LA-UR-97- 3502

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Reaction Kinetics Relevant to the Recycle Hydride-Dehydride Process for Plutonium Recovery

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Abstract

Objectives of this one-year, Laboratory Directed Research and Development (LDRD) project were the expansion of fundamental knowledge of plutonium chemistry and the development of information for enhancing plutonium recovery methods and weapons safety. Results of kinetic studies demonstrate that the monoxide monohydride, PuO(H), formed during corrosion of plutonium by water is pyrophoric when dry and acts as an initiator for hydride-catalyzed reaction of the metal with air. The catalyzed corrosion rate of Pu is 10^8 times faster than that in dry air and transforms plutonium into a readily aerosolized material. A potential application for the catalytic reaction is in the direct recovery of plutonium as oxide. Wet PuO(H) is non-pyrophoric and the safety hazard posed by its formation is reduced if the material is not allowed to dry.

Background and Research Objectives

Recycle hydride-dehydride recovery of plutonium is a demonstrated technology that is routinely applied in the recovery of metal from weapons components. The process, which employs the facile reaction of plutonium with hydrogen to separate the hydride product from other materials, includes a thermal decomposition step for regenerating metal and hydrogen from the isolated product. Safety concerns arise because large amounts of hydrogen and pyrophoric hydride are present in the plutonium facility during this two-step process. The recycle method maximizes safety and minimizes waste generation by limiting the amount of hydrogen used in the process. As a small amount of hydride is separated by reaction of the hydrogen with the plutonium component in a cool zone of the recovery reactor, the hydrogen is regenerated and recycled by simultaneous decomposition of the separated product in a hot zone. This one-step process reduces safety concerns and produces a metal casting ready for long-term storage.

A potential need for converting plutonium metal to oxide results from increasing interest in disposal of surplus plutonium as a mixed oxide (MOX) fuel of plutonium and

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uranium in light water reactors. In the current two-step process, hydride is first formed by reaction of metal with hydrogen and then converted to oxide by controlled reaction with oxygen. As with the two-step process for metal recovery, safety concerns associated with the process establish the desirability of developing an alternative method for producing oxide.

A primary objective of this one-year study is further definition of chemistry related to the hydride-catalyzed conversion of plutonium metal to oxide, a reaction with potential application in a one-step process for safe and direct recovery of plutonium as oxide. Enhanced corrosion of metal occurs in storage containers because small amounts of hydride are formed by hydrogen from radiolysis of plastic and other organic materials. Results of laboratory-scale experiments [Ref. 1] show that hydrided metal at 25°C reacts with air at a rate that is 10^8 greater than the corrosion rate of metal in dry air at room temperature [Ref. 2].

A novel chemical approach was pursued to determine if the hydride-catalyzed reaction is initiated by the presence of phases other than hydride. Metal coated with a layer of the oxide hydride product formed by reaction of plutonium with water [Ref. 3] was exposed to air at different conditions. In addition to expanding the fundamental knowledge of plutonium chemistry, results of the study are applicable in addressing issues of plutonium recovery and weapons safety.

Importance to LANL's Science and Technology Base and National R&D Needs

This work applies capabilities in nuclear and materials science to develop technical information that reduces the nuclear danger by supporting four central missions of the Laboratory. The results are relevant to nuclear materials management and safe disposition of plutonium because they provide additional evidence for the feasibility of a safe one-step process for direct recovery of plutonium from weapons components as an oxide suitable for MOX fuel fabrication. The area of environmental stewardship is impacted because a decrease in the number of process steps reduces the potential for generating hazardous waste. Stockpile Stewardship is addressed by an enhanced potential for safe dismantlement. Stockpile Stewardship and maintenance of stockpile safety are impacted because the experimental results are relevant to weapon disassembly incidents and accident scenarios in which plutonium is inadvertently exposed to water. Under appropriate conditions, the monoxide monohydride, PuO(H), a corrosion product formed on the metal surface by reaction of water, may be capable of initiating the highly exothermic hydride-catalyzed reaction of metal with air.

