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**A THERMODYNAMIC DATA
PROGRAM INVOLVING
PLUTONIA AND URANIA AT
HIGH TEMPERATURES**

QUARTERLY REPORT NO. 5

**E. A. AITKEN
S. K. EVANS**

**U. S. ATOMIC ENERGY COMMISSION
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**NUCLEONICS LABORATORY
NUCLEAR TECHNOLOGY DEPARTMENT**

GENERAL ELECTRIC

PLEASANTON, CALIFORNIA

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ABSTRACT

The first four quarterly reports on thermodynamic information about segregation of urania-plutonia solid solutions used in fast reactor environments appeared as GEAP-5358, GEAP-5395, GEAP-5634 and GEAP-5672. The over-all scope of the program was presented in GEAP-5358.

Work progress is reported on tasks related to the measurement of liquidus-solidus transformations, vaporization of urania and oxygen redistribution in a temperature gradient. Several thermal diffusion mechanisms are derived for oxygen redistribution in fast reactor fuel.

1. INTRODUCTION

Previous work was concentrated on the liquid-solid transformation of the hypostoichiometric composition of a urania-plutonia system. During this quarterly report period, several new activities were started on other aspects of the solid solution thermodynamics which have a bearing on Pu segregation. These activities include measurement of uranium activity in the solid solution by thermal transpiration and measurement of stoichiometry shifts due to an imposed thermal gradient.

2. LIQUID-SOLID TRANSFORMATION

In the previous quarterly report, the liquidus and solidus temperatures for hypostoichiometric urania-plutonia solutions were presented as a function of plutonia concentration. Melting point maxima were shown to occur for compositions which had an equivalent O-to-Pu ratio of 1.75 and a high Pu concentration. At present, it appears that the segregation of plutonium due to the phase separation will be about the same regardless of the stoichiometry. This reasoning is based on the assumption that the hypostoichiometric system is an ideal mixture of UO_2 and PuO_{2-z} which would allow one to claim that the O-to-Pu ratio of the coexisting liquid and solid phases are identical. Special melting experiments have been designed to determine if any stoichiometry shift does occur between the liquid and solid phase.

The measurement is based on an isothermal treatment of two different compositions at a temperature where one composition is molten and the other is solid. If the two materials are allowed to be in direct contact then the two compositions would dissolve in each other and result in only one composition. On the other hand, if the two compositions are separated by a semi-permeable membrane, such as Ta, then oxygen can migrate between the two compositions without mutual dissolution.

Molybdenum capsules have been fabricated for these special experiments. The sealed capsule will contain a large pellet containing a high Pu concentration. Inside this pellet will be a small sealed Ta tube which contains a second pellet at a lower Pu concentration than the first. The smaller pellet will remain as a solid during the heat treatment while the larger outer pellet will be molten.

After the heat treatment, the capsule will be opened and the oxygen-to-metal ratio of the solid pellet will be determined and compared with its initial value. The oxygen-to-metal ratio of the molten pellet after the heat treatment will also be measured if there is no contamination from the containers. The initial experiments will utilize compositions of 100% plutonia and 60% plutonia to give maximum sensitivity and allow ease of fabrication. The heat treatment temperature will be about 2550°C. If a stoichiometry shift is observed in this case, then further experiments will be carried out in the region of 20 to 40% plutonia. If no stoichiometry shift occurs (O-to-Pu ratio is the same) then the original assumption of ideal mixing will be considered valid and Pu segregation can be determined directly from this assumption.

3. DETERMINATION OF COMPONENT ACTIVITIES

Departures from ideal mixing are best determined by comparing component activities. Rand⁽¹⁾ has suggested that UO_2 and PuO_{2-z} are ideal mixtures from oxygen activity measurements on the solid solution at low temperatures. At low temperatures only the Pu species appears to be altermvalent in the hypostoichiometric region and only the uranium species is altermvalent in the hyperstoichiometric region. As the temperature is increased, both species will tend to become altermvalent so that the significant mixed valence character can coexist in an otherwise stoichiometric system. The presence of U^{V} , U^{VI} and Pu^{III} near the stoichiometric value can cause departures from ideality that would not have been detected previously and such a departure would have a bearing on a number of important properties, such as the U-to-Pu ratio in the vapor phase, and the reaction tendency of the fuel with sodium.

