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THE PSEUDO TERNARY SYSTEM $\text{BeO-UO}_2\text{-PuO}_2$

C. E. McNEILLY

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By

C. E. McNeilly

Ceramics and Graphite Research Section
Materials Department

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INTRODUCTION

Parametric core-design studies of the Fast Flux Test Facility (FFTF) have indicated a need for softening the neutron spectrum to obtain a more negative Doppler coefficient for high plutonium loadings (~25 vol% PuO_2). One method of achieving this softening is to incorporate BeO in a UO_2 - PuO_2 fuel in the approximate composition of 60 vol% UO_2 , 30 vol% PuO_2 , 10 vol% BeO, (which corresponds quite closely to 50 mole % UO_2 , 25 mole % PuO_2 and 25 mole % BeO). However, the possibility that a low-melting eutectic is formed in the ternary system must be ascertained before the performance of such a fuel can be evaluated. The purpose of this work was to determine the ternary diagram, $\text{BeO}-\text{PuO}_2-\text{UO}_2$.

The binary phase diagrams (Figures 1a, 1b, and 1c), have been partially determined for the systems $\text{BeO}-\text{UO}_2$ ⁽¹⁾, $\text{BeO}-\text{PuO}_2$ ⁽¹⁾, and PuO_2-UO_2 ^(2,3), and considerable information regarding the probable ternary diagram can be derived from these.

SUMMARY AND CONCLUSIONS

All of the results obtained in this study agree with our predictions made from the study of published binary phase diagrams and crystal chemistry considerations:

- BeO did not form a ternary

compound or solid solution with $(\text{Pu}, \text{U})\text{O}_2$.

- Under conditions of no oxygen loss, the lowest solidus in the ternary system is that of $\text{BeO}-\text{PuO}_2$ binary (~2135 °C).
- If oxygen loss could occur, the lowest solidus would be about 2000 °C.

PROCEDURE

Phase relationships in the $\text{BeO}-\text{UO}_2-\text{PuO}_2$ ternary were determined by metallography, X-ray diffraction analysis, and melting point determinations on sintered pellets. Nineteen samples were examined whose compositions were in the region of the expected eutectic "valley." These covered the range of 50 to 92 mole % BeO, 4 to 50 Mole % UO_2 and 4 to 30 mole % PuO_2 . (See Appendix for exact mole and volume percents.)

SAMPLE FABRICATION

One-quarter inch diameter by 1/4 in. high pellets were dry pressed from blended powders of the desired compositions. Since the BeO was in the form of submicron size particles, it acted as a very effective binder, and no additional binder was required. Sintering for 8 hr at 1600 to 1650 °C in an Ar-8% H_2 atmosphere produced complete solid solubility of the PuO_2-UO_2 .

FIGURE 1a. BeO-PuO₂ Binary Diagram

FIGURE 1b. PuO_2 - UO_2 Binary Diagram

FIGURE 1c. UO_2 -BeO Binary Diagram

DISCUSSION

METALLOGRAPHY

Metallography was performed primarily to detect any reaction zones between the BeO grains and the (Pu,U)O₂ solid solutions not detected by X-ray diffraction (Figures 2a, 2b, and 2c). In all photomicrographs the gray area is BeO, the white is (Pu,U)O₂, and the black is porosity. Figure 2c appears much different from 2a and 2b because the etchant used for all samples was not as suitable for a sample with so high a UO₂ content. Also, the sample was not quite as well sintered as the others.

As expected, no reaction zone was detected in any of the samples.

X-RAY DIFFRACTION

The extent of solid solution and/or compound formation was determined by X-ray diffraction. Complete solid solution of the PuO₂ and UO₂ was apparent in all samples. The lattice parameters observed for the (Pu,U)O₂ solid solution in contact with BeO were in quite good agreement with those calculated for a pure (Pu,U)O₂ solution (Table I), indicating no solubility of BeO. A solution of BeO in (Pu, U)O₂ would not be expected because: (1) BeO crystallizes in the hexagonal system while (Pu,U)O₂ is cubic, and (2) Be⁺² has an ionic radius of 0.35 Å compared to 0.98 Å for Pu⁺⁴ and U⁺⁴.

No diffraction lines attributable to any third phase were detected.

