Uranium molybdenum silicide U_3MoSi_2 and phase equilibria in the U–Mo–Si system

M. Ugajin [*], A. Itoh, S. Okayasu, Y. Kazumata

Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-1195, Japan

Abstract

The metallographic and X-ray diffraction data are given for the new ternary silicide U_3MoSi_2. This compound melts incongruently at approximately 1480°C according to: $U_3MoSi_2 \rightarrow U_4MoSi_3 + U_2Mo_3Si_4 + L$ (L = peritectic liquid). It was verified that molybdenum coexists with U_3Si_2 predominantly as U_3MoSi_2. Indexing of the powder pattern showed that U_3MoSi_2 has a simple cubic structure with lattice parameter $a_0 = 10.69 \pm 0.01$ Å.   © 1998 Elsevier Science B.V. All rights reserved.

PACS: 81.30.B; 61.82.Bg

1. Introduction

A potentiality of the uranium silicide U_3Si_2 for the power-reactor fuel application prompted us to perform a burnup-simulation experiment [1]. Molybdenum was found to play an important role in the fission-product chemistry of U_3Si_2 fuel. Supplementary study on the U–Mo–Si system revealed the existence of a new compound U_3MoSi_2. This finding was initiated by the analysis of small precipitates in a U_3Si_2–0.5 wt% Mo alloy described later. A number of ternary uranium silicides have been reported in the literature. However, studies on the U_3XSi_2-type compound have not been made except by us [1].

For the verification of this new compound and for the elucidation of the phase equilibria in the U–Mo–Si system, the results of the metallography, X-ray diffractometry (XRD) and electron-probe microanalysis (EPMA) will be presented. This paper constitutes a series of our recent investigations on the high U-density fuels: U_3Si [2] and U_6Me (Me = Fe, Mn, Ni) [3].

2. Experimental

The U–Mo–Si alloy ingots each weighing 10–11 g were prepared by arc melting the high-purity elements (U > 99.8; Mo > 99.95; Si > 99.999 wt%) on a water-cooled Cu hearth under Ar atmosphere. The ingots were turned over and remelted at least six times to ensure homogeneity. The loss in weight during the melting procedure was less than ~0.05%, so the nominal compositions were used throughout this paper. The arc-melted alloys emplaced in the sealed quartz tubes were annealed in a muffle furnace at 500–1100°C for 4–22 days, and then rapidly cooled to room temperature by water quenching. The melting point of U_3MoSi_2 was determined by a series of heat-treatments in a vacuum tungsten-mesh heater at 1400–1700°C. Melting was detected by corner rounding of the sample and its metallographic change. 'Power-off' cooling rate of ~150°C/min was enough to quench-in the high temperature phases. The temperature was checked by the melting point of Ni (1453°C). Density was measured by Archimedean immersion method with metaxylene as a replacement liquid.

The phases present before and after the heat-treatment were examined by optical microscopy and EPMA. Powder XRD was also utilized with Ni-filtered Cu Kα radiation [λ (Kα) = 1.54178 Å and λ (Kα$_1$) = 1.54051 Å].

_____
[*] Corresponding author. Fax.: +81-29282 6097; e-mail: ugajin@popsvr.tokai.jaeri.go.jp.

The compositions of the phases were determined by EPMA using the standards: U–6 wt% Mo, Mo_3Si_2, USi, U_3Si_2 and U_3Si. The crystal structure of the Si-dissolved (U, Mo) alloy that precipitated at the grain boundaries could not be determined by XRD due to its scarcity and the peak overlapping. However, we succeeded in identifying it by the detection of the superconductivity. Electrical resistivity of the as-annealed U_3MoSi_2 samples was measured with the four-terminal method from 1.8 K to room temperature. The d.c. magnetization measurements were performed using a SQUID magnetometer (Quantum Design, Inc.) in an applied field of 1000 Oe. The ac susceptibility data were also obtained. This electromagnetic method was found to be effective for detecting a trace amount of the bcc γ–(U, Mo, Si) that intervenes between the grain boundaries.

