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Journal of Nuclear Materials 277 (2000) 274–279

journal of nuclear materials

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Neutron diffraction study of U–10 wt% Mo alloy

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Received 28 August 1998; accepted 12 July 1999

Abstract

The structural properties of a U–10 wt% Mo powder sample prepared by the centrifugal atomization method were investigated by the Rietveld total profile analysis method. The high resolution neutron powder diffractometer at the HANARO research reactor in Taejon, Korea, was used for a series of neutron diffraction pattern measurements for the study. The sample was synthesized by the centrifugal atomization method and was found to consist of two γ-U solid solution phases having identical bcc structures, but slightly different lattice dimensions, and accordingly different Mo content. When the sample was annealed for 10 h at 600°C, the two solid solution phases with different Mo contents merged into a uniform single phased γ-U solid solution. The diffraction pattern of the annealed sample showed two additional weak reflections, which could be indexed as a super lattice structure U_3Mo derived from the bcc cell by a /1 1 0/−1 1 0/0 0 1/ type lattice transformation. The disorder–order phase transition leading to the formation of ordered metastable phase U_3Mo should be of the first-order. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years, the development of low enrichment uranium fuel has been the center of attraction for many researchers. Scientists are interested in having a neutron source with higher thermal neutron flux density for higher quality experiments, which necessarily requires a small core size. At the same time, international nuclear policy demands low enrichment of U-235 in the uranium fuel element. To obtain a higher neutron flux density using a low enrichment fuel, it is necessary to develop a new uranium alloy which gives a higher uranium loading to compensate for the low enrichment. It has been well-known among reactor designers that a pure uranium metal is not suitable for reactor fuel because of poor irradiation behavior, specifically physical deformation caused by thermal cycles combined with neutron irradiation. It is also known that no stable uranium compound contains enough uranium to satisfy the necessary uranium loading. One of the prospective materials is γ-phase uranium alloy which contains small amount of another metal to stabilize the γ-U solid solution [1–3]. A series of studies conducted by Kim et al. [1,2] recently reported that U–10 wt% Mo alloys synthesized by the centrifugal atomization method crystallize in a cubic γ-U structure (bcc) and have physical properties acceptable for reactor fuels. Among many alloys which have a tendency to crystallize in the γ-phase structure at a high temperature, U–Mo and U–Zr solid solution alloys are the most suitable because they form the γ-phase structure over a wide range of solute concentrations.

Below 560°C, the equilibrium state of U–Mo alloys is a mixture of α-U and γ′-phase (U_2Mo), as shown in Fig. 1 [4]. However, by rapid cooling from the γ-phase, it can retain a metastable γ-state at room temperature.

It has been reported [5,6] that the U-alloys containing up to 11 at.% Mo, when water quenched from the γ-phase region, form metastable α′ and α″ phase structures which are slight variations of the orthorhombic lattice of α-U [5,6]. Alloys containing

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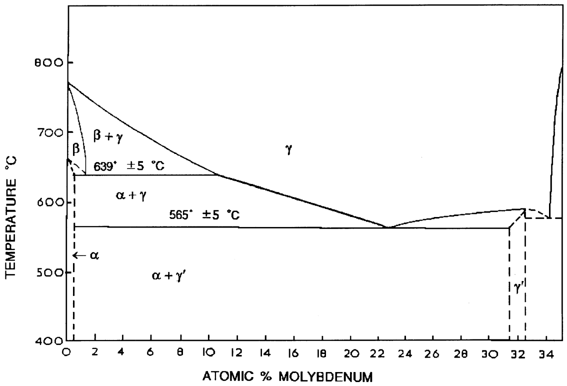

Fig. 1. Uranium–molybdenum phase diagram.

11.39–12.73 at.% Mo, when quenched, form γ^{o}-phase with an ordered tetragonal structure [6,7]. The tetragonal cell was transformed from the bcc cell by a / 2 0 0/0 2 0/0 0 1/ transformation so that $a_t \approx 2a_c$ and $c_t \approx a_c$, where a_c is the lattice parameter of the γ-phase bcc cell. An ordered structure proposed for metastable $U_{22}Mo_3$ (12.1 at.% Mo) [8] has the same tetragonal cell with a slightly different arrangement of Mo and U atoms.