TABLE I. Observed Lattice Parameter of the Ternary Solid Solution Compared to Calculated Values

Solid Solution Composition (mole %)		Å Calculated	Å Observed
UO ₂	PuO ₂		
30	70	5.419	5.420
36	64	5.423	5.425
50	50	5.433	5.435
62	38	5.442	5.443
70	30	5.448	5.447
84	16	5.458	5.456
88	12	5.461	5.459

MELTING POINTS

The liquidus of the ternary system in the vicinity of the eutectic "valley" was determined by observing melting of the samples in a tungsten "V" filament furnace filled with a helium atmosphere. Small, irregular chunks of material (1 to 2 mm in diameter) were placed in the bottom of the "V" filament and observed with a micro-optical brightness pyrometer. The melting point was determined by measuring the temperature of the tungsten filament when the sample melted. Two to five determinations were made on each composition. The system was calibrated by using materials of known melting point (Pt, Zr, Al₂O₃, Ir, Mo, and BeO), and overall accuracy of the system is estimated to be ± 25 °C.

Even though the samples were heated quite rapidly, the PuO₂-rich solutions would be expected to lose oxygen. From the results of the Hough and Marples⁽¹⁾ work on the BeO-PuO₂-ThO₂ system, we can assume

FIGURE 2. Polished and Etched Samples from BeO-UO₂-PuO₂ Ternary
[Areas are: gray-BeO, white-(Pu,U)O₂ and black-Porosity]

that the melting points observed in the present study for the PuO_2 -rich compositions may be as much as 135 °C too low. Figure 3 shows the melting points obtained in our work. If a reasonable correction is applied to allow for the lower melting points observed for the oxygen-deficient samples, we can construct a diagram as shown in Figure 4.

This would indicate that the lowest melting composition in the ternary would be the BeO-PuO_2 eutectic (ca. 34 mole % PuO_2) with a melting point of 2135 °C. Under conditions where the oxygen, which is driven off from the PuO_2 -rich solid solutions, could be permanently lost from the solid solution, a low melting point of about 2000 °C could be expected.

FIGURE 3. As-Determined Melting Points in the BeO-Rich Position of the $\text{BeO-PuO}_2\text{-UO}_2$ Ternary (mole %)

FIGURE 4. Proposed BeO-PuO₂-UO₂
Ternary Showing Melting Point
Corrected for Oxygen Loss (mole %)

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APPENDIX

TABLE IA. Compositions and Melting Points of Ternary Samples

Composition						Melting Point	
BeO		UO ₂		PuO ₂		Measured	Corrected ^(a)
Vol%	Mole %	Vol%	Mole %	Vol%	Mole %		
25.7	50.0	30.1	20.0	44.1	30.0	2165	2245
25.7	50.0	39.2	26.0	35.2	24.0	2240	2300
25.6	50.0	50.5	33.6	24.0	16.4	2250	2280
25.4	50.0	61.6	41.0	13.1	9.0	2260	2280
25.5	50.0	71.7	47.6	3.5	2.5	2270	2280
35.8	60.1	7.1	3.97	57.1	35.9	2060	2170
33.9	60.1	20.2	11.9	45.8	27.9	2150	2200
33.8	60.0	33.5	20.0	32.7	20.0	2175	2230
33.6	60.0	47.0	28.0	19.4	12.0	2230	2240
33.9	60.4	61.0	36.5	5.0	3.1	2230	2230
42.5	68.1	7.3	3.97	50.2	27.9	2090	2210
42.2	68.0	22.1	12.0	35.7	19.9	2130	2200
42.1	68.0	36.7	20.0	21.2	12.0	2240	2250
41.5	67.6	51.5	28.4	7.0	3.94	2235	2240
52.3	76.1	8.0	3.9	39.7	20.0	2115	2240
51.9	76.0	24.3	12.0	23.7	12.0	2245	2300
51.8	75.9	40.4	20.1	7.8	3.96	2280	2300
78.1	91.2	11.0	4.3	10.8	4.4	2430	2480
64.0	84.0	27.1	12.0	8.7	4.0	2330	2370

(a) This correction is based on an error of -135 °C at the BeO-PuO₂ eutectic. The amount of correction is decreased in proportion to the amount of PuO₂ in the (Pu,U)O₂ solid solution.

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