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**CALCULATION OF OXYGEN DIFFUSION IN PLUTONIUM OXIDE
FILMS DURING THE HIGH-TEMPERATURE OXIDATION OF
PLUTONIUM-1 WEIGHT PERCENT GALLIUM IN 500 TORR OF AIR**

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A C K N O W L E D G M E N T

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CALCULATION OF OXYGEN DIFFUSION IN PLUTONIUM OXIDE FILMS DURING THE HIGH-TEMPERATURE OXIDATION OF PLUTONIUM-1 WEIGHT PERCENT GALLIUM IN 500 TORR OF AIR

Jerry L. Stakebake

ABSTRACT

Oxygen self-diffusion in $\text{PuO}_{1.995}$ was calculated from rate constants obtained for the parabolic oxidation of the Pu-1 wt% Ga alloy in 500-torr dry air between 250 and 480 °C. Diffusion is described by the equation

$$D = 1.2 \times 10^{-6} \exp(-22,600/RT) \text{ m}^2/\text{sec}$$

The activation energy for oxygen vacancy diffusion in the n-type PuO_{2-x} is 22.6 kcal/mole. Results from this investigation are compared with other reported results, and a possible explanation for the difference in results is discussed.

INTRODUCTION

Plutonium is a very reactive metal that oxidizes readily when exposed to air, oxygen, or water vapor. In earlier work,¹ the high-temperature oxidation of plutonium in dry air was described by a three-stage process. Stage I involves the growth of an oxide film with a diffusion controlled parabolic rate. Stage II consists of a region of linear kinetics where the rate controlling process is thought to be the diffusion of oxygen through a dense plutonium dioxide film that has essentially reached a constant thickness. Stage III is a second linear process produced by the cracking and spalling of the oxide film.

The exact nature of the oxide film involved in Stages I and II is still uncertain. Phase diagrams for the plutonium oxygen system indicate a mixed phase of cubic PuO_{2-x} and cubic $\text{PuO}_{1.52}$ (α - Pu_2O_3) at temperatures below 300 °C and PuO_{2-x} plus $\text{PuO}_{1.61}$ above 300 °C.^{2,3} X-ray

studies⁴ of the oxidation of plutonium show that $\text{PuO}_{1.52}$ is produced in low oxygen pressures at 305 °C. When the temperature was increased to 420 °C, the primary oxide formed was referred to as PuO. Larson and Haschke⁵ subsequently showed that the PuO phase is actually the oxide carbide PuO_xC_y . In any case, this phase appears to exist only as a thin film and is readily oxidized to $\text{PuO}_{1.52}$ and PuO_2 .

The focus of this work was the Stage I oxidation process that forms a dense plutonium dioxide film and results in the diffusion controlled kinetics. Oxidation kinetics of Pu-1 wt% Ga were evaluated using the parabolic rate law. Oxygen self-diffusion coefficients were then calculated from the parabolic rate constants and compared to the results obtained using other methods.⁶⁻⁹ Activation energies for diffusion and parabolic oxidation were also calculated.

EXPERIMENTAL

The Pu-1 wt% Ga alloy used in this investigation and the experimental procedures for measuring the oxidation kinetics have been described elsewhere.¹ This alloy contained 502 ppm of impurities in addition to the gallium. Oxidation kinetics were determined using a Cahn vacuum microbalance. Measurements were carried out in 500-torr dry air (105-torr O_2) over the temperature range 250-500 °C. A data acquisition system was used to continuously collect data throughout the three-stage oxidation process. Data relating to the parabolic Stage I process were separated and analyzed by computer. Samples from coupons oxidized through the Stage I process were analyzed by metallography and x-ray diffraction to determine if more than one type of oxide was present.

RESULTS AND DISCUSSION

Evaluation of Oxide Formation

The exact composition of the oxide film formed during the parabolic oxidation of plutonium is unknown. The oxide product formed was analyzed by x-ray diffraction and the results showed only a single fcc PuO_2 phase with a lattice parameter of $5.398 \pm 0.002 \text{ \AA}$. The slightly expanded lattice ($5.398 \text{ \AA}$ compared to $5.396 \pm 0.0003 \text{ \AA}$ for stoichiometric $\text{PuO}_{2.00}$) indicates a composition of PuO_{2-x} . Gardner et al.² reported the lattice parameter for $\text{PuO}_{1.98}$ to be $5.405 \pm 0.002 \text{ \AA}$. The PuO_{2-x} film observed in this study would then have a composition between $\text{PuO}_{1.98}$ and $\text{PuO}_{2.00}$. Assuming Vegard's law, the composition would be $\text{PuO}_{1.995}$. No x-ray evidence was found for the formation of the bcc $\text{PuO}_{1.52}$ ($\alpha\text{-Pu}_2\text{O}_3$) phase. A cross section through the oxidized metal sample was examined by metallography and also showed no visible evidence of multiple oxide film formation. However, in this nonequilibrium system, it is still probable that a reduced oxide film near $\text{PuO}_{1.52}$ is present at the metal interface.