It is important to make a comprehensive characterization of the crystal structure, microstructure and phase composition of the subject alloys. In this paper, we present a neutron diffraction study of a U–10 wt% Mo alloy prepared by the centrifugal atomization method. The method involves a rapid cooling, and hence the high temperature is retained as a metastable state at room temperature. The X-ray method may not be an appropriate tool for the study of metastable uranium alloys because of the high X-ray absorption of U atoms and the intense localized heating by X-ray radiation.

2. Experimental

2.1. Diffraction measurements of the atomized U–Mo alloy powder

The powder diffraction data were obtained from the 32-detector HRPD of KAERI, using 0.18339 nm neutrons from a Ge (3 3 1) monochromator, and 0.12193 nm from a Ge (3 3 5) monochromator, both with a 90° take-off angle. Collimations used were: $\alpha_1 = 6'$, $10'$ or $20'$ for the inpile collimator, $\alpha_2 = 30'$ for the collimator before sample, and $\alpha_3 = 10'$ for the collimator before detectors. The sample was contained in a cylindrical vanadium can, 8 mm in diameter and 40 mm high. The absorption correction was ignored because its value was negligibly small. The diffraction pattern was measured from 5° to 155°.

2.2. Synthesized U–10 wt% Mo sample

The earlier X-ray study by Kim et al. [1] reported that the alloy synthesized by the centrifugal atomization method has a single phased γ-U structure. Our neutron diffraction study indicated that the as synthesized sample contains a smaller amount of two more phases, in addition to the γ-U phase found by the previous X-ray study. The neutron diffraction pattern could be interpreted if the sample consisted of three γ-U solid solution phases with the same bcc cell and a slightly different unit cell size. We denote them as phases I, II, and III. The different lattice dimensions may be caused by different Mo concentrations, but it is impossible to determine the Mo content in each phase by Bragg diffraction methods alone. Using the information from an earlier study by Dwight [4], the lattice parameter of γ-phase in a U–Mo system is related to the Mo concentration by the equation a (nm) = 0.34808 – 0.000314 × (at.% Mo). Based on these assumptions, the atomic concentration of Mo atoms in the solid solutions were found to be 22 at.% for phase I and 17.5 at.% for phase II. Phase III had very weak diffraction intensities, with the unit cell size ($a = 0.34996$ nm) close to but a little bit larger than that of pure γ-uranium from the Dwight equation.

Over 99% of the composition had crystallized in either phase I or II. Since the two primary phases (I and II) were so similar in unit cell sizes, the peaks of the two phases could be distinguished mostly at higher scattering angles with higher instrumental resolution, but never resolved completely as shown in the pattern in Fig. 2.

The γ-U structure, which has the given fraction of Mo solute atoms uniformly occupying the two U sites of the bcc cell, was assigned to both phases. No Mo atoms were assigned to the phase III structure, based on the judgment from the unit cell size. The Rietveld refinement of the structure converged normally to the χ^2-value of 1.92. The weight fraction [9] of phases I and II from the Rietveld refinement gave a total of 9.3 wt% (20.3 at.%) Mo, which is slightly less than the 10 wt% Mo expected from the sample fabrication. According to the previous study [4–6], uranium alloys containing less than 10 at.% Mo cannot retain the γ-phase by quenching to room temperature. Therefore, the possibility of the formation of different uranium phases was considered. It was found that uranium oxide, UO, with the NaCl type crystal structure, $a = 0.49488(3)$ nm, also gives a slightly better refinement of phase III than γ-phase. This, along with the mentioned difference in lattice parameters for pure uranium, testifies that phase III could be uranium oxide, UO. The final phase composition and structural parameters are listed in Table 1.