Scientific Approach and Accomplishments

The oxidation kinetics of plutonium metal coated with a layer of oxide hydride were defined using PVT (pressure-volume-temperature) methods. Samples of delta-phase Pu-Ga alloy with known masses and dimensions were sealed in volume-calibrated reaction vessels under 0.005 M NaCl solutions [Ref. 3]. Extents of aqueous corrosion were determined by monitoring the increase in hydrogen pressure over time due the following reaction:

$$\mathrm{Pu\ (s)} + \mathrm{H_2O\ (l)} \rightarrow \mathrm{PuO(H)\ (s)} + 1/2\ \mathrm{H_2\ (g)}.$$

In one case, this reaction was stopped by vacuum drying after about 10% of the metal had been consumed. In another case, the PuO(H)-coated metal was exposed to atmospheric air after evacuation of hydrogen formed during the corrosion process. Complete removal of residual moisture was verified in the first case by the absence of a detectable pressure rise in the sealed vessel over a period of several months. Continued generation of hydrogen over a six-month period shows that water remained in the other vessel.

Reactivities and kinetic behavior of the dried and undried products were determined by PVT measurements following pressurization of the reaction vessels with air. An initial air pressure of 1.0 atm (14.7 psia) was placed over the dried sample. The reactor containing the undried sample was filled to an air pressure of 6.8 atm (100 psia). In both cases, the pressures and gas-phase temperatures in the reactors were monitored over time. Instantaneous reaction rates (in mmol of gas reacted/cm^2-h) were calculated from experimental DP/Dt data with correction for gas-phase temperature. Residual gases were analyzed by mass spectrometry.

Pressure-time data for the dry PuO(H)-coated metal show that the hydride-catalyzed reaction of oxygen and nitrogen initiates following exposure to air. The corrosion rate rose exponentially after pressurization and reached a maximum of 110 mmol /cm^2-h after approximately 35 s. The increase in rate was accompanied by a thermal excursion and a progressive pressure drop that terminated at a residual pressure of 0.14 atm (2.1 psia) after about five minutes. The observed corrosion rate corresponds to reaction of 26 g Pu/cm^2-h and agrees with the value of 20 g Pu/cm^2-h measured in tests with hydride coated metal [Ref. 1]. Hydride catalysis is also demonstrated by extensive reaction of nitrogen.

Data for the undried sample show no evidence for reaction, even with a large over-pressure of air. The absence of reaction is confirmed by existence of a constant temperature and by a stable gas composition following pressurization.

When fully dried, plutonium oxide hydride is a pyrophoric material that acts as an initiator for the hydride-catalyzed reaction of plutonium with air. During the initial stage of reaction, oxidation is accompanied by formation of hydrogen. As with oxidation of hydride on the metal, the product hydrogen apparently does not appear as gas, but remains in the solid and reacts with underlying metal to form a catalytic layer of hydride that moves into the metal ahead of the advancing oxide layer. Heat produced by oxidation initiates the reaction between hydride and nitrogen and the catalyzed reaction of air with metal ensues. The process initiates at room temperature and rapidly transforms the metal from a nondispersible form into a powdered material with a large mass fraction in the plutonium-aerosolizable particle-size range.

Hydride catalysis of the plutonium-air reaction is also evident in rate data for high temperature oxidation processes of the metal. The ignition point of plutonium is 500 ± 25°C, and a self-sustained reaction occurs if metal is heated above this temperature in air. However, the reaction rate is independent of temperature and remains constant at a value of 8 ± 4 g Pu/cm^2-h over the 500-1000°C range due to formation of an oxygen-depleted boundary layer of nitrogen at the solid-gas interface [Ref. 4]. The hydride-catalyzed reaction of nitrogen diminishes the nitrogen layer and increases the corrosion rate by a factor of three.

The potential application of hydride-catalyzed oxidation for one-step recovery of metallic plutonium as oxide is confirmed. The quantity of hydrogen that would be used in such a process is limited by the amount required to deposit a thin hydride layer on the metal surface. The metal is separated as oxide particles formed during controlled oxidation with oxygen. Large amounts of hydride are not present and the release of hydrogen off-gas is markedly reduced.

The presence of moisture apparently prevents ignition of the oxide hydride and initiation of the hydride-catalyzed reaction with air. This observation is consistent with earlier work indicating that the products of aqueous corrosion are not pyrophoric when wet [Ref. 3]. Therefore, spontaneous ignition of products formed during accidental exposure of plutonium to water is unlikely if moist conditions are preserved.

Publication

Haschke, J. M. , Allen, T. H., and Stakebake, J. L., "Reaction Kinetics of Plutonium with Oxygen, Water and Humid Air: Moisture Enhancement of the Corrosion Rate," Journal of Alloys and Compounds, in press, 1996.

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