3. Results and discussion

Fig. 1 shows the phase diagram of the U–Mo–Si system constructed on the basis of our experimental results. Particular attention is paid to the U–Si binary side of the system that includes U_3MoSi_2, U_4MoSi_3, $U_2Mo_3Si_4$ and peritectic liquid. The existence of the new ternary compounds, U_3MoSi_2, and U_4MoSi_3, was for the first time observed with the respective compositions 82.4U–11.1Mo–6.5Si and 84.1U–8.5Mo–7.4Si wt%. An equilibrium reaction of the ternary peritectic involving these compounds was identified:

$$U_3MoSi_2 \rightleftharpoons U_4MoSi_3 + U_2Mo_3Si_4 + L. \tag{1}$$

The existence of $U_2Mo_3Si_4$ [5] was confirmed here by the present authors. The four-phase reaction triangle is indicated as a shaded area in Fig. 1. The composition of the peritectic liquid designated as L is located near 74U–16Mo–10Si at.% = 90.6U–7.9Mo–1.5Si wt%. The temperature of this invariant reaction, i.e., incongruent melting point of U_3MoSi_2, has been determined to be 1480 ± 30°C. As shown in Fig. 2, the as-melted U_3MoSi_2 alloy comprises the three high-temperature phases in Eq. (1): U_4MoSi_3 of large acicular grains with microcracks, a cloud-shaped $U_2Mo_3Si_4$ and the peritectic liquid of deeply etched areas between the U_4MoSi_3 grains. By rapid solidification, the metastable peritectic liquid is retained at room temperature as a mixture of U alloy and an unidentified ternary compound. These two phases tend to make up an extremely fine lamellar or mottled structure with the U alloy as a matrix constituent. The possibility that the unidentified compound is U_3MoSi_2 is not entirely excluded; however, any detectable amount of U_3MoSi_2 was not present in
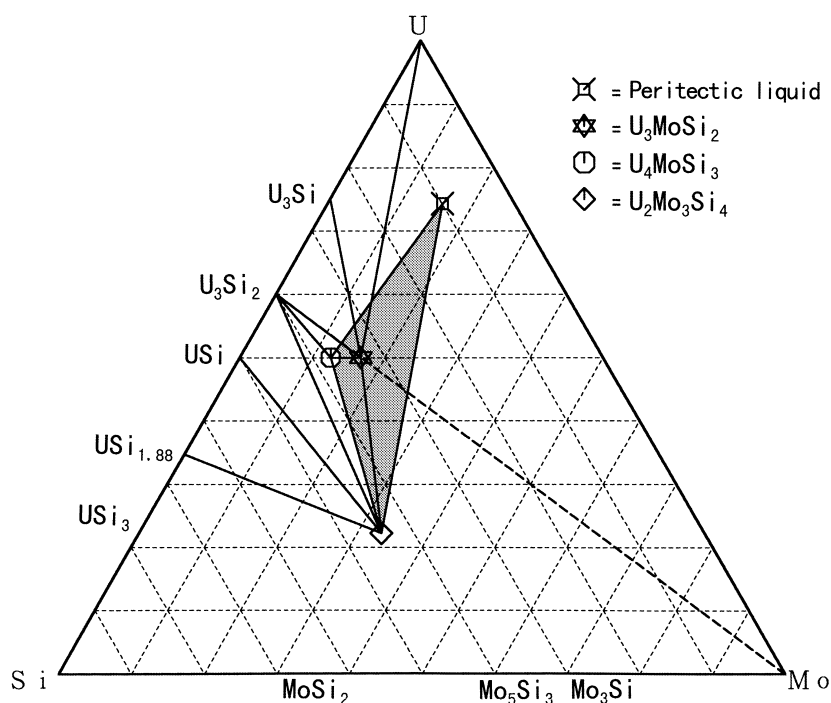