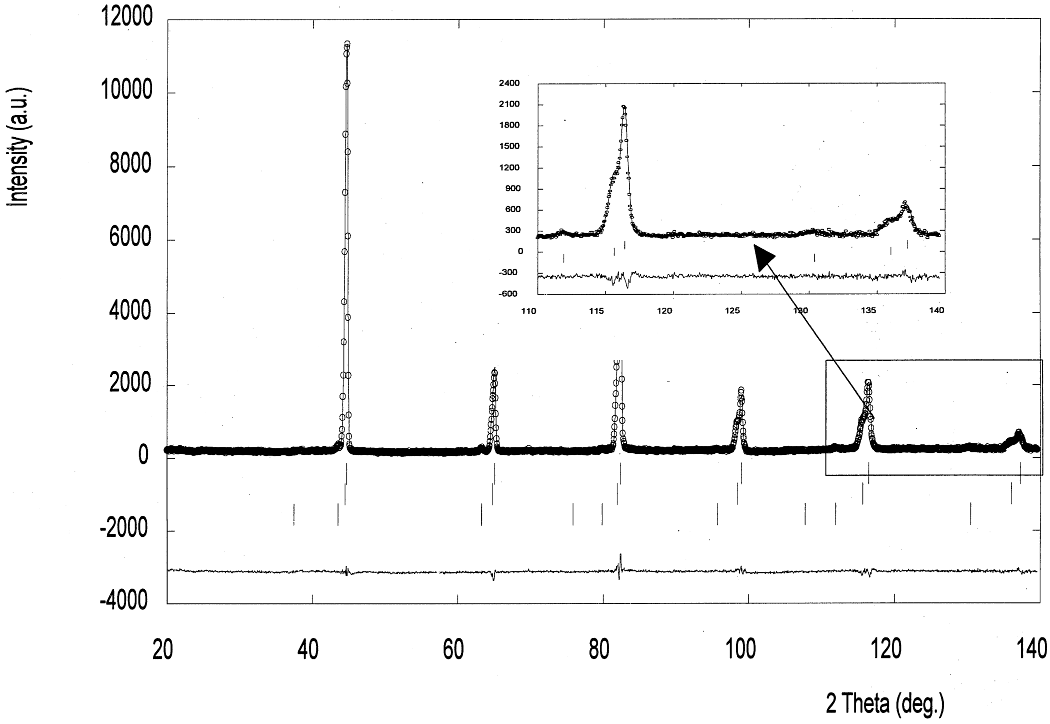

Fig. 2. Neutron diffraction pattern of U-10 wt% Mo alloy synthesized by the centrifugal atomization method.

2.3. Annealing at 600°C for 10 h

When the synthesized sample was annealed for 10 h at 600°C and then cooled to room temperature in the furnace, the two γ-U solid solution phases I and II found in the synthesized sample merged into a uniform single phased γ solid solution, as shown in Fig. 3.

Weak peaks corresponding to the UO phase decreased, but other weak peaks corresponding to UO_2 appeared in the diffraction pattern. A careful examination of the diffraction data has also revealed the presence of several additional weak peaks in the lower scattering angle region.

If we assume that all metal atoms of phases I and II after annealing are distributed uniformly on the atomic sites of the single phased γ solid solution, the Mo atomic concentration in the solid solution phase became 20.3 at.%. The Rietveld refinement of the structural model, consisting of the single phased γ-U solid solution and UO_2 phase, converged very well to $\chi = 1.77\%$. Lattice parameter $a = 0.34156$ nm, as obtained from the Rietveld refinement for the uniform γ solid solution phase, corresponds to 20.8 at.% Mo content, according to the Dwight equation. This is in good agreement with 20.6 at.% Mo, corresponding to the merger of phases I and II and the formation of about 2.4 wt% of UO_2.

Two additional rather weak were peaks were observed at scattering angles of $2\theta \approx 22.3°$ and $\approx 38.8°$ (for $\lambda = 0.18339$ nm) could be explained by superlattice reflections due to an ordering of the component atoms of

Table 1
Results of Rietveld refinements of the as synthesized sample[a]

Phase I	U–Mo solid solution	Phase II	U–Mo solid solution
	γ-phase, I m3m		γ-phase, I m3m
Unit cell	$a = 0.34116(1)$ nm	Unit cell	$a = 0.34261(2)$ nm
FWHM	$U = 0.195(26)$	FWHM	$U = 0.488(45)$
	$V = -0.208(27)$		$V = -0.360(6)$
	$W = 0.170(6)$		$W = 0.199(32)$
(x, y, z)	2(a) of I-m3m		2(a) of I-m3m
R-bragg	2.83		3.38
Wt. fraction	63.5%		35.6%

[a] UO-phase is not included.

