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GEAP-5634
AEC RESEARCH AND
DEVELOPMENT REPORT
MAY 1968

A THERMODYNAMIC DATA PROGRAM INVOLVING PLUTONIA AND URANIA AT HIGH TEMPERATURES

QUARTERLY REPORT NO. 3

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U.S. ATOMIC ENERGY COMMISSION
CONTRACT AT(04-3)-189
PROJECT AGREEMENT 53

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Prepared for the
United States Atomic Energy Commission
Contract No. AT(04-3)-189, Project Agreement 53

*Printed in U.S.A. Available from the
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A THERMODYNAMIC DATA PROGRAM INVOLVING PLUTONIA AND URANIA AT HIGH TEMPERATURES

E. A. Aitken
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ABSTRACT

Melting point data for PuO_{2-x} and $\text{U}_{.6}\text{Pu}_{.4}\text{O}_{2-x}$ solid solutions in the hypostoichiometric region were obtained by the thermal arrest method.

The data show a maximum at an oxygen-to-plutonium ratio between 1.70 and 1.80 for both compositions. The liquidus and solidus temperatures are nearly coincident for the PuO_{2-x} case and differ by about 35° for the mixed oxide composition. The melting point of PuO_{2-x} falls steeply at an oxygen-to-plutonium ratio below 1.73. The solidus temperature of $\text{PuO}_{1.61}$ was found to be 2300°C . The results on the melting behavior of PuO_{2-x} are compared with similar data for UO_{2-x} .

1. INTRODUCTION

This quarterly report is the third* in a series directed toward gathering thermodynamic information about segregation of urania-plutonia solid solutions used in fast reactor environments. The initial phase of the program is directed at one type of segregation which may arise from liquid-solid phase transformations. Emphasis is on the hypostoichiometric compositions. The over-all scope of the program was presented in the first quarterly report.⁽¹⁾

Data on the melting behavior of plutonia and 40 mole % plutonia solid solution are presented as a function of stoichiometry. The presence of a maximum in the melting temperature versus stoichiometry curve appears to be characteristic of the plutonia valence.

2. EXPERIMENTAL STUDY OF THE MELTING BEHAVIOR

General methods of preparation and determination of the melting point from cooling curves were described previously.⁽¹⁾

2.1 FABRICATION

The pellets were fabricated from calcined powder obtained by oxalate precipitation for urania-plutonia solutions. All pellets were sintered in a dry 6% hydrogen - 94% nitrogen or helium gas mixture at 1500°C for 4 hours. This operation gave pellets with a stoichiometry which corresponded to an oxygen-to-plutonium ratio of 1.80 to 1.90.**

* The previous reports issued in this series were GEAP-5358 and GEAP-5395, the first and second reports, respectively.

** The oxygen-to-plutonium ratio is calculated from the measured oxygen-to-metal ratio by assuming that the oxygen-to-uranium ratio is a fixed value of 2.00 for all hypostoichiometric compositions.

Other oxygen-to-plutonium ratios could be made by additional heat treatment in the appropriate gas environment. For pellets with an oxygen-to-plutonium ratio near 2.00, the sintered pellets were oxidized and then reduced in 6% hydrogen - 94% helium at 900°C; for pellets with an oxygen-to-plutonium ratio between 1.70 to 1.75, the pellets were heated in dry hydrogen with a zirconium-titanium gettering alloy nearby to facilitate removal of water evolved by the pellet.

To obtain oxygen-to-plutonium ratios of 1.6, pieces of 80% plutonium - 20% zirconium alloy wire or uranium metal were placed in the proper ratio in the capsule with the sintered pellet so that the net oxygen-to-plutonium ratio would be 1.6 after the capsule reached melting temperature. Several studies have shown that because of the high mobility of oxygen, the metal becomes quickly oxidized at temperatures above 2000°C and the composition of the oxidized metal is indistinguishable from that of the original pellet. The presence of zirconium which was less than 1% of the cation fraction was assumed to have a negligible effect on the melting temperature. The zirconium is expected to behave like plutonium or uranium metal by oxidizing to ZrO_2 which becomes part of the solution.

These heat treatments cover the practical range of oxygen-to-plutonium ratios for reactor applications. Intermediate values of oxygen-to-plutonium ratios may be obtained readily by variation of the oxygen activity of the hydrogen gas or by control of time at temperature.

2.2 TEMPERATURE MEASUREMENT

An Ircon model 11X30 Automatic Optical Pyrometer has been procured to provide a continuous temperature measurement during thermal arrest measurements. The pyrometer employs a silicon detector operating in the red end of the visible spectrum whose output is fed into a Moseley 680 variable speed strip chart recorder. The output of the Ircon pyrometer is calibrated with a micro-optical pyrometer.

