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A THERMODYNAMIC DATA PROGRAM INVOLVING PLUTONIA AND URANIA AT HIGH TEMPERATURES

QUARTERLY REPORT NO. 6

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U.S. ATOMIC ENERGY COMMISSION
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ABSTRACT

In the fifth quarterly report (GEAP-5720) the continuing scope of work related to measurement of liquidus-solidus transformations, vaporization of urania, and oxygen redistribution in a temperature gradient was presented. Work progress is reported on these tasks with preliminary data presented on UO_2 - 20% PuO_2 thermal gradient experiments carried out in the temperature range 1200 to 1600°C.

1. INTRODUCTION

This quarterly report is sixth in a series which describes experiments directed toward understanding plutonium segregation in urania-plutonia solid solutions used in fast reactor environments.

In the fifth quarterly report (GEAP-5720), the scope of several new activities initiated in that period which have a bearing on plutonium segregation is described.

In this report, progress made in each of these areas during the report period is described.

2. LIQUID-SOLID TRANSFORMATIONS

During the course of this report period, it was necessary to relocate the plutonium enclosure containing the melting point determination equipment. As a result, further melting experiments must be postponed until reinstallation of that equipment is completed. However, efforts have gone forward to prepare specimens for future experiments.

It was noted in the fourth quarterly report (GEAP-5672) that only visual determinations of the $\text{PuO}_{1.61}$ melting point were made. Plutonia pellets were fabricated, spiked with plutonium metal, and encapsulated in molybdenum to provide melting specimens with oxygen-to-plutonium ratios of 1.6 and 1.5. These measurements will complete the series of melting experiments and are necessary to provide data for further application of the solution theory model developed in the first quarterly report.

3. DETERMINATION OF COMPONENT ACTIVITIES

The fifth quarterly report described the scope of work to be followed in determination of uranium activity in mixed oxide solutions.

Initial measurements have been carried out with UO_2 using air as a carrier gas. Difficulties in maintaining a constant gas flow rate have resulted in failure to establish reproducibility in the measurements.

Addition of a metering valve has resulted in flow stability, but the nonreproducibility in the uranium deposition rates remains. Efforts are being made to identify the sources of error, such as leaks in the system, which would lead to unsatisfactory results.

When the system has been successfully operated and optimum flow rates have been established, the carrier gas will be changed to a CO-CO₂ mixture to provide oxygen activities more representative of fuel conditions.

Following measurements with 10/1 and 1/10 CO/CO₂ mixtures, experiments will be carried out with UO₂ - 40% PuO₂ to investigate possible departures from ideal behavior.

4. OXYGEN MIGRATION IN MIXED OXIDE SYSTEMS

During studies on oxygen migration in mixed oxide systems conducted under other AEC programs, ⁽¹⁾ several capsules containing UO₂ - 20% PuO₂ pellets of various stoichiometries were subjected to temperature gradients. Following the heat treatments, the pellets were subjected to a destructive thermogravimetric oxygen-to-metal ratio determination. Before the destructive examination, electrical conductivity measurements were carried out on the pellets from one capsule. The measurements were carried out with a tungsten probe device described elsewhere. ⁽²⁾ Briefly, the device measured current flow in a series circuit containing a voltage source, the tungsten probe, and the sample. The small (~100 micron) tungsten tip contacted the right circular specimens at various points on the cylindrical surface. A metal plate contacting the specimen on the opposite side was used as the bottom electrode. The small size of the probe made it possible to examine resistivity gradients which existed in individual pellets. As long as the sample geometry remained constant, the current measurement was indicative of the resistivity of the sample; i. e., it provided a comparative measure of resistivity between the sample being measured and other samples of the same geometry. Baily and Lyon ⁽³⁾ have shown that resistivity in UO₂ - 20% PuO₂ increases as the oxygen-to-metal ratio decreases below 2.00. The results of the tungsten probe measurements as shown in Figure 1 confirm the resistivity increase and also indicate that resistivity is more sensitive to changes in oxygen activity near a stoichiometry of 2.00 than thermogravimetric oxygen-to-metal ratio determinations. As a result of these data, it was decided to measure resistivity on all pellets from future thermal gradient experiments.