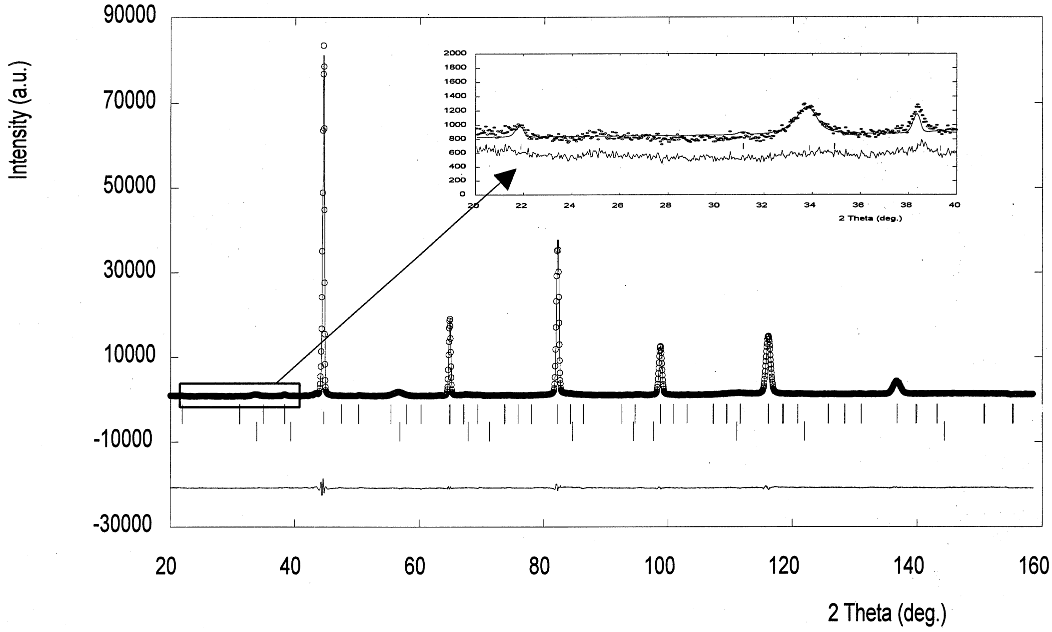

Fig. 3. Neutron diffraction pattern of U–10 wt% Mo alloy after annealing at 600°C for 10 h.

the γ solid solution. The two superlattice reflections could be indexed as (1/2 1/2 0) and (1/2 1/2 1) of the γ-phase bcc cell. The 20.8 at.% Mo content could be approximated closely to stoichiometric U_3Mo for the ordered model. In this case, the number of atoms in one unit cell of ordered U_3Mo phase should be a multiple of four, and hence the volume of the ordered supercell should be $V_{\mathrm{ord}} = 2nV_{\mathrm{c}}$, where $n = 1, 2, 3, \ldots$, and V_{c} – volume of bcc cell.

Doubling of the bcc cell ($V_{\mathrm{ord}} = 2V_{\mathrm{c}}$) may be achieved in two ways, either by the unit-cell transformation of / 1 0 0/0 1 0/0 0 2/ or by the transformation of /1 1 0/−1 1 0/ 0 0 1/. The former transformation yields a tetragonal unit cell with dimensions $a_{\mathrm{t}} \approx a_{\mathrm{c}}$ and $c_{\mathrm{t}} \approx 2a_{\mathrm{c}}$, and the latter yields a tetragonal cell with dimensions $a_{\mathrm{t}} \approx \sqrt{2}a_{\mathrm{c}}$ and $c_{\mathrm{t}} \approx a_{\mathrm{c}}$. Among the two possible superlattice structures, the latter was found to agree with the two observed weak reflections. The proposed superlattice structure of U_3Mo (Fig. 4) is given below.

Space group	P-4m2,
Mo: 1(a)	$0, 0, 0$
U1: 1(b)	$1/2, 1/2, 0,$
U2: 2(g)	$0, 1/2, z;\ 1/2, 0, -z \quad (z \approx 1/2)$

(The above structure becomes identical to the disordered γ-phase structure if the z-coordinate of (g) site is 1/2 and all sites are occupied by a uniform mixture of Mo and U atoms.)

The Rietveld refinement of the proposed superlattice showed good agreement with the superlattice reflections, as shown in the insert of Fig. 3. But taking into account the ordering has not noticeably decreased the χ^2-value and R-factor because of the relatively low intensity of the superlattice peaks in comparison with the fundamental peaks. As shown in Table 2, the structure is partially disordered, so that part of the molybdenum sites 1(a) (corners) are occupied by U atoms and part of the uranium sites 2(g) (centers of side faces) are occupied by Mo atoms, while sites 1(b) (centers of bottom and upper faces) are occupied only by U atoms.

The arrangement of atom sites in the superlattice model is essentially the same as that of the bcc structure, except for the small shift of the U2 position (centers of side faces) along the c-axis by $(0.5 - z = 0.014)$ in the super cell. It is possible to classify the lattice into three sublattices corresponding to positions 1(a), 1(b), and 2(g).

