Kinetics of the Reaction between Plutonium Dioxide and Water from 25°C to 350°C: Formation and Properties of the Phase PuO_{2+x}

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In the areas of plutonium waste disposition and storage, and medium to long-term retrievable Pu materials storage, the issue of water and other small molecule interactions with pure or impure Pu oxide materials and metal has become a major concern. Small molecule reactions in these types of systems has led to changes in materials stoichiometry, containment breaches and dispersal of material resulting from pressurization, corrosion of the containment, and the collapse of sealed containers due to the formation of partial vacuum. The exact nature of these reactions and the resulting implications for medium to long-term storage are not well understood, although there have been studies which attempted to explain them from a large body of observations and experiments [1-3].

The interaction of PuO_2 with water was investigated from 100°C to 350°C using a suite of experimental techniques which include microbalance and pressure-volume-temperature (PVT) methods, thermal gravimetric analysis (TGA), mass spectrometry (MS), x-ray and neutron diffraction. Reaction rates and oxide compositions were determined from measured increases in sample mass or pressure over time (t). Gaseous and solid products were analyzed using MS and diffraction methods, respectively. Oxide products have also been characterized by x-ray photoelectron spectroscopy (XPS). The plutonium oxide specimens used in this study were formed by oxidation of electrorefined alpha-phase metal containing approximately 100 ppm Am as the major metallic impurity. The specific surface area of the oxide was 4.8 m^2/g. The initial oxide stoichiometry was determined to be $PuO_{1.97}$ based on the measured lattice parameter and data from the correlation of the cubic lattice parameter (a_o) at fixed 0:Pu ratios with temperature reported by Gardner et al. [4].

PVT and microbalance measurements were made at 200°C to 350°C using techniques similar to those described for kinetic measurements at 25°C [5]. Accurately weighed samples (0.05-0.1 g) of oxide contained in Pt or Au crucibles were placed in volume-calibrated (36 cm^3) gold coated, stainless steel reactors sealed with nickel-gasket closures. After evacuation, a reactor was filled with H_2O vapor (24 Torr) supplied by a water reservoir held at constant temperature throughout the test. The sample temperature was measured by a thermocouple located near the specimen and was maintained at the desired constant value using a programmable controller. The system pressure was measured as a function of time using a capacitance manometer and was recorded using digital methods. After completion of the P-t measurements, samples of the gas and solid phase were obtained for MS and for XRD (or XPS analyses), respectively.

Results of PVT and microbalance measurements during exposure of plutonium dioxide to water vapor at 200°C to 350°C and 24 Torr show linear increases in pressure and mass as a function of time. Mass spectrometric analysis of gas samples taken after termination of the tests show that only H_2O and H_2 were present in the gas phase. These results are identical to those observed at 25°C [5] and suggest the following reaction:

$$PuO_2\,(s) + x\,H_2O \rightarrow PuO_{2+x}\,(s) + H_2\,(g)\ . \qquad (1)$$

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This equation implies that a fraction of the plutonium is oxidized to an oxidation state greater than Pu(IV); although difficult to unambiguously prove in an ex-situ settting, this result is consistent with earlier XPS data [2]. The kinetic results from the microbalance and PVT measurements are described by a single relationship:

$$1nR = - 6.441 - (4706/T) . \qquad (2)$$

The activation energy for reaction is 9.4 +/- 0.6 kcal/mol. The uncertainty in E, results primarily from the uncertainty in the average R at 25°C [5]. Rates from microbalance measurements are in good agreement with those from PVT data, but are consistently higher because of water adsorption on the microbalance and the sample.

X-ray diffraction data show that the oxide product formed during reaction (1) has a fluorite-related fcc structure derived from that of the dioxide. The results of eight measurements with calculated 0:Pu ratios from 2.016 to 2.169 show that the lattice parameter of PuO_{2+x} is a linear function of composition:

$$a_o\,(A) = 5.3643 + 0.01764\ 0:Pu\ . \qquad (3)$$

When the PuO_{2+x} oxide product was heated above 400°C in subsequent TGA experiments, a mass loss was observed at approximately 360°C and the lattice constant of the resulting oxide returns to that of PuO_2, indicating that PuO_{2+x} is stable only up to 360°C. The O:Pu ratio calculated from the measured mass loss in the TGA experiments and the hydrogen generation from the PVT experiments are in excellent agreement.

Kinetic results for oxidation of plutonium dioxide by water shows that the reaction has a normal temperature dependence over the 25°C to 350°C range. The temperature dependence observed for the rate demonstrates that the reaction of PuO_2 with H_2O is primarily chemical instead of radiolytic. The rate of a purely radiolytic process is expected to be temperature independent at a fixed water pressure. At isobaric conditions, the measured activation energy of a radiolytic process might actually be slightly positive because the rate is expected to decrease as the equilibrium surface concentration of H_2O adsorbed on the oxide decreases with increasing temperature. If formation of PuO_{2+x} is promoted by radiolysis of H_2O, the largest fractional contribution to the oxidation rate is anticipated at low temperature in a system with a high surface concentration of water.

The Vegard's law behavior shown by Equation 3 assists in defining important solid-state properties of PuO_{2+x}. The continuous variation of a_o with composition indicates that PuO_{2+x} is a solid-solution. Neutron diffraction studies indicate that additional oxygen is accommodated on interstitial sites in the fluorite lattice of PuO_2. Whereas oxidation of Pu(IV) on cationic sites of dioxide would tend to shrink the lattice, accommodation of oxide ions on vacant sites causes lattice expansion. The opposing changes are apparently of comparable magnitude, and the net effect is a low dependence of a_o on the composition of $Pu0_{2+x}$.

References

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