304
GEAP-12210
AEC RESEARCH AND
DEVELOPMENT REPORT
APRIL 1971

MASTER

RECEIVED BY DTIC OCT 26 1971

A THERMODYNAMIC DATA PROGRAM INVOLVING PLUTONIA AND URANIA AT HIGH TEMPERATURES

QUARTERLY REPORT NO. 15

E. A. AITKEN
M. J. ADAMSON
S. K. EVANS
T. E. LUDLOW

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

NUCLEONICS LABORATORY • GENERAL ELECTRIC COMPANY
VALLECITOS NUCLEAR CENTER, PLEASANTON, CALIFORNIA, 94566

GENERAL ELECTRIC

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

GEAP-12210
AEC Research and
Development Report
April 1971

A THERMODYNAMIC DATA PROGRAM INVOLVING PLUTONIA AND URANIA AT HIGH TEMPERATURES

Quarterly Report No. 15
February 1, 1971 — April 30, 1971

E. A. Aitken S. K. Evans
M. G. Adamson T. E. Ludlow

Approved:

H. W. Alter, Manager
Nucleonics Laboratory

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

*Printed in U.S.A. Available from the
Clearing House for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia*

Price: \$3.00 per copy

NUCLEONICS LABORATORY • GENERAL ELECTRIC COMPANY
VALLECITOS NUCLEAR CENTER, PLEASANTON, CALIFORNIA, 94566

GENERAL ELECTRIC

3466-NL-27
49-DAC/mea-7/71

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

CONTENTS

	<u>Page</u>
ABSTRACT	1
1. INTRODUCTION	1
2. THERMAL GRADIENT EXPERIMENTS WITH EXCESS SODIUM	1
3. DETERMINATION OF COMPONENT ACTIVITIES	2
4. OXYGEN MIGRATION IN (U,Pu)O ₂ SYSTEMS	2
ANALYTICAL MODEL	6
EXPERIMENTAL PROCEDURE	8
RESULTS	8
Composition and Stoichiometry Changes	8
Time Dependence of Heat of Transport	9
Spacer Experiments	15
Long Pellet Experiment	15
DISCUSSION	15
IMPLICATIONS TO FUEL IRRADIATION	20
5. A THEORETICAL STUDY OF PLUTONIUM-URANIUM SEGREGATION IN MIXED OXIDE FUELS	21
REFERENCES	21

ILLUSTRATIONS

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Arrhenius Plot of 1000 Hour Thermal Gradient Anneal of U _{0.75} Pu _{0.25} O _{1.966} with 49 mg Sodium	3
2.	Arrhenius Plot of 300 Hour Thermal Gradient Anneal of PuO _{1.8} with 138 mg Sodium	4
3.	UO ₃ Partial Pressure versus 1/T for UO _{2+x} and (U _{0.6} Pu _{0.4})O _{2+x} in Air	5
4.	Summary of Thermal Gradient Experiments between 2000 and 1500° with (U _{0.8} Pu _{0.2})O _{2-x}	10
5.	Arrhenius Plots of 1000-Hour Thermal Gradient Anneals	11
6.	Results of PuO _{2-x} Thermal Gradient Experiments	12
7.	Time Dependence of Mixed Oxide Thermal Gradient Experiments	13
8.	Time Dependence of Low Stoichiometry Thermal Gradient Experiments	14
9.	Thermal Gradient Experiments with Molybdenum Spacers	16
10.	Comparison of Spacer and Nonspacer Experiments	17
11.	Arrhenius Plot of 2000-Hour Thermal Gradient Anneal of Long Pellets of U _{0.75} Pu _{0.25} O _{1.956}	18
12.	Idealized Results for 2000-Hour Temperature Gradient Experiments	19

A THERMODYNAMIC DATA PROGRAM INVOLVING PLUTONIA AND URANIA AT HIGH TEMPERATURES

Quarterly Report No. 15
February 1, 1971 — April 30, 1971

E. A. Aitken S. K. Evans
M. G. Adamson T. E. Ludlow

ABSTRACT

Work progress is reported in the continuing scope of work related to vaporization of urania in urania-plutonia solid solutions, oxygen activities at high temperatures, oxygen redistribution in a temperature gradient, Pu/U segregation and sodium-fuel interactions.

1. INTRODUCTION

This quarterly report is the fifteenth in a series which describes experiments directed toward understanding plutonia segregation in urania-plutonia solid solutions and in fast reactor environments through a knowledge of its thermodynamic behavior. In the fourteenth quarterly (GEAP-12182) the progress of several experiments which have a bearing on plutonia segregation was described. In addition the thermodynamic aspects of the sodium-fuel reaction product were studied. Continued progress in these areas is described in this report.