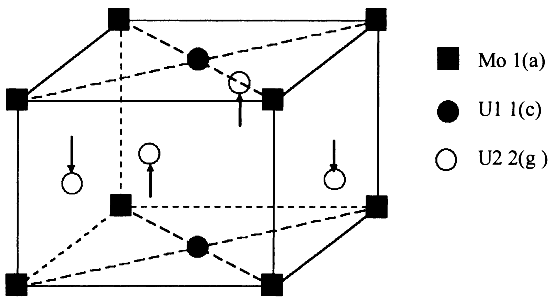

Fig. 4. Structure of metastable ordered phase U_3Mo.

Table 2
Result of Rietveld refinement of the annealed (600°C–10 h) sample[a]

Phase I	U_3Mo	Phase II	UO_2
Unit cell	$a = b = 0.48305(6)$ nm	Unit cell	$a = b = c = 0.5441(6)$ nm
	$c = 0.3418(2)$ nm		
Space group	P-4m2	Space group	Fm3m
0.66Mo + 0.34U	in 1(a)	U	in 4(a)
0.91U+0.09Mo	in 2(g); $z = 0.514$	O	in 8(c)
1U	in 1(b)		
FWHM	$U = 0.410(13)$	FWHM	$U = 30.971(12)$
	$V = -0.337(09)$		$V = -19.859(13)$
	$W = 0.177(26)$		$W = 3.980(79)$
R-bragg	2.4	R-bragg	12.6

[a] Phase composition (wt): $U_3Mo(97.3) + UO_2(2.4) + UO(0.3)$, $\chi^2 = 1.72$.

The model suggested that γ^0-phase [7] could not be ascribed to U_3Mo because the observed superlattice reflection (1/2 1/2 0) was extinguished in this model (indices are given relative to the bcc cell). In the model suggested by Tangri [8] for $U_{22}Mo_3$, one more superlattice reflection (0 0 1) should be observed between the (1/2 1/2 0) and (1/2 1/2 1) reflections. Therefore, this model, too, could not be ascribed to the U_3Mo.

3. Discussion

3.1. Phase composition and oxidation

The formation of two γ solid solutions with very slightly different cell parameters in the synthesized sample may be attributed to the extremely rapid cooling by the centrifugal atomization method or to the non-uniformity of the solute element in the state of molten alloy. True reasons are not clear now. Annealing of the synthesized sample for 10 h at 600°C was quite enough for the Mo to become homogeneously distributed so that two γ-phases merged into one γ-phase with 20.3 at.% Mo. The single γ-phase state for this composition at 600°C is consistent with the equilibrium phase diagram [4]. Subsequent furnace cooling has not led to the decomposition of the U–Mo alloy or the loss of the retained bcc lattice of the γ solid solution, but the structure has been modified by ordering.

The UO_2 phase was likely to form during the annealing process. Diffraction peaks of the UO_2 phase that formed in the annealed sample were very much broader than those of the U_3Mo phase. It is interesting to notice that such peak broadening was not observed in the small amount of UO phase observed in the as-synthesized sample. The oxide UO_2 is apparently in the form of a thin layer covering the surface of the particles and grains. The thickness of the UO_2 layer estimated from the broadening of two peaks is approximately 8 nm.

3.2. Structure of the metastable ordered phase U_3Mo

As was shown above, in the ordered U_3Mo phase, the lattice is composed of three sublattices. Consequently, two long range order parameters should define the distribution of atoms and degree of order. Two long range order parameters point out that order–disorder phase transition is connected with two stars of ordering wave vectors. The suggested structure for U_3Mo can be constructed using two Lifshits stars of wave-vectors $\mathbf{k}_1 = 2\pi(\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)$ and $\mathbf{k}_2 = \pi(\mathbf{b}_1 + \mathbf{b}_2)$ [10]. The vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ are reciprocal lattice vectors in the [1 0 0], [0 1 0] and [0 0 1] directions, respectively, and their modulus is equal to $1/a$, where $a$is the real space lattice parameter of the γ-phase bcc cell. According to Khachaturyan's theory [10], the structure is one of those which could be formed as a result of a disorder–order phase transition in a substitutional bcc alloy. The star of wave-vector $\mathbf{k}_2 = \pi(\mathbf{b}_1 + \mathbf{b}_2)$ consists of six vectors: (0 1/2 1/2), (1/2 0 1/2), (1/2 1/2 0), (0 1/2 −1/2), (−1/2 0 1/2), (1/2 −1/2 0). The star does not satisfy the necessary Landau criteria for second-order type phase transitions because it contains three vectors which give the reciprocal lattice wave-vector of the bcc disordered lattice