Fig. 1. Phase diagram of the U–Mo–Si system at 850°C. The four-phase reaction represented by Eq. (1) has been proved to occur at about 1480°C in the shaded triangular area. In the U–Mo binary system [4], the body-centered cubic solid solution, γ-(U$_{1-x}$Mo$_x$), extends from $x = 0$ to $x = \sim0.4$ ($\sim$21 wt% Mo) at 850–1100°C.
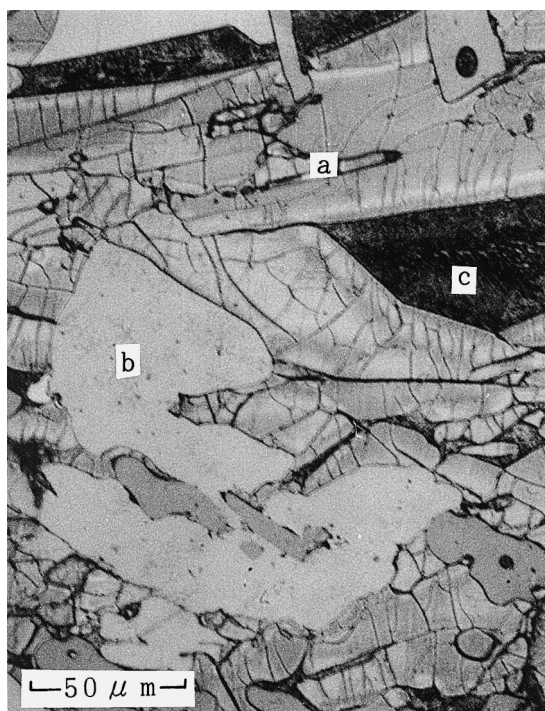
Fig. 2. Microstructure of as-arc-melted U_3MoSi_2, showing the coexistence of U_4MoSi_3 (a), $U_2Mo_3Si_4$ (b) and the peritectic liquid (c) that has been retained at room temperature as a mixture of a probable phase of γ-(U, Mo, Si) and an unidentified ternary compound.

Fig. 3. Microstructure of U_3MoSi_2 arc-melted and annealed at 1100°C for 5 days, showing almost single-phase U_3MoSi_2 (see Fig. 5).

the as-melted alloy. This means that the high-temperature state was almost completely frozen-in to room temperature.

Heat-treatment of the as-melted sample led to change remarkably the microstructure. As seen in Fig. 3, the microstructure of the U_3MoSi_2 sample annealed at 1100°C for 5 days shows the almost single-phase U_3MoSi_2 with the near-equiaxed and well-developed grains. Practically no change was observed in the XRD patterns of the two U_3MoSi_2 samples. The one was heated at 1100°C for 5 days, 650°C for 5 days and finally at 500°C for 22 days, and the other one at 1100°C for 5 days. This fact indicates that phase transition does not occur in the U_3MoSi_2 compound at least between 500°C and 1100°C. Fig. 4 shows an example of the XRD pattern taken for U_3MoSi_2. The observed diffraction peaks were tentatively indexed according to the simple cubic cell. Table 1 lists the values of diffraction angle (2θ), interplanar distance (d), relative intensity (I/I_0) and the (hkl) data so obtained. The lattice parameter of U_3MoSi_2 was determined to be 10.69 ± 0.01 Å by a least-squares fit on the powder data. Although a few weak peaks were omitted in the lattice parameter calculation, fitting of the assigned indices to the proposed cell was not poor. The density measured for the 1100°C-
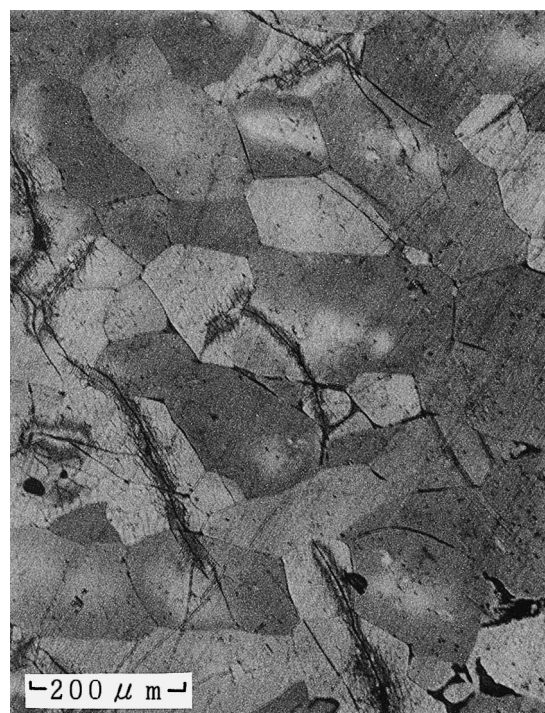
annealed U_3MoSi_2 is 12.1 g/cm³, whereas that for the as-arc-melted is higher (12.6 g/cm³) due to the presence of a large amount of U alloy. Consequently, theoretical density of U_3MoSi_2 is deduced as 11.8 g/cm³ by assuming 10 formula units per cell.