2. THERMAL GRADIENT EXPERIMENTS WITH EXCESS SODIUM

In the fourteenth quarterly report, a description of an experimental system to study reactions of sodium with mixed oxide fuel in a temperature gradient was reported. The first series of experiments was described and the results were reported where available. The remaining results of the first series of investigations are reported here along with the description of the second series of experiments.

The major results of each test conducted to date are given in Table 1. Figure 1 illustrates the result of a 1000-hour thermal gradient anneal of $(U_{0.75}Pu_{0.25})O_{2-x}$ containing 49 mg of sodium. The observed heat of transport, -15.4 kcal/mole, closely matched that of Test 5 described in the fourteenth quarterly progress report. No evidence of a reaction product between the mixed oxide fuel and sodium could be found in this test. The lack of a reaction product indicates that the sodium may have leaked out during the anneal.

The result of a 300 hour thermal gradient anneal of PuO_{2-x} containing 138 mg of sodium is shown in Figure 2. The coldest five pellets in this experiment exhibited swelling and cracking from a possible reaction with sodium. However, oxygen-to-metal ratio determinations on three of these five pellets showed no deviation from the trend observed in the pellets at higher temperatures; therefore, the sodium may have been removed during the anneal, possibly through a leak in the capsule. It cannot be determined whether the heat of transport observed is indicative of oxygen transport through a sodium-bearing gas phase or not, since the PuO_{2-x} system exhibits a similar heat of transport without sodium.

A second series is planned to investigate the reaction tendencies of sodium with mixed oxide fuel in which the sodium reservoir is at a known temperature. Six molybdenum capsules containing $(U_{0.75}Pu_{0.25})O_{2-x}$ and excess sodium will be fabricated and annealed in the temperature gradient so that the sodium reservoirs will be at 500, 700, and 900°C. Three tubes will contain fuel of nominal 1.93 stoichiometry at 500, 700, and 900°C sodium temperature; two tubes will contain nominal 1.97 stoichiometry fuel at 500 and 700°C sodium temperature; one tube will contain stoichiometric fuel at 500°C sodium temperature.

The thermal gradient anneals will begin during the next quarter.

TABLE 1. Summary of Experimental Conditions and Results from Thermal Gradient Capsules Heated in a Temperature Gradient

Capsule	Internal Temperature ($^{\circ}\text{C}$)	Heat Treatment (h)	Na (mg)	Initial O:M	T_N ($^{\circ}\text{C}$)	T_R ($^{\circ}\text{C}$)	2-y at T_R	Q^* (kcal/mole)	Remarks
1	500-1150	100	35	1.965	500	750	1.965	NM [†]	Not at steady state
2	900-1450	300	32	1.965	900	975	1.970	-5.7	Reaction bands $< 1000^{\circ}\text{C}$
3	900-1450	300	85	1.965	900	980	1.975	-5.7	Reaction bands $< 1000^{\circ}\text{C}$
4	1105-1475	300	37	1.933	1110	1110	1.94-1.95	-2.4	Reaction at coldest pellet only
5	1240-1500	300	36	1.964	1240	—	NM	-15.7	No reaction product, no visual evidence Na Capsule may have failed.
6	1105-1475	100	39	1.958	1060	~ 1100	NM	—	1 inch long pellet at cold end. Not at steady state
7	1105-1475	1000	49	1.966	1110	—	NM	-15.4	No reaction product Capsule may have failed
8	1105-1475	300	138	1.80	1110	1190	1.832	-4.81	Some pellet swelling $< 1190^{\circ}\text{C}$ 100% $\text{PuO}_{1.8}$

[†]NM = not measured

3. DETERMINATION OF COMPONENT ACTIVITIES

The determination of uranium activity in $\text{UO}_2\text{-PuO}_2$ solid solutions is being studied by means of a transpiration technique with air and CO/CO_2 as the carrier gases. Experiments were conducted with UO_{2+x} and $(\text{U}_{0.6}\text{Pu}_{0.4})\text{O}_{2+x}$ between 1300 and 1500°C with air as the carrier gas. The results of these experiments are shown in Figure 3. The data at 1405 and 1515°C exhibit a 35% decrease in UO_3 pressure compared to UO_{2+x} . At 1303°C only a 15% decrease in UO_3 pressure was observed. It may be that below 1300°C , the $(\text{U}_{0.6}\text{Pu}_{0.4})\text{O}_{2+x}$ system separates into two phases, U_3O_{8-y} and a mixed oxide phase enriched in plutonium. For this system, the resultant UO_3 pressure would correspond to that of U_3O_{8-y} . Further experimental work is planned to study this phenomenon in more detail.

4. OXYGEN MIGRATION IN $(\text{U,Pu})\text{O}_2$ SYSTEMS

The current series of experiments designed to probe the mechanisms involved in migration of oxygen in the $(\text{U,Pu})\text{O}_{2-x}$ system in a temperature gradient has been completed. In the interest of clarity, a synopsis of the experiments conducted is presented to give the reader a basic understanding of the necessity for elucidation of the oxygen transport mechanisms in oxide nuclear fuel materials.

