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A THERMODYNAMIC DATA PROGRAM INVOLVING PLUTONIA AND URANIA AT HIGH TEMPERATURES

MASTER

QUARTERLY REPORT NO. 10
DECEMBER 1969 TO FEBRUARY 1970

E. A. AITKEN
S. K. EVANS

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Quarterly Report No. 10 — December 1969 to February 1970

E. A. Aitken
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CONTENTS

	<u>Page</u>
ABSTRACT	1
1. INTRODUCTION	1
2. DETERMINATION OF COMPONENT ACTIVITIES	1
3. OXYGEN MIGRATION IN (U,Pu)O _{2-x} SYSTEMS	2
4. SODIUM-FUEL INTERACTIONS	2
5. OXYGEN ACTIVITY STUDIES	2
REFERENCES	3

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E. A. Aitken and S. K. Evans

ABSTRACT

In the ninth quarterly report (GEAP-12047) the continuing scope of work related to vaporization of urania, oxygen redistribution in a temperature gradient, and sodium fuel interactions was presented. Work progress is presented on these tasks.

In addition, the scope of new experiments to extend the study of oxygen activity in $\text{UO}_2\text{-PuO}_2$ systems to higher temperatures is described.

1. INTRODUCTION

This quarterly report is the tenth in a series; experiments directed toward understanding plutonium segregation in urania-plutonia solid solutions used in fast reactor environments are described. In the ninth quarterly report (GEAP-12047) the progress of several experiments on plutonium segregation was described. Continued progress in these areas is described. New experiments to determine oxygen activity in the $\text{UO}_2\text{-PuO}_2$ system at high temperatures are discussed.

2. DETERMINATION OF COMPONENT ACTIVITIES

The determination of uranium activity in $\text{UO}_2\text{-PuO}_2$ solid solutions is being studied with a transpiration technique, air and CO/CO_2 are used as the carrier gases. Preliminary runs with U_3O_8 in air to establish the optimum flow rate were completed and reported in the last quarterly report (GEAP-12047). The data obtained were in general agreement with Alexander's¹ work.

Several experiments have been undertaken to determine the system response to lower uranium-bearing gas pressures than those produced by heating U_3O_8 in an air atmosphere. Samples of UO_{2+x} were heated in 10 CO_2/CO and $\text{CO}_2/10 \text{ CO}$ flowing gas mixtures to determine the UO_3 vapor pressures for these oxygen activities in the 1300 to 1400°C temperature range. The results of experiments conducted to date are summarized (Table 1). The data reported here for the 10 CO_2/CO mixture at 1407°C is about 40% lower than that reported by Alexander,¹ and agree with an earlier comparison made with Alexander's¹ data in the last quarterly report. The other experiments give higher values than Alexander's¹ data indicate, probably because the coulometric analysis used to detect the uranium in the transpiration tube leach solution loses accuracy for values of uranium much less than 1 mg. Also, small amounts of uranium may be introduced from the outside of the tube during the leaching process.

TABLE 1. Comparison of Transpiration Experiment Results with Alexander's¹ Data

Temperature (°C)	Gas	Total U Collected (mg)	UO_3 Pressure (atm)	Extrapolation from Alexander's Data (atm)
1320	10/1 CO_2/CO	1.23	3.05×10^{-7}	1.42×10^{-7}
1315	1/10 CO_2/CO	0.107	3.26×10^{-8}	1.20×10^{-9}
1400	1/10 CO_2/CO	0.081	2.14×10^{-8}	9.67×10^{-9}
1407	10/1 CO_2/CO	2.40	6.11×10^{-7}	1.06×10^{-6}

Two future experiments will be conducted at 1500°C using the carrier gases 10 CO₂/CO and CO₂/10 CO to ensure reproducibility in the results. Once the calibration of the apparatus with UO_{2+x} at different oxygen activities is complete, experiments will begin with compositions in the UO₂-PuO₂ system. These experiments will be conducted to investigate the affect of plutonium additions on the UO₃ partial pressure. If the UO₂-PuO₂ system exhibits ideal solution behavior, then the UO₃ partial pressure will be a linear function of the composition. If departures from ideality exist, more extensive experiments will be undertaken at higher temperatures to investigate them.