Oxidation Kinetics

The mechanism for plutonium oxidation depends upon the nature of the oxide film being formed. The primary factor to be considered is whether the oxide is compact or porous. A compact oxide acts as a barrier separating the metal from oxygen. Oxidation rates then depend on the solid-state diffusion of oxygen through the oxide. As the oxide grows, the diffusion distance increases and the reaction rate decreases with time. This process has been observed in the initial oxidation of plutonium and explained by the parabolic rate model.

Oxidation of Pu-1 wt% Ga in 500 torr of air is illustrated in Figure 1. This run was made at 405°C and is typical of all the oxidation runs made below about 480°C .¹ A parabolic growth of the oxide film began at time zero and eventually transformed into a linear rate of oxidation. At temperatures above about 480°C , the oxidation process was linear throughout the run.

FIGURE 1. Parabolic oxidation of Pu-1 wt% Ga at 405°C in 500 Torr of Air

Parabolic oxidation kinetics were evaluated using the equation

$$x^2 = k_p t + C \quad (1)$$

where x is the amount of oxygen reacted (mg/cm^2), k_p is the parabolic rate constant, and C is the integration constant. The activation energy for this process was determined from the temperature dependence of k_p by using the Arrhenius equation

$$k_p = A \exp(-E_a/RT) \quad (2)$$

A plot of this equation is shown in Figure 2. The activation energy for the parabolic oxidation process was calculated to be 23.4 kcal/mole . Since parabolic kinetic behavior is typically caused by the formation of a dense product layer, the rate limiting step is the diffusion of oxygen through this oxide. In this situation, the activation energy for parabolic oxidation is also the activation energy for oxygen diffusion.

Oxygen Diffusion in Plutonium Dioxide

The theory of parabolic oxidation has been described by Wagner.¹⁰ This theory assumes that the volume diffusion of reacting ions (corresponding point defects) or the transport of electrons across

FIGURE 2. Temperature Dependence of the Parabolic Oxidation Rate Constants for Pu-1 wt% Ga Oxidation in 500-Torr Air

the oxide layer is the rate-determining process. Reaction at the metal-oxide interface is then very rapid. Rate controlling lattice diffusion occurs by the formation of point defects with different types of defects resulting in different diffusion mechanisms.

Wagner^{11,12} derived an expression for relating parabolic rate constants and diffusion coefficients. Wach^{13,14} further related the rational rate coefficient used by Wagner to the parabolic rate coefficient, k_p , and the diffusion coefficient, D , for oxygen diffusion in V_2O_5 . This method has now been applied to the oxygen/plutonium dioxide system. The diffusion coefficient for oxygen diffusion in $PuO_{1.995}$ was determined from the experimentally determined parabolic rate constant, k_p , by the equation

$$k_p = 2DW^2\rho^2 \quad (3)$$

where W is the mass fraction of oxygen in PuO_2 and ρ is the density of PuO_2 .

Following the calculation of the diffusion coefficients as a function of temperature, the

activation energy for diffusion may be determined from the Arrhenius relationship

$$D = D_0 \exp(-Q_D/RT) \quad (4)$$

Evaluation of numerous data on the diffusion of hydrogen in metals and non-metals revealed a linear dependence between the logarithm of D or D_0 and the activation energy Q_D .¹⁵ This relationship can be described by the equation

$$D_0 = D_\theta \exp(Q_D/R\theta) \quad (5)$$

where D_θ is the intercept at $Q_D = 0$ and θ has units of temperature. At any temperature, T , the diffusion coefficient is given by

$$D = D_\theta \exp(Q_D/R\theta) \exp(-Q_D/RT) \quad (6)$$

or

$$D = D_\theta \exp(Q_D/R\theta - Q_D/RT) \quad (7)$$

This relationship is significant in that it permits the determination of the activation energy for a diffusion process from a single value of the diffusion coefficient. Numerical values for D_θ and θ have been determined directly from $\log D_0$ versus

Q_D plots.¹⁵ Since D_θ and θ are characteristics of the diffusant, they also may be determined independently. The constant D_θ was derived from Heisenberg's uncertainty principle and is given by

$$D_\theta = h/4\pi m \quad (8)$$

For oxygen, D_θ is equal to 1.99×10^{-9} m²/sec. The constant θ is the vibrational characteristic temperature and is determined by

$$\theta = h\nu/k \quad (9)$$

Oxygen has a calculated value for θ of 2230 K¹⁶ while the value determined experimentally was 2010 K.¹⁵