Stoichiometry control in fast reactor fuel is of great importance due to the predicted effects of high oxygen activity on cladding integrity and fuel-coolant reactions. The presence of temperature gradients in all fuels and the attendant gradient in oxygen potential require that the properties of the oxygen potential gradient be well established so that proper predictions on fuel behavior can be made.

Several aspects of the thermomigration problem require attention. It is well known that oxygen migrates to the cooler regions of hypostoichiometric urania-plutonia fuel leaving the center deficient in oxygen when compared to the average fuel composition. The cladding may act as a sink for the excess oxygen which appears in its vicinity. In the presence of cesium fission products, the excess oxygen may enhance corrosion of the cladding materials. In the event of the failure of a fast reactor fuel pin in sodium coolant, fuel-sodium reaction products may form which cause swelling of the ruptured fuel pin with possible detrimental effects on coolant flow and fuel integrity.

FIGURE 1. ARRHENIUS PLOT OF 1000 HOUR THERMAL GRADIENT ANNEAL OF $U_{0.75}Pu_{0.25}O_{1.966}$ WITH 49 mg SODIUM

FIGURE 2. ARRHENIUS PLOT OF 300 HOUR THERMAL GRADIENT ANNEAL OF $PuO_{1.8}$ WITH 138 mg SODIUM

FIGURE 3. UO_3 PARTIAL PRESSURE VERSUS $1/T$ FOR UO_{2+x} AND $(\text{U}_{0.6}\text{Pu}_{0.4})\text{O}_{2+x}$ IN AIR

ANALYTICAL MODEL

Aitken¹ has treated the problem of thermomigration of oxygen in urania-plutonia systems in terms of irreversible thermodynamics. A single component, oxygen, is considered to be migrating both in the solid and gas phases. This migration results in a flux of oxygen which can be expressed in the form

$$J_{\text{oxygen}} = L_g X_g + L_s X_s + L_{Hs} X_H \quad (1)$$

The L coefficients represent mobility rates in the gas, L_g , and the solid, L_s . The X variables are driving forces for oxygen transport in the gas, X_g , and solid, X_s . The thermal driving force is X_H . These driving forces have the following forms:

$$X_g = -T \text{ grad } (\mu_{ZO}/T), \quad (2)$$

$$X_s = -1/2 T \text{ grad } (\mu_{O_2}/T), \quad (3)$$

and

$$X_H = T \text{ grad } (1/T). \quad (4)$$

Such a cyclic mechanism can operate when local equilibrium exists between the solid and gas phases at every point in the temperature gradient. Sintered urania-plutonia pellets normally contain enough hydrogen or carbon to provide a significant hydrogen or CO over-pressure. Under these conditions, the local equilibrium situation can be represented by

$$\text{grad}(\mu_{ZO}/T) = 1/2 \text{ grad } (\mu_{O_2}/T) + \text{grad } (\mu_Z/T) \quad (5)$$

when ZO/Z is assigned to be either H_2O/H_2 or CO_2/CO .

The equilibrium can be expressed as

$$\mu_Z = \mu_Z + RT \ln P_Z \quad (6)$$

and

$$\mu_{ZO} = \mu_{ZO} + RT \ln P_{ZO} \quad (7)$$

For the chemical potential of oxygen in the hypostoichiometric urania-plutonia lattice, it is preferable to express the chemistry in terms of oxygen vacancies using the relative system of Schottky for describing the solid state defect chemistry in MO_{2-x} . In the Schottky system of notation only relative changes from the host crystal lattice are considered. Thus for creation of a vacancy of M in the binary compound MX by removal of an M atom to the gas phase, we can write

$$0 \text{ (or nil)} = M_g + |M| \quad (8)$$

where $|M|$ implies an atom removed from the lattice, resulting in a vacancy.

The free energy change for this reaction is

$$\Delta G = \mu_{M_g} + \mu_{|M|} \quad (9)$$

Considering the mixed oxide system, then, the above reaction becomes

$$\text{nil} = 1/2 O_2 (g) + |O| \quad (10)$$

and

$$\Delta G = 1/2 \mu_{O_2} + \mu_{|O|} \quad (11)$$

Since local chemical equilibrium is assumed, $\Delta G = 0$ and

$$1/2 \mu_{O_2} = -\mu_{|O|} \quad (12)$$

and

$$\mu_{|O|} = \mu_{|O|}^0 + RT \ln x \quad (13)$$

thus

$$1/2 \mu_{O_2} = +1/2 \mu_{O_2}^0 - RT \ln x. \quad (14)$$

By dividing Equations (6), (7), and (14) by T and taking the gradient, we obtain

$$\text{grad } (\mu_Z/T) = \Delta H_{ZO} \text{ grad } (1/T) + R \text{ grad } \ln P_Z, \quad (15)$$

$$\text{grad } (\mu_{ZO}/T) = \Delta H_{ZO} \text{ grad } (1/T) + R \text{ grad } \ln P_{ZO}, \quad (16)$$

$$1/2 \text{ grad } (\mu_{O_2}/T) = 1/2 \bar{h}_{O_2} \text{ grad } (1/T) - R \text{ grad } \ln x. \quad (17)$$