The major advantage of the Ircon pyrometer is the elimination of reliance on visual observation of the beginning of a thermal arrest. In the past, temperature measurements have been made every 10 seconds visually, with a micro-optical pyrometer. Experience has shown that observer fatigue introduces random errors into the temperature measurement which can alter an indication of the onset of a thermal arrest. The use of a pyrometer with a continuous readout eliminates this problem.

The procedure consists the following steps:

1. Bring capsule to a temperature within 100°C of melting temperature.
2. Read blackbody hole temperature with micro-optical pyrometer.
3. Measure output on recorder for same setting.
4. Raise temperature of sample at controlled rate to above melting temperature and record output continuously.
5. Read blackbody temperature with micro-optical pyrometer.
6. Lower temperature of sample at controlled rate and record output continuously until original temperature is obtained.
7. Read blackbody temperature with micro-optical pyrometer.

By this method the thermal arrest can be detected on both heating and cooling as shown in Figure 1. The thermal arrest curve on heating tends to define the solidus temperature more clearly, while the liquidus temperature is more sharply defined on the cooling curve.

During this quarter, the efficiency of the induction generator was improved so that temperatures in excess of 3000°C were possible in the melting point apparatus. This improvement enabled the extension of the calibration curve for the apparatus to the melting point of tantalum (2996°C). The observed temperature for the melting point of tantalum coincided with a linear extrapolation of the calibration curve obtained from melting standards used at lower temperatures.

2.3 RESULTS

A summary of the results of the melting study are presented in Table 1 together with the method of fabrication and the oxygen-to-plutonium ratio. The capsules containing 60 mole % plutonia are being prepared for measurement next quarter. Future studies will include a re-examination of the 20 mole % composition series and a special measurement to detect oxygen-to-metal ratio differences between the

FIGURE 1. THERMAL ARREST HEATING AND COOLING CURVES BY RECORDING PYROMETER TECHNIQUE FOR $\text{PuO}_{1.846}$

TABLE 1. Summary of Melting Point Behavior of Urania-Plutonia Solid Solutions

Mole Fraction PuO _{2-x}	Heat Treatment ^(a)	O:M Ratio	O:Pu Ratio	Solidus-Liquidus Range, °C	Remarks	
1.0	A	2.00	2.00	2445 - 2445	2390 by visual observation	
	B	1.84 ₆	1.84 ₆	2445 - 2470		
	B ^(b)	1.78 ₅	1.78 ₅	2467 - 2472		
	C	1.73	1.73	2470 - 2470	2490-2510 by visual obser- vation By visual ob- servation only	
	D	1.61	1.61	2300 - ?		
0.4	A	2.00	2.00	2685 - 2745		
	B	1.96	1.90	2737 - 2772		
	C	1.91	1.78	2750 - 2782		
	D	1.84	1.60	2730 - 2765		
0.6	A	2.00	2.00	To be completed		
	B	1.91	1.85			
	D	1.84	1.73			
	D	1.76	1.60			

(a) The types of heat treatments are identified as follows:

A - Sinter in dry H for 4 h at 1500°C - oxidize in air at 900°C - reduce in hydrogen at 900°C

B - Sinter in dry H₂ for 4 h at 1500°C

C - Sinter in dry H₂ for 4 h at 1500°C - reduce in H₂ for 50 to 70 h at 1500°C with Zr-Ti getter

D - Sinter in dry H₂ for 4 h at 1500°C - add Pu and U metal to adjust O:M ratio

(b) Sample heated for an additional 4 h

liquid and solid phase. The solidus and liquidus temperatures shown in Table 1, column 5 represent data obtained by the electronic sensor during repeated cycling through the melting point.

The values for PuO_{2-x} have been revised slightly from those reported last quarter when the data were taken by visual observation of the cooling curve only. The observed melting point for the stoichiometric composition was slightly higher than reported by visual means last quarter. The earlier result was obtained on air-fired PuO_2 pellets and capsule failure rate was high. By reducing the pellet in hydrogen at 900°C , the oxygen activity was reduced significantly with very little change in stoichiometry. As a result, an increased number of cycles was obtained and enabled a better opportunity for determining the melting temperature. No capsule failures have occurred in hypostoichiometric compositions.

The liquidus and solidus temperatures are shown in Figure 2 as a function of oxygen-to-plutonium ratio. The appearance of a maximum in the melting point appears to occur near an oxygen-to-plutonium ratio of 1.80 for both PuO_{2-x} and $\text{Pu}_{0.4}\text{U}_{0.6}\text{O}_{2-x}$ compositions. The data suggest that the melting point variation with stoichiometry is controlled by the oxygen-to-plutonium ratio rather than oxygen-to-metal ratio.

For PuO_{2-x} , there is a rapid decrease in melting temperature below an oxygen-to-plutonium ratio of 1.7. One data point at an O:Pu ratio of 1.61 which was obtained visually on an open capsule gave a clear indication that the solidus temperature was 2300°C . The liquidus temperature could not be distinguished in this experiment.