Diffusion coefficients for oxygen diffusion in $\text{PuO}_{1.995}$ were calculated from the parabolic rate constants obtained for the oxidation of the Pu-1 wt% Ga alloy in 500 torr of dry air. These results are summarized in Table 1. Data were obtained over the temperature range 250 to 465 °C. The Q_D values included in this table were obtained using the single point method of Equation 7. The average value for all runs was 20.3 kcal/mole, which compares favorably with the value of 22.6 kcal/mole obtained from the Arrhenius plot of Figure 3. This value is essentially identical with the 22 kcal/mole calculated from Figure 2 for the activation energy of parabolic oxidation. Diffusion of oxygen in $\text{PuO}_{1.995}$, at a single oxygen partial pressure of 105 torr, can be described by the equation

$$D = 1.2 \times 10^{-6} \exp(-22,600/RT) \quad (10)$$

Results from this investigation compare favorably with the limited number of results available from earlier studies.⁶⁻⁹ Curves A⁶ and B⁷ in Figure 3 were obtained by an isotope exchange method using stoichiometric $\text{PuO}_{2.00}$. The activation energy for oxygen diffusion in these materials was 45 and 42 kcal/mole respectively. Diffusion coefficients in Curve C⁸ were determined by the gravimetric oxidation of PuO_{2-x} . The activation energy for oxygen vacancy diffusion was 11 kcal/mole. The single value at point D⁹ was obtained from electrical resistivity measurements of $\text{PuO}_{1.98}$. Activation energies for self-diffusion were calculated

TABLE 1. Self-Diffusion of Oxygen in $\text{PuO}_{1.995}$ During the Parabolic Oxidation of Plutonium-1 Weight Percent Gallium in 500 Torr of Air

Temperature (°C)	k_p (g ² /cm ⁴ sec × 10 ¹¹)	D (m ² /sec × 10 ¹⁶)	Q_D^* (kcal/mole)
251	2.00	5.46	20.5
279	3.40	9.28	21.2
296	14.20	38.8	19.9
304	9.89	27.0	20.9
326	21.60	59.0	20.7
350	26.10	71.1	21.5
377	64.60	176	21.2
400	147	401	20.6
401	196	536	20.2
402	130	354	21.1
405	127	346	21.3
417	244	666	20.4
422	642	1750	18.7
442	948	2590	18.7
464	1680	4570	18.3
Average			20.3

*Determined by Equation 7.

FIGURE 3. Temperature Dependence for Oxygen Self-Diffusion Coefficients in Plutonium Dioxide

FIGURE 4. Effect of Oxygen Partial Pressure on the Oxygen Diffusion Coefficients

using Equation 7 described above. For $\text{PuO}_{1.98}$ the value was 26 kcal/mole.

Pressure Dependence of Oxygen Diffusion

The pressure dependence of the oxygen diffusion coefficient is influenced by the mechanism for oxygen transfer through the oxide film. In general, if the diffusion coefficient is directly proportional to pressure, oxygen diffuses by an interstitial mechanism. If the dependence is inversely proportional to pressure, diffusion is controlled by an oxygen vacancy mechanism.

Larson and Cash¹⁷ measured the parabolic oxidation of Pu-1 wt% Ga in 0.05-torr oxygen in the temperature range 30-90 °C. Oxygen diffusion coefficients were calculated from these data using Equation 3. Figure 4 compares these results with those

calculated from the current high-temperature study. Activation energies for diffusion were in reasonable agreement for the two studies, 30 kcal/mole at low temperature and pressure compared to 22.6 kcal/mole at high temperature and pressure. Earlier data obtained by Stakebake¹⁸ for Pu-1 wt% Ga oxidation in 300 torr of air (63 torr of O_2) also were used to evaluate the pressure effects on diffusion coefficients. Data obtained between 250 and 350 °C are included in Figure 4. The activation energy for diffusion under these conditions was 33 kcal/mole. The agreement between activation energies is indicative of similar diffusion processes. These data show an inverse pressure dependence for diffusion, which supports an oxygen vacancy diffusion mechanism.