After combining Equations (15), (16), and (17) into Equation (5), we have

$$-R \text{ grad } \ln x = -(1/2 \bar{h}_{O_2} - \Delta H_{ZO} + \Delta H_Z) \text{ grad } (1/T) + R \text{ grad } \ln (P_{ZO}/P_Z) \quad (18)$$

If the variation in Equation (18) is examined at a constant temperature gradient, the result is

$$\frac{\partial \text{grad } \ln (P_{ZO}/P_Z)}{\partial \text{grad } \ln x} = -1 \quad \text{grad } T = \text{constant} \quad (19)$$

The fundamental criterion for cyclic flow of oxygen at steady state is that the entropy production be minimized with respect to the state variables in the system. Under the condition of a constant temperature gradient, the state variables are the composition of the solid and the partial pressure of the gas phase.

The entropy production rate is given by

$$\sigma' = \sum J_i X_i \quad (20)$$

By neglecting cross coefficients between thermal and material transfer, we find the part of the entropy rate from gas and solid phase flow is

$$\sigma' = L_g (\text{grad } \ln P_{ZO}/P_Z)^2 + L_s (\text{grad } \ln x)^2 \quad (21)$$

The constraint in Equation (19) allows us to minimize the entropy production rate with respect to one variable only, $\text{grad } \ln x$, to give

$$L_g \text{ grad } \ln P_{ZO}/P_Z = L_s \text{ grad } \ln x. \quad (22)$$

When Equation (22) is substituted in Equation (18), the result is

$$-(1 + L_s/L_g) R \text{ grad } \ln x = (1/2 \bar{h}_{O_2} - \Delta H_{ZO} + \Delta H_Z) \text{ grad } (1/T). \quad (23)$$

By integrating Equation (23) with respect to the space coordinates we have

$$\ln x = \frac{(1/2 \bar{h}_{O_2} - \Delta H_{ZO} + \Delta H_Z)/RT}{(1 + L_s/L_g)} + C. \quad (24)$$

Aitken¹ has pointed out the heat of transport

$$Q^* = (1/2 \bar{h}_{O_2} - \Delta H_{ZO} + \Delta H_Z) \quad (25)$$

corresponds to the situation described by Rand and Roberts² therefore, effective heat of transport observed for the cyclic flow situation is

$$Q^*_{eff} = \frac{Q^*_{RR}}{1 + L_s/L_g} \quad (26)$$

Prigogine³ has pointed out that L_s is proportional to the oxygen vacancy concentration. At constant oxygen-to-plutonium ratio (or constant L_g), then the effective heat of transport can be reduced to

$$Q^*_{eff} = \frac{Q^*_{RR}}{1 + Kx} \quad (27)$$

where K is a constant and x is the oxygen vacancy concentration.

The data reported in this study were examined with the results of this model; conclusions reached are discussed in the following sections.

EXPERIMENTAL PROCEDURE

Thermal gradient experiments were carried out by sealing 36 to 40 UO_2 - PuO_2 pellets of the desired composition and stoichiometry in a 12-inch long molybdenum tube with an inside diameter of 0.250 inch. The pellets were nominally 0.250 inch long and 0.220 inch in diameter. Pellet densities were variable, but nominally 92% of theoretical. The sealed molybdenum tubes were placed in a molybdenum-wound, N_2 - 6% H_2 furnace with a known temperature gradient from 1600 to 900°C. After temperature gradient anneals which varied from 100 to 2000 hours, the tubes were opened and the pellets removed. Oxygen-to-metal ratio determinations using Lyon's method were made on each of the pellets.

The furnace temperature profile was measured with a Pyro micro-optical pyrometer at specified locations in the furnace. Corrections to the pyrometer readings were made by observing melting temperatures of copper, iron, nickel, and cobalt samples which were slowly entered into the furnace hot zone.

RESULTS

Composition and Stoichiometry Changes

Thermal gradient experiments conducted with $(U_{0.8}Pu_{0.2})O_{2-x}$ in the temperature range of 2000 to 1200°C were reported by Evans, Aitken, and Craig.⁴ The results of their experiments are shown in Figure 4; The observed heat of transport is shown to become more negative as the average deviation from stoichiometry decreases. The data for $1.942 < O:M < 1.996$ exhibit a change in heat of transport at 1400 to 1600°C and resulted in much more negative values at lower temperatures.