As stated in the fifth quarterly report, thermal diffusion measurements in the region 1200 to 1600°C have been undertaken. Five 12-inch molybdenum tubes (0.25 inch inside diameter) were loaded with UO₂ - 20% PuO₂ pellets at an initial oxygen-to-metal ratio of 1.97. The tubes were heated in the gradient for 4, 15, 120, 300, and 1000 hours, respectively. Following the heat treatment, each tube was opened, and the pellets removed.

Resistivity measurements on the 4-, 15-, and 1000-hour pins have shown a lack of reproducibility primarily because cracks occurred in the pellets during fabrication. Consequently, those results are not presented here.

The oxygen-to-metal ratio determinations for the 4- and 15-hour pins are shown in Figures 2 and 3, respectively. No evidence for a trend toward oxygen migration was observed in either of these pins. The small variations observed in the oxygen-to-metal ratios are due to initial variability or limits in precision of the oxygen-to-metal ratio determination. The greater scatter in the 4-hour results is due to the use of a slightly less sensitive balance in those measurements.

Initial O:M = 2.000
Final O:M = 1.996

FIGURE 1. THERMAL GRADIENT CAPSULE NO. 9

Since the two pins annealed for the shortest time exhibited no oxygen migration, it was decided to examine next the pin which was annealed for the longest time period in the test, the 1000-hour anneal. The same balance was used for these O:M measurements as in the 15-hour test and will be used in all future O:M determinations.

Partially complete O:M measurements are shown in Figure 4 for the 1000-hour test with the temperature gradient existing during the test. Since the data exhibit evidence for oxygen migration in the pin, the logarithm of the deviation from stoichiometry was plotted as a function of reciprocal temperature as shown in Figure 5. The approximate arithmetic mean of the stoichiometry data was used in constructing the plot. A heat of transport of -65.5 kcal/mole was calculated from the linear plot obtained. This value is much more negative than those obtained from similar experiments carried out at higher temperatures on other AEC programs, ⁽¹⁾ and indicates that a different mechanism for oxygen transport is operating at lower temperatures.

FIGURE 2. THERMAL GRADIENT TEST, UO_2 -20% PuO_2 (4 hours)

FIGURE 3. THERMAL GRADIENT TEST, $\text{UO}_2\text{-20\% PuO}_2$ (15 hours)

FIGURE 4. PARTIALLY COMPLETE THERMAL GRADIENT TEST FOR UO_2 -20% PuO_2 (1000 hours)

FIGURE 5. PARTIAL RESULTS FOR $\text{UO}_2\text{-}25\%\text{PuO}_2$ 1000-HOUR THERMAL GRADIENT TEST

It was shown in these experiments^(1, 4) that the oxygen migration behavior can be explained on the basis of one component transport by a cyclic mechanism involving both solid phase diffusion of oxygen and gas phase diffusion with a $\text{H}_2/\text{H}_2\text{O}$ medium. This mechanism can result in a heat of transport of the order of -10 kcal/mole as observed. Migration by either solid state diffusion or by gas phase transport alone give more negative values for the heat of transport. Since gas phase transport would be expected to decrease faster with a temperature decrease than solid state diffusion, the mechanism which is observed in the current study is probably solid state diffusion of oxygen in the temperature gradient. However, the data obtained to date are incomplete and may be subject to revision when more complete information is available.

An understanding of the processes involved in oxygen migration under temperature gradients in the urania-plutonia system cannot be obtained without knowledge of the migration behavior on the end members of the system. Studies have already been carried out for UO_{2-x} ⁽⁵⁾ but no similar information is available for PuO_{2-x} . Consequently experiments are in progress to define oxygen transport behavior in hypostoichiometric plutonia which is subjected to a temperature gradient.

Pellets of PuO_{2-x} with a stoichiometry of 1.79 oxygen-to-plutonium ratio have been fabricated and loaded into 12-inch molybdenum tubes (0.25 inch inside diameter). The tubes were sealed and are undergoing exposure to a constant temperature gradient in the region 1200 to 1600°C. Tests are being run on five tubes heated for increasing lengths of time up to 3000 hours. After a given heat treatment, the pellets will be removed for resistivity and oxygen-to-metal ratio determinations. The results are expected to yield kinetic and steady-state data concerning PuO_{2-x} to supplement information obtained for urania-plutonia solutions.

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