In contrast the 40 mole % plutonia composition exhibited only a small decrease in melting temperature below an O:Pu ratio of 1.7. Since the PuO_{2-x} lattice is highly deficient at an O:Pu ratio of 1.6 and transforms to the body-centered cubic structure, it is not surprising that a sudden change in melting temperature should occur. The $\text{Pu}_{0.4}\text{U}_{0.6}\text{O}_{2-x}$ lattice is not nearly as deficient for the same oxygen-to-plutonium ratio so that defect fluorite structure remains stable.

The difference in the liquidus and solidus temperatures for the PuO_{2-x} composition is small especially near the maximum. This observation would be expected from thermodynamic principles for a two-component system. The data for the 40 mole % PuO_2 composition indicate an almost constant difference of about 35°C between the solidus and liquidus temperatures even near the maximum. Since this composition has three components, coincidence of the liquidus and solidus temperature at the maximum point in the figure is not required by thermodynamics.

3. DISCUSSION OF RESULTS

The results obtained so far suggest that the oxygen-to-plutonium ratio is the governing factor. It is interesting to note that the maximum melting temperature has appeared near an oxygen-to-plutonium ratio of 1.75. This value corresponds to equal fractions of Pu^{III} and Pu^{IV} cations.

FIGURE 2. MELTING POINT OF HYPOSTOICHIOMETRIC PLUTONIA AND 40% Pu-60% U MIXED OXIDES VERSUS STOICHIOMETRY

In an earlier report⁽¹⁾ a model for predicting melting behavior as a function of stoichiometry was developed. In the model an interaction parameter between the components in the liquid and in the solid phase was used to express nonideal behavior. It was assumed that the strength of the interaction parameter in the solid phase was proportional to the Pu^{III} content. If this interaction term was negative then a maximum in the melting temperature would occur in the hypostoichiometric region. A tentative indication from the data so far suggests that the interaction term instead is proportional to the product of the Pu^{III} and Pu^{IV} content. In this way, the maximum melting temperature would occur at an oxygen-to-plutonium ratio of 1.75.

With only a few changes in the computer program the liquid-solid transformation model was applied to the two-component case, PuO_{2-x} . The interaction parameter was adjusted to give the best fit. Figure 3 shows a comparison of the experimental data with calculated curve from the model for the case where the interaction term, B_s^* , is -5000 and -3500 cal/mole. For the calculation, it was assumed that the melting temperature of $\text{PuO}_{1.5}$ was 2085°C and that of PuO_2 was 2445°C. Since the $\text{PuO}_{1.5}$ composition exists as a different structure than PuO_2 , the model is not applicable at compositions near $\text{PuO}_{1.5}$.

The system UO_{2-x} exists over a wide hypostoichiometric range and is structurally similar to PuO_{2-x} . A comparison of its liquid-solid transformation would be a useful means of understanding the effect of stoichiometry on the melting behavior of these fuel materials. Recently melting data by filament methods were presented by Bannister⁽²⁾ which showed no maximum in the melting temperature and considerable spread in the liquidus-solidus temperatures at hypostoichiometric compositions. Earlier, Bates⁽³⁾ used the filament method also and obtained indications of a maximum melting temperature. Latta and Fryxell⁽⁴⁾ used the thermal arrest method and obtained no maximum on the hypostoichiometric composition side but no distinction was made between liquidus and solidus temperatures at that time. The liquidus and solidus curves reported by Bannister are shown in Figure 3. The data of Latta and Fryxell follow closely the solidus curve rather than the liquidus. Comparison of the experimental curves with the liquidus and solidus curves obtained by adjustment of the interaction parameter in the calculated model indicates that the closest fit occurs when B_s is zero or slightly positive. In this calculation, it was assumed that the melting point of $\text{UO}_{2.00}$ was 2855°C and the melting point of $\text{UO}_{1.5}$ was 2380°C. Since $\text{UO}_{1.5}$ is not stable, the choice of a melting point represents the approximate convergence of the liquidus and solidus at the monotectic composition. The actual spread between the liquidus and solidus is somewhat larger than what would be predicted by the model and may be the result of the invalid assumption of complete miscibility in the $\text{UO}_{2.0}$ - $\text{UO}_{1.5}$ range.

FIGURE 3. COMPARISON OF LIQUIDUS-SOLIDUS CURVES OF UO_{2-x} AND PuO_{2-x} WITH CALCULATED CURVES FROM MODEL

* As used in GEAP-5538, B_ℓ , the interaction term for the liquid phase, is assumed zero.

The negative value of the interaction term, B_s , for PuO_{2-x} suggests that the presence of Pu^{III} ion stabilizes the solid phase relative to the liquid phase whereas the presence of U^{III} ion does not. It is difficult to describe how stabilization occurs since both the entropy and enthalpy of the solution are affected by nonstoichiometry. It is known that Pu^{III} is easier to form than the U^{III} hence the extra energy required for U^{III} formation is not offset by the other stabilizing factors and no maximum in the melting point is observed.

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