Transpiration measurements to determine the U activity near the stoichiometric composition have been initiated. A Marshall Pt-50% Rh wire-wound air furnace has been fitted with a sealed alumina tube in which will be placed powder samples of oxide material. A known quantity of air or a CO-CO_2 gas mixture will be passed over the powder and through an orifice in a Pt tube at 1200 to 1500°C. The vapor (principally UO_3) deposited on the interior of the Pt tube will be leached in nitric acid and analyzed for U and Pu. From this vapor, pressures will be determined which, in turn, will determine the U activity in the solid solution. The effect of stoichiometry on vaporization properties will be studied by altering the oxygen partial pressure of a buffering gas mixture.

Initial measurements will be made on UO_2 and $\text{UO}_{2-40\%} \text{PuO}_2$ to provide evidence for departures from ideality. If a significant departure is observed, then more compositions will be run to determine the character of the nonideal behavior.

4. OXYGEN MIGRATION IN MIXED OXIDE SYSTEMS

Temperature gradients in the fuel will cause composition changes to occur. This aspect of segregation is a complex interplay between transport rates and thermodynamic properties. During this quarter, considerable effort was expended in deriving mechanisms for thermal diffusion in fuel compounds. The results of the study and some experimental work on UO_{2-x} and $(\text{U, Pu})\text{O}_{2-x}$ carried out on other AEC programs will appear in the Journal of Nuclear Materials.⁽²⁾ Only a brief description of the mechanisms of oxygen transport in fuel oxides and its implications on fuel behavior will be given here.

It is known from experimental work that oxygen migrates rapidly along a stack of pellets heated in a closed container in an axial temperature gradient. Measurements at temperatures above 1700°C show that a steady-state composition gradient is established in a few hours. The composition changes uniformly along the gradient and even changes uniformly within the pellet itself. For hypostoichiometric compositions the oxygen tends to concentrate at the colder end of the temperature profile. Plots of the logarithm of the deviation from stoichiometry versus reciprocal temperature give a slope which is identified as the heat of transport, Q^* . Depending on the mechanism of transport, all or part of the heat of transport can be determined from the thermodynamic properties of the system.

A special feature of transport in fuels is that molecular species can migrate along the gradient in the vapor phase and solid phase. There are several vapor species which exist in equilibrium with the fuel at high temperatures and the relative importance of each depends on (a) the stoichiometry, (b) temperature and (c) the presence of auxiliary constituents. It is important to consider each of these factors in deriving a thermal diffusion mechanism. In the solid phase, oxygen diffusion occurs more rapidly than the cations, therefore, the cations are essentially fixed in the lattice during the time period to reach steady state. Cation mobility will be significant only when a vapor species containing the cation is present at a high enough vapor pressure. For the urania-plutonia solid solution, these vapor species do not appear to be as important as H_2O or CO_2 auxiliary gases present in most fuel pins.

In fuel bodies, vapor flow will occur by diffusion along cracks. Consequently, the free flow area for vapor transport will be smaller than the fuel flow area for solid phase transport. The mobility of the vapor phase constituents, however, is larger by several orders of magnitude than the mobility of oxygen in solid phase so that the net flow of constituents in the gas phase and the solid phase can be comparable at high temperatures. These parallel paths for transport give rise to three cases which may govern the type of thermal diffusion mechanism operating in a given system:

1. Dominant flow in the gas phase,
2. Dominant flow in the solid phase,
3. Comparable flow in both phases.

In urania-plutonia solutions, gas phase flow will be dominant when the oxygen-to-metal ratio is high, since the H_2O or CO_2 content of H_2 or CO cover gas becomes appreciable (i. e., $> 10^{-3}$ atm). A dominant gas phase flow requires that the H_2O or CO_2 partial pressure gradient vanish at steady state. If equilibrium is maintained between the gas phase and solid phase constituents at each point along the temperature gradient then the heat of transport, Q^* , may be determined from the following equation:

$$Q^* = \frac{1}{2} \bar{h}_{O_2} - \Delta H_{H_2O} + \Delta H_{H_2} \quad (1)$$

where $\bar{h}_{O_2}$ is the partial molar enthalpy of oxygen in the fuel phase, ΔH_{H_2O} and ΔH_{H_2} are the heats of formation of water and hydrogen, respectively. For a CO_2 - CO cover gas, the corresponding heats of formation for these gases should be used in place of H_2O - H_2 .

This condition was postulated by Markin and Rand⁽¹⁾ where they showed relationships between stoichiometry and temperature by graphical methods. The analytical method described above agrees with their observations in that the heat of transport should be about 60 to 70 kcal/mole

for hypostoichiometric urania-plutonia and that the oxygen should concentrate at the low temperature side. For hyperstoichiometric composition, Equation (1) predicts migration to the high temperature side of the profile.

The experimental results for urania-plutonia indicate much smaller heats of transport than predicted by Equation (1) except when the average oxygen-to-metal ratio is near stoichiometry. As the stoichiometric composition approaches 2.0, then H_2O partial pressure rises steeply so that gas phase transport of oxygen will become dominant and the conditions for applicability of Equation (1) are met. At lower oxygen-to-metal ratios, the H_2O partial pressure is lower and gas phase transport of H_2O becomes comparable to oxygen transport by diffusion in the solid. In this case, a pressure gradient of H_2O will develop. At steady state there will be a pressure gradient of H_2O and a composition gradient in the system. The situation may be visualized as equivalent to a cyclic flow of oxygen in the solid up the temperature gradient and a flow of H_2O in the gas phase down the temperature gradient. The flows balance each other at steady state. The result of this condition is that Q_{cyclic}^* is some fraction of Q^* from Equation (1). The experimental results suggest that the fraction is about 0.25. The reason for this value is not clear at this time.

Another interesting observation from the experimental results is that there is a small but significant change in the heat of transport with oxygen-to-metal ratio. This change is in the same direction and has the same magnitude that would be expected from the change in the partial molar enthalpy of oxygen in the fuel with oxygen-to-metal ratio.

The partial pressure of gas constituents in equilibrium with the fuel decreases with decreasing temperature and the gas phase transport rates diminish. The mobility of oxygen in the solid phase also decreases with decreasing temperature but to a lesser extent. Consequently, at low temperatures solid phase transport of oxygen may become the dominant transport mechanism. In the absence of a gas phase, the arguments used above do not apply since equilibrium between the gas and solid phase is not necessary. In this case, the analytical treatment is more complex and it is difficult to predict the heat of transport from thermodynamic data. Measurement of the heat of transport from thermal diffusion experiments is more fruitful.

Previous experiments have been confined to temperature gradients at temperatures above 1600°C , where high partial pressures of gases are present and steady-state conditions are established rapidly. At lower temperatures the mechanism may be different because of the expected dominance of solid state diffusion of oxygen. Thermal diffusion measurements in the region 900 to 1600°C have been started. Twelve-inch molybdenum tubes (0.25 inch inside diameter) have been fabricated for encapsulation of a stack of 20% PuO_2 pellets at an initial oxygen-to-metal ratio of 1.97. The molybdenum tubes will be sealed and exposed to a constant temperature gradient. Tests will be run on five tubes, each heated for increasing lengths of time up to 1000 hours. After a given heat treatment, the pellets will be removed and the oxygen-to-metal ratio will be determined and correlated with temperature at each position along the tube. The results are expected to yield kinetic and steady-state data about the thermal diffusion process in the lower temperature range of fuel temperatures.

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