The metastable retention of the U alloy is due to the sluggishness of the reverse reaction of Eq. (1), and it is characteristic of the peritectoid and peritectic reactions. As we experienced, it also occurs in the binary peritectoid reaction [6]

$$U_3Si \rightleftharpoons U_3Si_2 + U$$
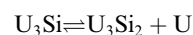
at 930°C [7] and in the ternary peritecto-eutectic reaction [1]

$$U_3Si + URuSi \rightleftharpoons U_3Si_2 + L$$

at about 840°C with the accompanied transformation L $\rightarrow$ URuSi + U upon rapid cooling. The latter type of reaction was also encountered in the uranium carbide system: UC + W $\rightleftharpoons$ $UWC_{1.75}$ + L at 2150°C [8,9]. In these cases, the solid solubilities of Si, Ru and W to γ-U are limited (<5 at.%), thus forming the α-U metal instead of the γ-U alloy at room temperature. The metallic grain-boundary phase seen in the 1100°C-annealed sample (Fig. 5) was confirmed to be metastable bcc γ-(U, Mo) retained at room temperature. Namely, it was
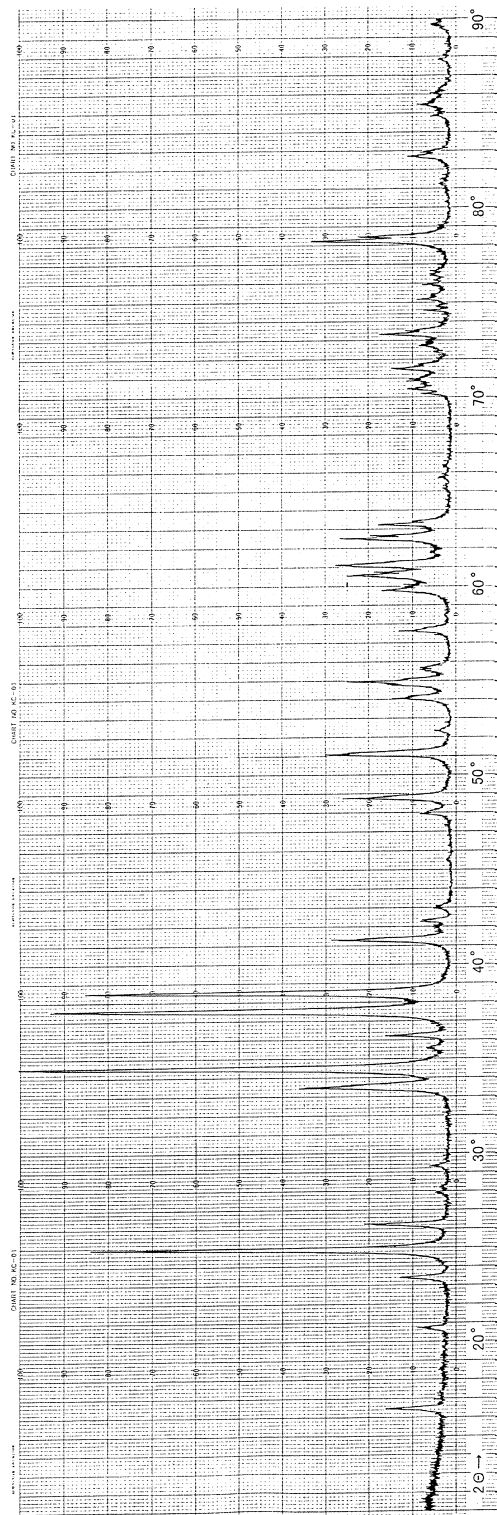
Fig. 4. Powder XRD pattern of U_3MoSi_2 arc-melted and annealed at 1100°C for 5 days, 650°C for 5 days and finally at 500°C for 22 days ($2\theta = 11$–$90°$). The essentially same pattern was obtained with the U_3MoSi_2 sample annealed at 1100°C for 5 days. The strong peaks of (0 2 1) and (1 1 1) of α-U should appear at $2\theta = 35.7°$ and $39.6°$, respectively; the strongest (1 1 0) peak of γ-(U, Mo) should appear at $\sim37°$, if each phase is present.

