposition at temperature below the critical temperature of ordering T_c [4,5]. Both ordering and decomposition decrease the free energy of the alloy but because the ordering process is usually much faster than decomposition, ordering instead of decomposition can decrease the free energy. Such a metastable ordered state can retard the process of decomposition because the energy barrier that must be overcome by atoms to form the nuclei of new phases, arising during decomposition, increases.

It was shown that the ordered γ^0-phase can be formed in alloys containing 11.39–12.73 at.% Mo after water quenching from the γ-phase region [7,8]. The phase was observed when the cooling rate was higher than the rate necessary to retain the γ-phase state and the degree of order increased with cooling rate. This was explained by retaining to low temperature, below the ordering temperature T_c for γ^0-phase, the equilibrium thermal vacancies existing at high temperature [8]. We did not observe any signs of ordering in the γ-phase after annealing of the U–5.4 wt% Mo alloy at 400°C and 500°C. At the same time the diffusion mobility at these temperatures was high enough to observe the decomposition of the γ-phase. It means that the ordering temperature, T_c, of possible superstructures lies below 400°C. It is also true for the γ^0-phase observed in [7,8]. Therefore formation of the ordered γ^0-phase will not retard the process of decomposition at 400°C.

The content of Mo in the α-phase given in Table 1 is higher than the 0.5% proposed by Dwight [2]. Our result shows that the contraction of the *b* lattice parameter is caused by molybdenum and takes place not only in metastable α′-phase but in stable α-phase as well.

Thus, we can make the conclusion that there is no formation of ordered phase in U–5.4 wt% Mo alloy after annealing at 400°C and 500°C. The formation of the ordered metastable γ^0-phase, observed after quenching with a high cooling rate, cannot retard the process of γ-phase decomposition. The phase boundary of the α-phase region at 500°C lies near 2.6 at.% Mo and *b* parameter of the α-phase is contracted like in the metastable α′-phase.

Acknowledgements

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