Aitken showed these data agreed well with the model predictions for $L_s/L_g = 3$ as is indicated in Table 2. This analysis does not take into account changes in the L_s/L_g ratio since the over-all oxygen activity in the tube is varied.

TABLE 2. Enthalpies and Heats of Transport (kcal/mole) for Specific Models of Thermal Diffusion of Oxygen in Various Oxide Fuels

Oxide	Heat of Solution	One-Component Gas Phase Models		Experiment
		$Q^* (H_2O/H_{2atm})^a$ (Rand-Roberts model)	$Q^*_{eff} (L_s/L_g=3)$	Q^*
$U_{0.8}Pu_{0.2}O_{2-n}$				
at O/Pu				
1.98	-241	-64	-16	≈ -100
1.90	-220	-53	-13	- 12
1.80	-193	-40	-10	- 8
1.70	-176	-31	- 8	- 7

a The enthalpy of formation is -56 kcal/mole for H₂O and 0 for H₂ gas.

Figure 5 illustrates the results of thermal gradient tests of urania-plutonia specimens of varying composition, but roughly constant oxygen activity (O-to-Pu ratio). The cyclic flow model was applied and these data are shown in Table 3. Since the oxygen activity was kept approximately constant in these tests, L_g is assumed to be constant and the oxygen vacancy concentration varies with plutonium content. The calculated values of Q*_{eff} were generated by using the values for PuO_{2-x} as a base.

TABLE 3. Thermal Gradient Experiment Results for Various Plutonium Compositions

Content (%)	O:M	X	Q* (kcal/mole)	Q* _{eff}	Q* _{eff}
				Calculation (kcal/mole)	Measurement (kcal/mole)
100	1.817	0.183	- 43	- 4.1	- 4.1
40	1.950	0.050	- 49	-13.7	-11.0
20	1.973	0.027	- 48	-20.2	-21.9

Time Dependence of Heat of Transport

Several experiments were carried out with PuO_{2-x} and hypostoichiometric urania-plutonia to determine the length of time necessary to reach steady state. Figure 6 illustrates the results of 1600 to 900°C anneals of PuO_{2-x} for 15, 100, 300, and 1070 hours. The heat of transport is observed to become less negative with time and approaches a steady-state value near -4 kcal/mole at 1070 hours.

The results of 1600 to 900°C anneals of U_{0.8}Pu_{0.2}O_{1.97} and (U_{0.75}Pu_{0.25})O_{1.96} for 300, 1000, and 2000 hours are shown in Figure 7. As in the plutonia case, the high-temperature heat of transport becomes less negative with time. At low temperatures up to 1000 hours, the fuel does not exhibit a stoichiometry gradient, but the deviation from stoichiometry in this region is less than the average value. The 2000-hour tube contained a slightly greater plutonium concentration (25% Pu) than the shorter time tests which would cause the heat of transport to become slightly less negative for a given oxygen activity than for fuel containing 20% plutonium. However, in this long-term test, a high-temperature heat of transport of -6 kcal/mole is observed which is similar to that found in the 2000 to 1200°C tests. The lower temperature heat of transport is similar to that which would be calculated under the conditions given in Table 2 (-14.1 kcal/mole observed versus -17.7 kcal/mole calculated). No region with an absence of a stoichiometry gradient exists in the 2000-hour case.

Figure 8 illustrates the results of 1600 to 900°C anneals of (U_{0.75}Pu_{0.25})O_{1.93} for 100, 300, and 1000 hours. The heat of transport is not large for any of these experiments. The absence of such a large value in the shortest test indicates the heat of transport changes monotonically from zero to its final steady-state value at such low oxygen activities.

FIGURE 4. SUMMARY OF THERMAL GRADIENT EXPERIMENTS BETWEEN 2000 AND 1500° WITH $(U_{0.8}Pu_{0.2})O_{2-x}$

FIGURE 5: ARRHENIUS PLOTS OF 1000-HOUR THERMAL GRADIENT ANNEALS

FIGURE 6. RESULTS OF PuO_{2-x} THERMAL GRADIENT EXPERIMENTS

FIGURE 7: TIME DEPENDENCE OF MIXED OXIDE THERMAL GRADIENT EXPERIMENTS

FIGURE 8. TIME DEPENDENCE OF LOW STOICHIOMETRY THERMAL GRADIENT EXPERIMENTS

Spacer Experiments

Two 1600 to 900°C anneals of $(U_{0.75}Pu_{0.25})O_{2-x}$ with molybdenum spacers separating the pellets were conducted to 1000 and 2000 hours. The results of these experiments are shown in Figure 9. The lowest temperature pellets did not exhibit any stoichiometry gradient in the 1000-hour test. The lowest temperatures produced a large negative heat of transport for the long-term tests, but the high-temperature heats of transports were similar (differences observed are probably due to slight stoichiometry differences between the two pins). The high-temperature heats of transport in the 2000-hour anneals with and without spacers were virtually identical as is shown in Figure 10, indicating similar mechanisms for oxygen transport above 1250°C.

