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Experimental investigations on the chemical state of solid fission-product elements in U_3Si_2

M. Ugajin and A. Itoh
Department of Chemistry and Fuel Research, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-11 (Japan)

Abstract

The uranium silicide U_3Si_2 has a congruent melting point of 1665 °C and possesses higher uranium density (11.3 g U cm^{-3}) and higher thermal conductivity than the uranium dioxide currently used in light water reactors. U_3Si_2 is in use as a research reactor fuel (US Nuclear Regulatory Commission, *NUREG-1313*, July, 1988), representing a potentiality for power reactor fuel. A first attempt is made in this study to predict the chemical state of the solid fission-product elements comprising zirconium, molybdenum, rare earth elements, alkaline earth metals and elements of the platinum group. Ternary phase equilibria in the U–Mo–Si and U–Ru–Si systems are also investigated to supplement the fission product chemistry in U_3Si_2.

1. Experimental details

Alloys were obtained by melting the proper amounts of metallic elements or compounds of silicon on a water-cooled copper hearth in an arc furnace under an Ar atmosphere. The purity of the starting materials was better than 99.95 wt.%; uranium metal had a purity of more than 99.8 wt.%. The ingots were turned over and remelted more than six times to ensure homogeneity. The loss in weight during the melting procedure was less than about 0.05% for U–Mo, Ru–Si alloys; therefore, nominal compositions are used throughout this paper. Duplicate alloys were prepared, where necessary, to check the reproducibility of the results. Arc-melted alloys were heat treated in muffle furnaces at temperatures of 800–1100 °C. Alloy specimens were water quenched to room temperature after heating for 3–10 days. Phases present before and after the heat treatments were examined by electron probe microanalysis and X-ray diffractometry using Cu Kα radiation.

2. Results

2.1. High burn-up simulation

The U_3Si_2 with 19.7% ^{235}U was assumed to have been irradiated under the likely operating conditions of research reactor: thermal neutron flux, 1.0×10^{15} n cm^{-2} s^{-1}; irradiation time, 75 effective full power days (EFPD). Burn-ups and inventories of actinide and fission products were calculated using the ORIGEN code. The burn-up thus obtained, about 97% of the initially contained ^{235}U, may be the maximum expected for this type of fuel in reactor service. Three alloys fuels simulated at 80% and 97% burn-ups were prepared by arc melting together elements according to the calculated inventories and were heat treated at 900 °C for 17 days or at 1100 °C for 4 days. The following 13 elements were simulated: U, Si, Mo, Ru, Rh, Pd, Nd, Ce, La, Pr, Y, Zr and Sr. Other rare earth, alkaline earth and actinide elements were considered by adding their equivalent quantities to the charges using these elements. It has been found that the chemical forms of the solid fission products can be classified into the following five categories (Fig. 1).

(1) *Matrix phase U_3Si_2.* The major constituents, uranium and silicon, form the matrix phase of tetragonal U_3Si_2. The solubility limits of other elements for the U_3Si_2 phase were found to be comparatively small, *e.g.* about 0.1 wt.% for Mo. Zirconium is soluble up to 1.2 wt.%; the majority of the Zr forms an unidentified U–Zr–Si compound.

(2) *U_3MoSi_2-type precipitate.* Mo and part of the Ru form a solid solution based on the new ternary compound U_3MoSi_2. Palladium added as one of the platinum group elements does not coexist in solution with these elements.

(3) *URuSi-type precipitate.* Ru and U form a new ternary compound URuSi; Rh dissolves selectively in it. Ru was thus found to partition between the U_3MoSi_2 and the URuSi, depending on the temperature of heat treatment.

(4) *(RE)Si-type (RE≡rare earth elements) precipitate.* Rare earth elements (Nd, Ce, La, Pr and Y) form

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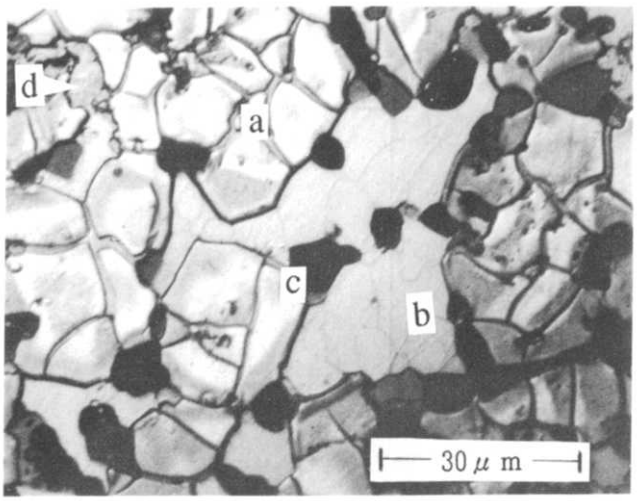

Fig. 1. Ceramography of 97% burn-up-simulated U_3Si_2 (arc melted and annealed at 1100 °C): region a, U_3Si_2 matrix; region b, $U_3(Mo,Ru)Si_2$; region c, (RE)Si (dark black); region d, U–Zr–Si compound.