3. OXYGEN MIGRATION IN (U, Pu)O_{2-x} SYSTEMS

Interpretations of previous data based on Aitken's² one-component cyclic model were presented in the ninth quarterly report (GEAP-12047). According to the model, heats of transport observed during oxygen migration in a temperature gradient are dependent upon the concentration of oxygen vacancies in the crystal lattice. Since for any given oxygen activity, the number of oxygen vacancies are controlled by the plutonium content, then by varying the plutonium content while keeping the oxygen-to-plutonium ratio constant should have a predictable effect on the heat of transport in a temperature gradient. A similar effect should be observed where the plutonium content is kept constant, but the stoichiometry is varied. To investigate the validity of these hypotheses, thermal gradient experiments have been designed using three different fuel compositions: (U_{0.8}Pu_{0.2})O_{1.93}, (U_{0.8}Pu_{0.2})O_{1.99}, and (U_{0.6}Pu_{0.4})O_{1.94}. The last two compositions are undergoing 1000-hour anneals in a temperature gradient from 1200 to 1600°C. The first composition will begin a 1000-hour anneal during the next quarter.

The experiment described in the ninth quarterly report involving PuO_{2-x} pellets separated by molybdenum spacers to inhibit solid state diffusion is also scheduled to begin a temperature gradient anneal during the next quarter.

4. SODIUM-FUEL INTERACTIONS

The second set of nickel capsules has been fabricated and will be annealed at 600°C for 7 days. Following the anneal, the sodium and fuel will be characterized as described in the eighth quarterly report (GEAP-12032).

5. OXYGEN ACTIVITY STUDIES

As fast reactor research continues, it becomes apparent that fuel oxygen activity plays an important role in determining the life of the fuel assembly through effects on the cladding materials and possibly the sodium coolant if it allowed to come in contact with the fuel. Therefore, a knowledge of the initial oxygen activity in the fuel assembly is necessary to assess the performance potential of the fuel carefully.

Markin and McIver³ have studied oxygen activity in the UO₂-PuO₂ system as functions of composition and stoichiometry up to 1100°C using electrochemical techniques. They found that for hypostoichiometric compositions, the oxygen activity is dependent only upon the oxygen-to-plutonium ratio, while for hyperstoichiometric compositions, the oxygen activity is dependent only upon the oxygen-to-uranium ratio. These findings greatly simplify relationships in the mixed oxide system.

It is becoming increasingly well known that the most desirable fuel compositions are hypostoichiometric to reduce oxygen activity levels which lead to cladding attack and gross swelling upon introduction of sodium to the fuel-cladding system. The fabrication of such fuels thus becomes of increasing concern to the nuclear fuel manufacturer since the production of hypostoichiometric fuel of specified oxygen activity requires careful control of sintering furnace atmosphere conditions. Also, since the majority of the fuel in a typical fuel pin operates at temperatures greater than 1100°C, a knowledge of oxygen activity relationships at elevated temperatures is necessary for proper understanding of fuel behavior during irradiation. A series of experiments have been conceived to study oxygen activity relationships in the UO₂-PuO₂ system. Pellets consisting of UO₂-25% PuO₂ will be clad in tantalum and then annealed in a N₂-6%H₂ gas mixture of predetermined oxygen activity for a sufficient period to assure that equilibrium has been attained between the pellets and the atmosphere. Tantalum has been shown⁴ to be quite permeable to oxygen at elevated temperatures, therefore, its use as a cladding material in these experiments is well indicated.

Initial experiments must be performed to determine the length of anneal necessary to attain equilibration. Three capsules containing stoichiometric UO_2 -25% PuO_2 clad in tantalum will be annealed in dry N_2 -6% H_2 for various times at 1700°C to determine the length of time required to reduce the pellets to a constant hypostoichiometric condition. Following these experiments, a similar set of three capsules containing hypostoichiometric UO_2 -25% PuO_2 will be annealed at 1700°C in wet N_2 -6% H_2 to determine the length of time necessary to oxidize the pellets to the stoichiometric composition. These findings will serve as benchmarks in conducting higher temperature tests.

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