Long Pellet Experiment

Three-inch long pellets were fabricated to provide an experimental test bed in the temperature gradient where solid state migration of oxygen is assured by eliminating the pellet interfaces. Only four interfaces were present in the entire pin and they provided enough "pellets" after post-test slicing to observe a data trend within individual long rods. The results of this 2000-hour experiment are shown in Figure 11. When comparing these results with those of Figure 10, it is observed that differences in heat of transport are apparent among the tests. A summary of these differences is given in Table 4. Since the average stoichiometry in the long pellet experiment is lower than in the experiment without spacers, the heat of transport for a given mechanism would be less negative for the long pellet experiment. Thus, it is reasonable to assume the -10.2 kcal/mole heat of transport observed in the long pellet experiment corresponds to the same mechanism as the -14.1 kcal/mole heat of transport in the pellet experiment without spacers. The lowest temperature heats of transport in the long pellet and spacer experiments appear to be similar.

TABLE 4. Results of 2000-Hour Temperature Gradient Experiments

Experiment	High Temperature Region		Low Temperature Region	
	Temperature, °C	Heat of Transport kcal/mole	Temperature, °C	Heat of Transport kcal/mole
No molybdenum spacers	1410-1220	-6.2	1220-980	-14.1
Molybdenum spacers	1410-1060	-6.3	1060-980	-30.7
Long pellets	1445-1070	-10.2	1070-1005	-26

DISCUSSION

The results of thermal gradient experiments presented above exhibit basically three separate regions of behavior. At high temperatures (1500 to 2000°C) all heats of transport observed fall in the range -7 to -12 kcal/mole except for the stoichiometric test which is considered to be a different mechanism.¹ At lower temperatures, (1500 to 900°C), the heats of transport are more negative. In the 2000-hour tests, transitions between the three types of behavior are seen.

At temperatures below 1070°C in the 2000-hour long pellet and spacer experiments, heats of transport in the -26 to -30 kcal/mole range are observed. This region may be present in the 2000-hour experiment without spacers, but the data are inconclusive. A idealized plot of the 2000-hour data is shown in Figure 12. The mechanism in the low temperature region is probably that described by Rand and Roberts² in which the deviation from stoichiometry is small enough to permit a constant H_2O pressure along the length of the tube. This mechanism in which oxygen transport occurs overwhelmingly in the gas phase, would be indifferent to experiment geometry. This is basically what is observed.

The two higher temperature regions of behavior exhibit similar properties in that the heat of transport becomes more negative as the deviation from stoichiometry is decreased. The high temperature data are more difficult to interpret because of the great differences in partial pressures of the oxygen-bearing gases as the stoichiometry was changed. The effect of these changes on L_g has not been studied in detail. Since the lower temperature tests which are compared were similar in oxygen activity, the variation in L_g is not so significant for this region.

FIGURE 9. THERMAL GRADIENT EXPERIMENTS WITH MOLYBDENUM SPACERS

FIGURE 10. COMPARISON OF SPACER AND NONSPACER EXPERIMENTS

FIGURE 11. ARRHENIUS PLOT OF 2000-HOUR THERMAL GRADIENT ANNEAL OF LONG PELLETS OF $U_{0.75}Pu_{0.25}O_{1.956}$

FIGURE 12. IDEALIZED RESULTS FOR 2000-HOUR TEMPERATURE GRADIENT EXPERIMENTS

The decrease in absolute value of the heat of transport with time observed in those tests with oxygen-to-plutonium ratios above 1.75 is probably because the high temperature stoichiometry was higher at the start of the thermal gradient anneals than later on. The large negative heat of transport was generated only in the first few pellets in the beginning, but as oxygen moved down the temperature gradient, encountering additional pellets, the oxygen activity at the high-temperature end decreased and resulted in a less negative heat of transport as the experiment progressed. The low-stoichiometry tests did not show the same type time dependence described above since the oxygen activity was so low that a large stoichiometry gradient could not be developed.

The 2000-hour spacer and long pellet experiments were conducted to investigate the elimination and enhancement of solid phase oxygen migration. These two experiments represent the extreme conditions regarding solid phase oxygen migration. The result of the 2000-hour experiment with 1/4 inch pellets alone should represent a compromise between the two extremes. The results indicate that above 1220°C the short pellet experiment exhibits behavior similar to the spacer experiment, while below that temperature, the short pellet experiment behaves similarly to the long pellet experiment.