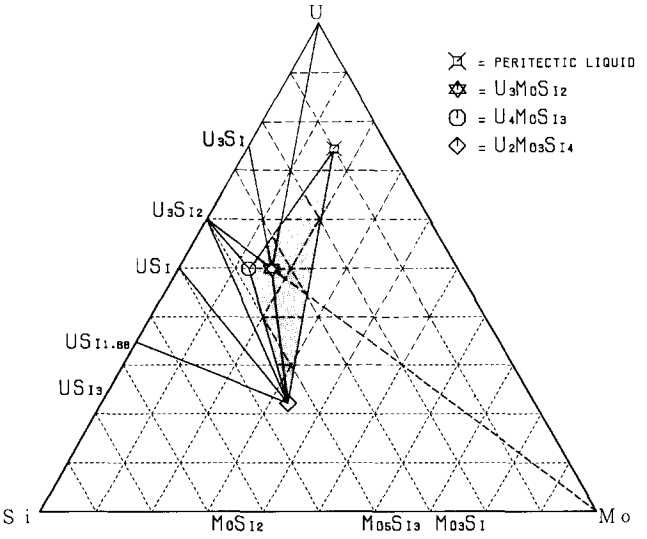

Fig. 2. Partial phase diagram of the U–Mo–Si system at 850 °C. The four-phase reaction triangle at temperatures above 1100 °C is indicated as a shaded area.

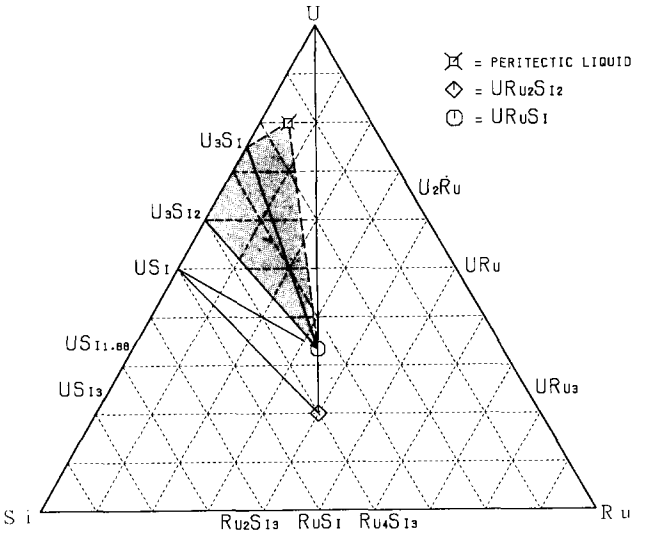

Fig. 3. Partial phase diagram of the U–Ru–Si system at 820 °C. The four-phase reaction quadrilateral is indicated as a shaded area; the invariant reaction temperature T is in the range 820 °C $< T <$ 850 °C.

monosilicide. Palladium enters into the lattice to form the solid solution (RE,Pd)Si.

(5) *Free metal.* Attempts using $SrSi_2$ or Sr metal as a starting material failed to form any type of Sr silicide. Strontium thus appears not to react with other elements; the Sr remaining in the metallic state, however, disappears from the specimens as a result of its evaporation during arc melting. Barium seems to behave similarly.

2.2. *Phase equilibria in the ternary systems U–Mo–Si and U–Ru–Si*

No ternary phase diagrams are so far available although ternary silicides URu_2Si_2, $U_2Ru_3Si_5$ and $U_2Mo_3Si_4$ have been reported to exist [1, 2, 3]. Figures 2 and 3 show partial phase diagrams of U–Mo–Si and U–Ru–Si systems, constructed in the present study, that are important to assess silicide fuels' performance. The existence of new ternary compounds has been discovered: U_3MoSi_2, U_4MoSi_3 and URuSi. An equilibrium reaction of the ternary peritectic involving these new ternary compounds was identified in the U–Mo–Si system:

$$U_4MoSi_3 + U_2Mo_3Si_4 + L \rightleftharpoons U_3MoSi_2$$

The four-phase reaction triangle is indicated as a shaded area in Fig. 2; the composition of the peritectic liquid (L) is located near 74U–16Mo–10Si (atomic per cent). The temperature of this invariant reaction has not yet been determined, but confirmed to lie at some temperature higher than 1100 °C. The as-melted U_3MoSi_2 alloy comprises U_4MoSi_3, $U_2Mo_3Si_4$ and Si-dissolved (U, Mo) phase.

In the U–Ru–Si system, the new ternary compound URuSi melts congruently in contrast to the U_3MoSi_2. This compound gave an X-ray pattern similar in relative intensity and d spacing to the data reported for the orthorhombic CoMnSi with TiNiSi-type structure [4]. Lattice parameters of URuSi are now tentatively determined as $a_0 = 6.37$ Å, $b_0 = 3.99$ Å and $c_0 = 7.25$ Å. The following ternary peritectoeutectic reaction has been proved to occur:

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

for which the four-phase reaction quadrilateral is shown as a shaded area in Fig. 3. The invariant reaction temperature was found to be at some temperature between 820 and 850 °C. The peritectic liquid (designated as L) may undergo the transformation

$$L \longrightarrow URuSi + U$$

on rapid cooling from the liquid state of the alloy. The metallic uranium phase remains in the metastable condition at room temperature. The reverse reaction to form U_3Si is sluggish as in the binary peritectoid reaction

$$U_3Si \rightleftharpoons U_3Si_2 + U$$

that occurs at 930 °C [5]. It should be noted that U_3Si does not have tie lines with Ru and Mo but forms those with URuSi and U_3MoSi_2.

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