Table 1
U_3MoSi_2 XRD data with the preliminary indexing to the simple cubic cell [a]

2θ (obs) (°)	2θ (calc) (°)	d (obs) (Å)	I/I_0 (%)	hkl
16.53	16.58	5.363	13	200
23.50	23.53	3.786	15	220
24.98	24.98	3.564	74	300
26.30	26.35	3.388	20	310
33.57	33.52	2.669	43	400
34.55	34.58	2.596	100	410
35.68	35.62	2.516	4	411
37.58	37.61	2.393	93	420
38.53	38.58	2.336	73	421
41.35	41.36	2.183	21	422
43.08	43.13	2.100	4	510
48.03	48.13	1.894	9	440
48.84	48.93	1.865	25	522
51.17	51.25	1.785	33	600
54.14	54.25	1.694	21	620
55.00	54.98	1.669	22	540
55.69	55.70	1.650	8	541
57.73	57.84	1.597	9	630
59.87	59.87	1.544	22	444
60.62	60.56	1.526	21	700
61.18	61.24	1.514	26	710
62.58	62.58	1.483	27	640
63.30	63.25	1.468	15	720

[a] 2θ (obs) > 59.0° obtained with Cu Kα_1 radiation.

Fig. 5. Microstructure of U_3MoSi_2; the near-central part of Fig. 3 is enlarged. The 0.6 wt% Si–dissolved γ-(U, 8.4 wt% Mo) alloy precipitates along the grain boundaries of U_3MoSi_2. An unidentified impurity phase is also present as small globules.

revealed that the 1100°C-annealed U_3MoSi_2 sample has a superconducting transition temperature T_C of 2 K (Fig. 6), whereas the 500°C-annealed U_3MoSi_2 sample does not show superconductivity in the investigated range of temperature. In this connection, Lindsay and co-workers [10,11] reported that the bcc γ-(U,Mo) phase exhibits superconductivity with the identical T_C value of $\sim$2.1 K, and the α–U phase appears to be nonsuperconducting above $\sim$0.2 K. Our γ-(U, Mo) phase slightly containing Si is considered to have transformed to the stable α-U and U_2Mo after heating at 500°C for 22 days; therefore, the sample no longer exhibited superconductivity. This temperature of heat-treatment is well below 560°C, i.e., eutectoid temperature for γ-(U, Mo) $\rightleftharpoons$ α-U + U_2Mo. Thus, the already-mentioned U alloy in the as-arc-melted sample (Fig. 2), being transformed from the peritectic liquid, is believed to be Mo-stabilized γ-U phase similar to that in the 1100°C-annealed sample. Ref. [10] may provide a support for this belief, which indicates that γ-($U_{0.82}Mo_{0.18}$) alloy could be made even in the as-arc-melted state without quenching from the γ-phase region.

Because the compound is a newly found one, U_3MoSi_2 was separately prepared and examined; the reproducibility of the results was good. The ternary compound $U_2Mo_3Si_4$ was also prepared in this study. Both the as-arc-melted and as-850°C-annealed samples comprised essentially single-phase $U_2Mo_3Si_4$ with traces