The implications of these observations are not yet completely clear, but some tentative conclusions may be reached. At high temperatures, the gas phase transport of oxygen is such that the presence of spacers is immaterial to the experimental geometry, yet the pellet interfaces do alter the transport mechanism. At lower temperatures, the pellet interfaces have little effect on the oxygen transport mechanisms, but interposition of spacers alters the transport. These tentative conclusions warrant further study into both experimental details and re-examination of the model for solid and gas phase transport of oxygen. This study and re-examination are continuing.

IMPLICATIONS TO FUEL IRRADIATION

The existence of a temperature gradient in a fuel rod undergoing neutron irradiation necessarily results in migration of oxygen from the center or the periphery of the rod, depending on whether the fuel is hypostoichiometric (oxygen-to-metal ratio less than 2.00) or hyperstoichiometric (oxygen-to-metal ratio greater than 2.00). $\text{UO}_2\text{--PuO}_2$ fuel for breeder reactor applications is limited to hypostoichiometric compositions initially by the requirement that extensive cladding oxidation be prevented. The results of the axial temperature gradient experiments described in this report indicate that oxygen migrates from the warmer to the cooler regions of the gradient. The same mechanisms for oxygen migration should occur in a radial temperature gradient such as exists in a reactor fuel rod during irradiation. This means that in such a rod loaded with hypostoichiometric fuel, the oxygen will migrate in a reproducible manner from the axis of the rod to the outer periphery. The resulting oxygen concentration profile is such that the fuel at the outer radius is near stoichiometric, and the oxygen-to-metal ratio decreases to possibly 1.93 or lower in the center of the rod. The actual profile observed is dependent upon the initial stoichiometry, the plutonium content, and the irradiation time (burnup).

It is instructive to examine the details of the oxygen transport mechanisms in terms of the observed heats of transports. In order to do this, consider again the equation relating heat of transport to deviation from stoichiometry

$$\ln x = Q^*/RT + C \quad (28)$$

where x is the deviation from stoichiometry in the mixed oxide (e.g., $x = 2.00\text{--O:M}$ for hypostoichiometric fuel), R is the gas constant, T is the absolute temperature in Kelvin degrees, C is a constant, and Q^* is the heat of transport which is measured from the slopes of the logarithm of the deviation from stoichiometry versus reciprocal temperature plots. When the heat of transport is a negative quantity as it is for hypostoichiometric $\text{UO}_2\text{--PuO}_2$, x increases as the temperature rises. Thus, the heat of transport, Q^* , is a measure of the driving force for migration of oxygen down the temperature gradient; the more negative the heat of transport, the greater the driving force.

As has been already mentioned, in a fuel rod the oxygen migrates from the center to the periphery (fuel-cladding interface) of the fuel rod. The extent to which this migration occurs is dependent upon the average fuel stoichiometry. As the average fuel stoichiometry decreases (average x gets larger) the oxygen-to-metal ratio at the fuel-cladding interface also decreases, the heat of transport becomes less negative, so there is less tendency for the oxygen to migrate to the fuel-cladding interface. The end result is that, for very low stoichiometry fuel (average oxygen-to-metal ratio less than 1.95), the fuel at the cladding interface can be expected to be substantially hypostoichiometric.

It is well known that, as burnup progresses, the fission product distribution is such that oxygen is released to increase the stoichiometry of the fuel at the rate of approximately 0.01 oxygen-to-metal ratio units per 1 at. % burnup.⁶ As the average fuel stoichiometry increases through burnup the oxygen-to-metal ratio at the fuel-cladding interface approaches more nearly the stoichiometric composition. This tendency is accelerated by the more negative heat of transport as the fuel stoichiometry increases. This process continues with burnup until eventually the average fuel oxygen-to-metal ratio is very close to 2.00. During the approach to this condition, the values for x along the temperature gradient have been decreasing. Since x is the deviation from stoichiometry, as the oxygen-to-metal ratio nears 2.00, x becomes so small as to be unmeasurable (the precision of the stoichiometry determination is about 0.003 in units of x). At such a time as the value of x at the center of the fuel rod becomes less than 0.003, no stoichiometry gradient can be detected even though the deviation from stoichiometry at the fuel-cladding interface is an order of magnitude less than 0.003. At this point, from an observable standpoint, the average fuel composition is essentially stoichiometric.

A judgment must be made as to which of the observed long term heats of transport would more accurately describe the oxygen redistribution in an actual fuel rod under irradiation. It would be expected that heats of transport measured from long pellet experiments would correspond more closely to the actual situation than would experiments where pellet interfaces are more numerous. At small values of x , the Rand-Roberts mechanism appears to prevail in all cases.

Modeling studies are under way to quantify these ideas in terms of expected LMFBR fuel conditions. Data such as reported here can be of significant assistance to understanding of oxygen redistribution in proposed fuels and in correlating cladding attack thresholds with initial stoichiometry and burnup.

