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Solidus and liquidus temperatures in the UO_2–PuO_2 system

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Abstract

The melting of plutonium and uranium mixed oxide containing Pu of more than 30% was investigated using a tungsten capsule and a rhenium inner capsule. In the conventional measurements of $(Pu,U)O_{2.00}$ in the tungsten capsule, a liquid phase of tungsten and plutonium oxide appeared in the mixed oxide during melting. This liquid phase was found to have an effect on the measurement of melting point. Therefore, the rhenium inner capsule was used to avoid the effect. The solidus and liquidus temperatures in the UO_2–PuO_2 system were decided from the $(Pu,U)O_{2.00}$ data measured using the rhenium capsule, and the effect of the Am content on the solidus temperature was evaluated. The variation of the solidus and liquidus temperatures in the UO_2–PuO_2–AmO_2 ternary system was represented to an accuracy of $\sigma = \pm 9$ K and $\sigma = \pm 16$ K, respectively, by the ideal solution model.

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1. Introduction

Plutonium and uranium mixed oxide (MOX) containing 30%Pu has been developed as the core fuel pellet of the fast reactor *Monju* [1]. The fuel pellet temperature rises to over 2300 K during irradiation because of the high linear heating power. The large temperature gradient in the radial direction causes redistribution of Pu and U, and Pu content increases to about 40% at the pellet center [2,3]. The maximum temperature of the fuel pellet during irradiation is limited within the design criterion to prevent fuel melting. So, it is essential to know the melting point of MOX as a function of Pu content.

Plutonium material used in the fuel contains a small amount of americium which is a daughter nuclide of ^{241}Pu. Americium content in the fuel for the fast reactor will be increased and this must be taken into account for long-term storage. Therefore, it is also necessary to investigate the effect of Am content on the melting point of MOX.

Lyon and Baily [4] and Aitken and Evans [5] measured the melting points of MOX systematically using the thermal arrest technique. In both reports, however, after the experiment, the samples were not analyzed for any change which might have occurred during heating. Most recently the authors [6] also measured the melting point of MOX as a function of Pu content, and reported that the measured solidus temperatures were in good agreement with the data of Lyon and Baily [4]. The authors also showed the solidus temperature decreased with increasing PuO_2 content and suddenly dropped at the composition between 20% and 30%Pu [6]. The melted samples were analyzed and were observed to contain a large amount of metallic W and Pu oxide along the grain boundary of the samples with 30% and 40%Pu content. It was suggested that the discontinuous variation of the solidus was caused by reaction with W that came from the capsule which the sample was sealed inside.

To investigate the effect of the reaction between W and the specimen on the measured melting point, it is necessary to carry out experiments eliminating the effect of the capsule material. In this work, a Re inner capsule was

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employed to prevent the reaction and the melting points were measured. The dependence of changes of the microstructure on heating temperature was investigated for both W and Re capsules, and the melting temperatures were decided for the UO_2–PuO_2 system. In addition, the effect of the Am content on solidus temperature was evaluated.

2. Experimental

2.1. Sample preparation

The sintered pellets listed in Table 1 were prepared by a mechanical blending method, and powders of UO_2, $(U_{0.513}Pu_{0.463}Am_{0.024})O_2$, $(Pu_{0.979}Am_{0.021})O_2$ and $(Pu_{0.926}Am_{0.074})O_2$ were used as raw materials. Americium included in the powders was accumulated during the long-term storage due to β-decay of ^{241}Pu. The mixed powder was pressed and sintered at 1973 K for 3 h in an atmosphere of Ar and 5%H_2 gas mixture with added moisture. The oxygen-to-metal (O/M) ratio of the sintered pellets was adjusted to 2.00 by annealing at 1023 K for 5 h at the oxygen potential of $\Delta\overline{G}_{O_2} \cong -400$ kJ/mol. The sum of metallic impurities in the pellet was less than 500 ppm. All of the samples were analyzed with an X-ray diffractometer (XRD: Rigaku RINT-1100) and an electron probe micro analyzer (EPMA: JEOL JXA8800), and were confirmed to be homogeneous.

2.2. Measurement procedure

Five types of capsules (Fig. 1) were prepared. Types C, D and E had a Re inner capsule. The W capsules were sealed in vacuum by electron beam welding. Two kinds of experiments were carried out to measure the melting point and to observe the dependence of the change of the microstructure on heating temperature; the conditions are listed in Tables 1 and 2, respectively.

In the measurement of the melting point the samples shown in Fig. 1 were heated above the melting points at a constant heating rate of 40–80 K/min, and heating temperature curves were obtained. The apparatus and procedures used in this experiment were similar to those described previously [4–10] for determining the melting point of MOX.

Temperatures were measured with a pyrometer placed in the black body well at the bottom end cap of the W capsule

Table 1
Samples and measured melting temperature

No.	Composition				Type of cell	Temperature of arrest		W content (%) after heating
	U (%)	Pu (%)	Am (%)	O/M		Starting point (K)	Ending point (K)	
1	69.6	29.8	0.6	2.000	C	3030	3074	–
2	59.6	39.7	0.7	2.000	C	2997	3029	–
3	59.6	39.7	0.7	2.000	C	3009	3020	–
4	58.5	39.6	1.9	2.000	C	3000	3052	–
5	58.5	39.6	1.9	2.000	C	3006	3043	–
6	58.4	38.3	3.3	2.000	C	2988	3017	–
7	58.4	38.3	3.3	2.000	C	2998	3050	–
8	58.4	38.3	3.3	2.000	C	3010	3039	–
9	51.4	46.3	2.4	2.000	C	2971	2998	–
10	37.7	60.0	2.3	2.000	C	2940	–[b]	
11	–	97.9	2.1	2.000	C	2822	2938	–
12	100	0	0	2.000	A	3140[a]	–	0
13	88.0	11.7	0.3	2.000	A	3077[a]	3117[a]	0
14	88.0	11.7	0.3	1.989	A	3093[a]	3135[a]	0
15	88.0	11.7	0.3	1.983	A	3084[a]	3105[a]	0
16	88.0	11.7	0.3	1.975	A	3085[a]	3107[a]	0
17	88.0	11.7	0.3	1.974	A	3054[a]	3069[a]	0
18	88.0	11.7	0.3	1.971	A	3100[a]	3124[a]	0
19	79.8	19.8	0.4	2.000	A	3052[a]	3090[a]	<1
20	79.8	19.8	0.4	1.982	A	3059[a]	3089[a]	<1
21	79.8	19.8	0.4	1.967	A	3066[a]	3079[a]	<1
22	79.8	19.8	0.4	1.954	A	3074[a]	3109[a]	<1
23	79.8	19.8	0.4	1.950	A	3079[a]	3097[a]	<1
24	79.8	19.8	0.4	1.942	A	3092[a]	3118[a]	<1
25	70.0	29.7	0.3	2.000	A	2967[a]	3047[a]	14
26	70.0	29.7	0.3	1.983	A	2979[a]	3073[a]	8
27	70.0	29.7	0.3	1.966	A	3025[a]	3062[a]	7
28	70.0	29.7	0.3	1.939	A	2995	3038	10
29	70.0	29.7	0.3	1.922	A	3041	3055	4
30	59.7	39.8	0.5	2.000	A	2910[a]	3024[a]	19–20
31	59.0	40.0	1.0	1.885	A	2981	3018	11.2

[a] Melting points were reported in previous works [6,10].
[b] The arrest was not detected during heating up to 2992 K.