of U_3Si_2 and USi. The formation of the latter two phases must be caused by the minor shift of composition during arc-melting. It is thus indicated that the $U_2Mo_3Si_4$ compound melts congruently in contrast to U_3MoSi_2. The 44U–20Mo–36Si at.% alloy was found to consist of these two ternary compounds at 850°C. The 25U–25Mo–50Si at.% alloy comprised $U_2Mo_3Si_4$ and $USi_{1.88}$ at the same temperature. Furthermore, it was confirmed that at 850°C the alloy of composition 50U–10Mo–40Si (at.%) consists of the three phases: U_3Si_2 + U_4MoSi_3 + $U_2Mo_3Si_4$. Unfortunately, single-phase U_4MoSi_3 has not yet been obtained. The U_4MoSi_3 sample annealed at 850°C for 4 days comprised U_4MoSi_3, U–1.0 wt% Mo alloy, U_3Si_2 and $U_2Mo_3Si_4$; even after annealing for 8 days, it still contained considerable amounts of the parasitic phases U_3Si + U_3Si_2 + $U_2Mo_3Si_4$. It seems reasonable to assume that the equilibrium state could not be attained due possibly to the complexity and sluggishness of the reaction associated with the occurence of the U_4MoSi_3 compound. On the other hand, the tetragonal U_3Si_2 (Fig. 7) that has a theoretical density of 12.20 g/cm^3 and melts congruently at 1665°C [7] was found to dissolve molybdenum up to $\sim$0.1 wt% Mo at 850°C. The heat-treatments of the U_3Si_2–0.5, 2.0 and 3.0 wt%Mo alloys
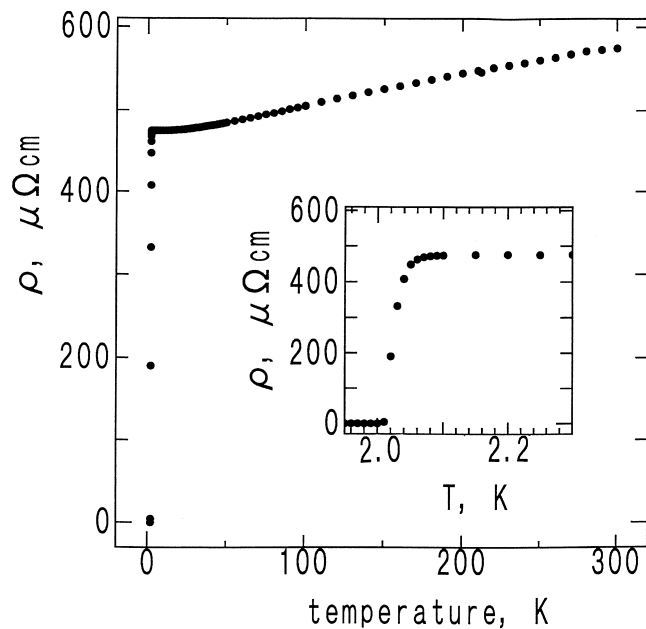
Fig. 6. Electrical resistivity (ρ) of the sample shown in Figs. 3 and 5 as a function of temperature. Inset shows data below 2.3 K; zero resistivity is achieved at 2 K. This sample was also proved to exhibit the Meissner effect.

Fig. 7. Microstructure of pure U_3Si_2 alloy arc-melted and annealed at 850°C for 4 days, showing single-phase U_3Si_2 (measured density = 12.2 g/cm^3).
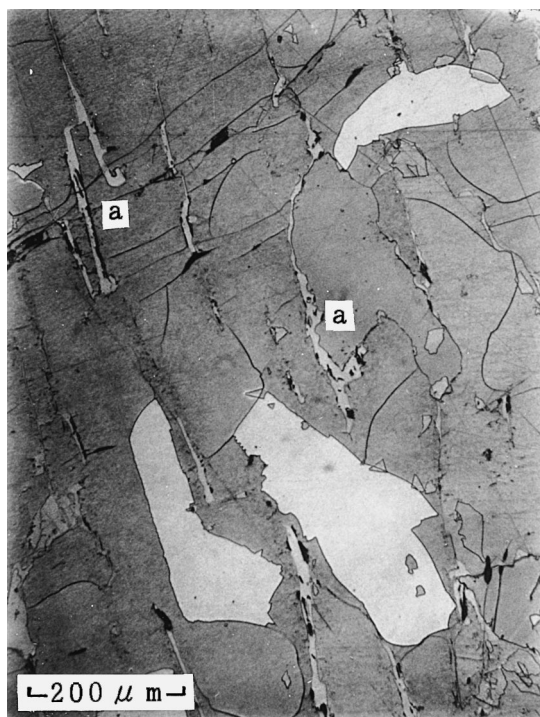