5. A THEORETICAL STUDY OF PLUTONIUM-URANIUM SEGREGATION IN MIXED OXIDE FUELS

The objective of this study is to generate a thermodynamic description of U:Pu segregation in mixed oxide fuels. The cation segregation is being considered in terms of the possible transport mechanisms. The theoretical model is under study at present and an analysis of current progress will be presented in the next quarterly report.

REFERENCES

1. Alexander, C. A., *Vapor-Solid Equilibria in the Uranium Oxide-Uranium System*, Doctoral Dissertation, The Ohio State University, 1961.
2. Aitken, E. A., "Thermal Diffusion in Closed Oxide Fuel Systems," *J. Nucl. Matl.*, **30**, 62-73 (1969).
3. Rand, M. H., and Roberts, L. H., *Symposium Thermodynamics of Nuclear Materials*, **1**, (IAEA, Vienna 1965) p. 3.
4. Prigogine, I., *Thermodynamics of Irreversible Processes*, Interscience Publishers, New York, 1961.
5. Evans, S. K., Aitken, E. A., and Craig, C. N., "Effect of a Temperature Gradient on the Stoichiometry of Urania-Plutonia Fuel," *J. Nucl. Matl.*, **30**, 57-61 (1969).
6. Anselin, F., *The Role of Fission Products in the Swelling of Irradiated $UO_2-(U, Pu)O_2$ Fuels*, General Electric Company, January 1969 (GEAP-5583).

Other Reports in This Series

GEAP-5358	No. 1.	through October 31, 1967
GEAP-5395	No. 2.	November 1, 1967 through January 31, 1968
GEAP-5634	No. 3.	February 1 through April 30, 1968
GEAP-5672	No. 4.	May 1 through July 31, 1968
GEAP-5720	No. 5.	August 1 through October 31, 1968
GEAP-5777	No. 6.	November 1 through January 31, 1969
GEAP-12017	No. 7.	February 1 through April 30, 1969
GEAP-12032	No. 8.	May 1 through July 31, 1969
GEAP-12047	No. 9.	August 1 through October 31, 1969
GEAP-12066	No. 10.	November 1, 1969 through January 31, 1970
GEAP-12099	No. 11.	February 1 through April 30, 1970
GEAP-12133	No. 12.	May 1 to July 31, 1970
GEAP-12153	No. 13.	August 1 to October 31, 1970
GEAP-12182	No. 14.	November 1, 1970 to January 31, 1971

DISTRIBUTION

<u>Copies</u>	<u>Copies</u>
Battelle Memorial Institute Pacific Northwest Laboratory P.O. Box 999 Richland, Washington 99352 Attn: T. Chikala 1	USAEC Division of Technical Information Extension P.O. Box 62 Oak Ridge, Tennessee 37831 3*
Battelle Memorial Institute Columbus Laboratory 505 King Avenue Columbus, Ohio 43201 Attn: C. A. Alexander 1	Los Alamos Scientific Laboratory P.O. Box 1663 Los Alamos, New Mexico 87544 Attn: J. A. Leary 1 R. D. Baker 1
Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois 60439 Attn: P. E. Blackburn 1 L. R. Kelman, LMFBP 1 Program Office	Westinghouse Electric Corporation Nuclear Fuels Division Pittsburgh, Pennsylvania 15230 Attn: W. L. Lyon 1
Oak Ridge National Laboratory P.O. Box X Oak Ridge, Tennessee 37830 Attn: J. L. Scott 1	Westinghouse Electric Corporation Advanced Reactors Division P.O. Box 217 Cheswick, Pennsylvania Attn: P. Murray 1
USAEC Fuels and Materials Development Branch Division of Reactor Development and Technology Washington, D.C. 20545 Attn: J. M. Simmons 4 G. W. Cunningham 1	Babcock & Wilcox Company Atomic Energy Division Lynchburg, Virginia 24501 Attn: C. J. Baroch 1
USAEC San Francisco Operations Office 2111 Bancroft Way Berkeley, California 94704 1	Atomics International P.O. Box 309 Canoga Park, California 91304 Attn: H. Pearlman 1
RDT Site Office USAEC c/o General Electric Company 310 De Guigne Drive Sunnyvale, California Attn: A. W. Larsen 1	United Nuclear Corporation Grasslands Road Elmsford, New York 10523 Attn: A. Strasser 1
USAEC Fuel Recycle Branch Division of Reactor Development and Technology Washington, D. C. 20545 Attn: W. H. McVey, Chief 1	WADCO Corporation Hanford Engineering Development Laboratory P. O. Box 999 Richland, Washington 99352 Attn: E. A. Evans 1
	Massachusetts Institute of Technology Department of Metallurgy and Material Science Cambridge, Mass. 02139 Attn: H. K. Bowen 1

*Submitted with transmittal form AEC-426

GENERAL ELECTRIC