$$(0\,1/2\,1/2) + (1/2\,1/2\,0) + (-1/2\,0\,1/2) = (0\,1\,1).$$

Therefore, the order–disorder phase transition should be of the first-order type. After annealing at 600°C, one of the sublattices 1(b) (centers of upper and bottom faces) is occupied only by uranium atoms. Therefore, one of the two long-range order parameters has reached its maximum value. Further ordering and increase of the second long-range order parameter will be related to the ordering of U and Mo atoms on the other two remaining sublattices 1(a) and 2(g). Thus, two long-range order parameters may not reach their maximum values simultaneously, but rather step by step (one after the another). In the perfectly ordered state, besides the observed peaks (1 0 0) and (1 0 1) of the tetragonal cell, one more superlattice peak corresponding to two overlapped peaks of reflections (0 0 1) and (1 1 0) (see Fig. 3) should be observed because its intensity increases and becomes comparable with the (1 0 0) and (1 0 1) peaks.

3.3. Ordering and stability of metastable gamma phase

Metastable ordered phases γ° and $U_{22}Mo_3$ were observed in [5–8] in samples containing about 12 at.% Mo after quenching the γ-phase from the γ region temperature. Our study showed that for a higher Mo content (21.6 at.%), metastable ordered phases can be formed during rather slow furnace cooling. The formation of a transient ordered state in phase separating alloys when both ordering and decomposition processes are going on simultaneously was considered theoretically in [11,12]. Chen and Khachaturyan [11] considered order–disorder kinetics using the microscopic kinetic theory. Reinhard and Turchi [12] used the Monte–Carlo kinetic Ising model which allowed accounting for fluctuational nucleation. A physical picture of the formation of the metastable ordered phase is rather clear [11,12]. The existence of different ordered phases (U_2Mo, γ°, $U_{22}Mo_3$) based on a disordered bcc lattice indicates the tendency for ordering in the bcc γ solid solution. Then, at relatively low temperatures during cooling when the decomposition process of the γ-phase is retarded, the free energy of the alloy can be decreased by ordering instead of decomposition. In contrast to the decomposition, where atoms should be transported through macroscopic distances much longer than the interatomic distance, the ordering is correlated to the movement of atoms on the order of the interatomic distance. Therefore, ordering takes place in the metastable γ solid solution, although the free energy of the ordered state is at a minimum. It is a local minimum since an absolute minimum corresponds to the decomposition into two stable states: α-U + U_2Mo. Formation of the ordered phase decreases the alloy's free energy and therefore increases its activation energy and decreases diffusion mobility. On the other hand, a decrease of free energy leads to the rise of the energetic barrier which must be overcome by small regions of alloy to form the seeds of new phases during decomposition. Thus, ordering can retard the process of decomposition.

From the above mentioned point of view, it seems interesting to study the influence of the impurity of a third metal on ordering. It is well-known that doping with a third metal can increase the order–disorder transition temperature, which decreases free energy and therefore makes the alloy more stable. It even may happen that such an alloy would transform from a metastable to a stable state.

4. Conclusion

The neutron diffraction study showed that a U-10 wt% Mo alloy prepared by the centrifugal atomization method consists of three phase constituents: two γ-U solid solutions with slightly different Mo contents and lattice parameters, and a small amount (~1 wt%) of uranium oxide UO. Annealing at 600°C for 10 h and furnace cooling to room temperature results in a merger of the two solid solutions into one single phased uniform solution with an ordered arrangement of atoms – superlattice U_3Mo. Further oxidation is going on during annealing so that about 2.5 wt% of UO_2 is formed. The unit cell volume of the superlattice U_3Mo corresponds to a doubling of the bcc unit cell of the γ solid solution and is related with the latter by /1 1 0/−1 1 0/0 0 1/ type lattice transformations. Analyses showed that the U_3Mo superlattice can be formed only by a first-order type phase transition.

Acknowledgements

The authors are deeply grateful to Dr C.S. Choi, C.T. Lee, and H.J. Kim, who helped us throughout this study. This Project has been carried out under the Nuclear R&D Program by the Ministry of Science and Technology.

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