Fig. 8. Microstructure of U_3Si_2–0.5 wt% Mo alloy arc-melted and annealed at 850°C for 4 days, showing the presence of small elongated islands of the U_3MoSi_2 precipitate (a) in the U_3Si_2 matrix (measured density = 12.12 g/cm^3).

revealed that only the two phases, U_3Si_2 and U_3MoSi_2, coexist in equilibrium at 850°C; microstructure of U_3Si_2–0.5 wt% Mo alloy is given in Fig. 8. Thus, it becomes clear that molybdenum exists with U_3Si_2 predominantly as U_3MoSi_2 rather than U_4MoSi_3. Such a predominant nature of U_3MoSi_2 is consistent with the results of the previous experiments on the U_3Si_2 burn-up simulation [1]. The U_3Si–5.0 wt% (9.2 at.%) Mo alloy lying beside the U_3MoSi_2–U join consisted of the three phases at 850°C: U_3MoSi_2, U and a small amount of U_3Si. The U metal dissolved approximately 0.4 wt% Mo and 0.1 wt% Si. The results of all these experimental observations were incorporated in the U–Mo–Si phase diagram to delineate the phase boundaries at 850°C and the four-phase reaction triangle at around 1480°C.

According to the recent investigation by Le Bihan and co-workers [12], another ternary compound $U_4Mo_5Si_3$ exists and has the structure isotypic with the $MgZn_2$-type hexagonal $U_4Mn_5Si_3$ [13]. This high-Mo and high-Si compound is located far from the U–Si binary region, and it might not directly concern the behavior of the irradiated U_3Si_2 fuel. Namely, from a practical point of view of fuel performance, it is important that the compounds U_3MoSi_2, U_4MoSi_3 and $U_2Mo_3Si_4$ have tie-lines with U_3Si_2.

Further study is needed to verify the existence of single-phase U_4MoSi_3 and to determine closely the crystal structure of U_3MoSi_2.

References

[1] M. Ugajin, A. Itoh, J. Alloys Comp. 213&214 (1994) 369.

[2] M. Ugajin, M. Akabori, A. Itoh, N. Ooka, Y. Nakakura, J. Nucl. Mater. 248 (1997) 204.

[3] M. Ugajin, A. Itoh, M. Akabori, N. Ooka, Y. Nakakura, J. Nucl. Mater. 254 (1998) 78.

[4] T.B. Massalski et al. (Eds.), Binary Alloy Phase Diagrams, 2nd ed., vol. 3, ASM International, Metals Park, OH, 1990, p. 2683.

[5] F.G. Aliev, L.G. Aksel'rud, V.V. Kozyr'kov, V.V. Moshchalkov, Sov. Phys.Solid State 30 (5) (1988) 742.

[6] M. Ugajin, A. Itoh, M. Akabori, Preparation of U–Si/U–Me (Me = Fe, Ni, Mn) Al-dispersion plate type fuel (miniplates) for capsule irradiation, JAERI-M 93–121, 1993 (in Japanese).

[7] T.B. Massalski et al. (Eds.), Binary Alloy Phase Diagrams, 2nd ed., vol. 3, ASM International, Metals Park, OH, 1990, p. 3375.

[8] M. Ugajin, I. Takahashi, J. Nucl. Mater. 37 (1970) 303.

[9] M. Ugajin, Y. Suzuki, J. Shimokawa, J. Nucl. Mater. 43 (1972) 277.

[10] J.D. Lindsay, R.W. White, M.C. Tinkle, S.W. Hayter, R.D. Fowler, Phys. Rev. B 7 (1973) 4290.

[11] H.H. Hill, R.W. White, J.D.G. Lindsay, V.O. Streubing, Solid State Commun. 15 (1974) 49.

[12] T. Le Bihan, J.C. Levet, H. Noel, J. Solid State Chem. 121 (1996) 479.

[13] Joint Committee on Powder Diffraction Standards-ASTM, Powder Diffraction File, Card 18-822 ($U_4Mn_5Si_3$).