Effect of Oxide Structure on Oxygen Diffusion

The complete phase diagram for the plutonium/oxygen system has not been firmly established and may be more complex than currently recognized.¹⁹ In the nonstoichiometric region below 300 °C, the phase diagram for the plutonium/oxygen system shows the existence of two oxide phases for oxygen/plutonium ratios between 1.5 and 2.0.² (See Figure 5.) One is an fcc PuO_{2-x} and the other a bcc $\text{PuO}_{1.52}$. The bcc phase converts to $\text{PuO}_{1.61}$ during oxidation at temperatures above 300 °C. McNeilly²⁰ measured the resistivity and thermoelectric properties of plutonium oxides and found them to exhibit typical oxide semiconductor properties. Oxides with compositions between 1.72 and 1.92 are p-type semiconductors at temperatures up to 300 °C due to the presence of $\text{PuO}_{1.52}$ with its large number of vacant sites. On oxidation above 300 °C, this oxide converts to an oxygen deficient PuO_{2-x} , which is an n-type semiconductor. The temperature for oxide transformation from $\text{PuO}_{1.52}$ (p-type) to PuO_{2-x} (n-type) increases with decreasing oxygen/plutonium composition. The cubic oxide $\text{PuO}_{1.985}$ remains n-type down to room temperature. Therefore, depending upon the oxidation temperature and oxide composition, the oxide may exhibit p- or n-type properties and contiguous layers may have a p-n junction, which can affect the diffusion process.

FIGURE 5. Plutonium/Oxygen Phase Diagram (Reference 2)

The defect structure in the plutonium oxide system is an anion type. Stoichiometric $\text{PuO}_{2.00}$ is assumed to have Frenkel-type defects.²¹ In this case, the defect pair consists of both oxygen vacancies and interstitials (V_o , O_i). Substoichiometric n-type PuO_{2-x} is oxygen deficient and the point defects are oxygen vacancies. The p-type oxide has an excess of oxygen with respect to the $\text{PuO}_{1.52}$ stoichiometry, e.g., $\text{PuO}_{1.52+y}$ with the oxygen being located in interstitial positions. Oxygen diffusion in the plutonium oxides described occurs by the migration of either oxygen vacancies or interstitials. The driving force for oxygen diffusion during oxidation is the free energy change associated with the formation of oxide from plutonium metal and oxygen gas. This potential difference is seen in the concentration gradient across the oxide film and drives oxygen diffusion. The rate of oxide growth is determined by the gradient and is proportional to the rate of

diffusion of oxygen. This mechanism leads to the parabolic rate of oxidation and provides the basis for measuring the diffusion coefficient.

Activation energies for diffusion may be grouped into two categories based on the properties of the oxide. Data for stoichiometric $\text{PuO}_{2.00}$ are in good agreement with an average activation energy of 43.5 kcal/mole. This material has a Frenkel (V_o , O_i) defect structure, which has an energy of formation of about 70 kcal/mole.⁹ At the oxidation temperatures of this investigation, it behaves like a p-type semiconductor with oxygen interstitials. The lower diffusion coefficient, higher activation energy, may well be caused by the restriction for interstitial ions in this stoichiometric fluorite phase. The average activation energy for five (Figures 3 and 4) substoichiometric PuO_{2-x} samples was 24.5 kcal/mole. This material is n-type with inherent oxygen vacancies providing the vehicle for oxygen diffusion. Dependence of oxygen diffusion on the oxygen/plutonium ratio may account for the variation in diffusion coefficients and activation energies being reported.

CONCLUSION

Oxygen diffusion through the plutonium oxide film formed during the oxidation of plutonium was evaluated. The only oxide detected was identified by x-ray diffraction as an fcc $\text{PuO}_{1.995}$. However, because of the nonequilibrium system, the presence of a bcc $\text{PuO}_{1.52}$ film at the oxide/metal interface is suspected. The thickness calculated for the rate controlling dense oxide layer was on the order of 15 to 25 μm . If this film were $\text{PuO}_{1.52}$, it easily would have been identified by x-ray diffraction and metallography. Therefore, the rate controlling oxide is assumed to be PuO_{2-x} and any $\text{PuO}_{1.52}$ present would exist as a very thin film. Oxygen diffusion coefficients were calculated from the parabolic rate constants for the air oxidation of Pu-1 wt% Ga. These coefficients compared well with those previously reported for oxygen diffusion in PuO_{2-x} . Any differences may be the result of differences in oxide composition or oxygen partial pressure. The difference between the results obtained for $\text{PuO}_{1.995}$ and those reported for stoichiometric $\text{PuO}_{2.00}$ may well be due to two

different diffusion mechanisms. The $\text{PuO}_{1.995}$ was an n-type semiconductor with oxygen vacancies providing the vehicle for oxygen diffusion. The activation energy for diffusion in $\text{PuO}_{1.995}$ was 22.6 kcal/mole, which was nearly identical with the activation energy of 23.4 kcal/mole obtained for the parabolic oxidation of plutonium. Evidence indicates that the diffusion coefficient increases and the activation energy for diffusion decreases as the oxygen/plutonium composition decreases for fcc PuO_{2-x} . Higher diffusion coefficients and lower activation energies are expected for bcc $\text{PuO}_{1.52}$. A technique for calculating activation energies from single values of the diffusion coefficient was evaluated. This activation energy was in agreement with the value calculated from the Arrhenius equation.

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