THERMALLY-INDUCED GALLIUM REMOVAL FROM PLUTONIUM DIOXIDE
FOR MOX FUEL PRODUCTION

David Kolman
Los Alamos National Lab.
Mail Stop E510
Los Alamos, NM 87545
(505) 665-6773

Manuel Griego
Los Alamos National Lab.
Mail Stop E511
Los Alamos, NM 87545
(505) 667-2572

Chris James
Los Alamos National Lab.
Mail Stop E510
Los Alamos, NM 87545
(505) 665-9263

Darryl Butt
Ceramtec, Inc.
2425 South 900 West
Salt Lake City, UT 84119
(801) 956-1022

ABSTRACT

A process for the separation of gallium oxide from plutonium dioxide using a "dry" process has been developed. The process uses a reducing gas to generate a volatile gallium specie which is collected downstream. The effects of temperature, duration, flow rate, and sample size have been examined. Results indicate that temperature plays a strong role in the efficacy of gallium removal. Other variables have a much smaller effect on gallium removal efficiency. Gallium removal to approximately 1 ppm (atomic) has been observed. Gallium removal to sub-ppm levels appears feasible based on results-to-date.

I. INTRODUCTION

In January 1997, the Secretary of Energy signed a Record of Decision finalizing a dual-track strategy to irreversibly dispose of the Nation's surplus plutonium. The strategy allows for immobilizing plutonium in inert forms or burning plutonium as mixed oxide (MOX) fuel in existing reactors. There is one potential drawback to using weapons grade plutonium as feed for MOX fuel - weapons grade plutonium contains approximately 1% gallium. Gallium is known to degrade the properties of many metallic materials via corrosion, embrittlement, or intermetallic compound formation. Thus, there is significant concern that gallium present in MOX fuel will compromise zirconium-based fuel cladding. Removal of gallium from MOX fuel is therefore imperative.

The aim of this work is to develop a "dry" process to reduce the Ga concentration of weapons-derived PuO_2 that is integrable into the pit disassembly and conversion process. A dry

method for Ga removal is desirable for a variety of reasons including waste reduction and relative ease of facility licensing. A dry method for removing Ga from PuO_2 was thought to be possible, based upon initial calculations. It was theorized that a reducing gas could be passed over the powder thereby reducing the solid Ga_2O_3 to Ga_2O gas:

Initial tests incorporating CeO_2 surrogates and Ar - H_2 gas confirmed that such a process was viable.

II. EXPERIMENTAL DETAILS

A. Material Characteristics

The process development tests incorporate weapons-derived PuO_2 . This material was produced from Pu metal using a three-step process (hydride - nitride - oxide). Analysis of the powder (Figure 1) indicated a bimodal particle size distribution with a significant

Figure 1 - Particle size distribution and micrograph of three-step PuO_2 powder used in this study.

UNCLASSIFIED AND UCNI

LA-UR-99-1760
All Case Group

APR 15 1999

date

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, 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. 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.

fraction of the powder comprising sub-micron particles. This powder was found to have a surface area of $6.4 \text{ m}^2/\text{g}$ ($\pm 0.3 \text{ m}^2/\text{g}$). Chemical analysis of this powder (using inductively coupled plasma - mass spectroscopy) indicated a Ga concentration of 0.87 wt% ($8700 \text{ } \mu\text{g}/\text{g}$ (ppm)) or 1.1 atomic%.

B. Test Procedure

Thermally-induced gallium removal (TIGR) tests comprised the exposure of PuO_2 to Ar - 6% H_2 gas ($\text{O}_2 < 8 \text{ ppm}$, $\text{H}_2\text{O} < 0.7 \text{ ppm}$). PuO_2 samples (typically 0.3 g, 0.9 g, and 2.5 g) were weighed, placed in nonreactive alumina boats, and then reweighed, noting the gross weight of each boat. These small boats were then placed in a large alumina boat to facilitate handling. The large boat was inserted into the hot zone of a tube furnace (see Figure 2). The temperature was ramped at a rate of $20^\circ\text{C} / \text{min}$. until the temperature of interest was reached. The samples were held at temperature for a fixed period of time. At the end of this period, the furnace was turned off and the samples were allowed to furnace cool. Following cooling to nearly room temperature ($< 50^\circ\text{C}$), the samples were removed from the furnace, the gas flow was stopped, and the gross weight of the boats recorded. Note that a sample exposed to a higher temperature for the same duration of time as one exposed to lower temperature is exposed to elevated temperature for a longer period of time due to the increased ramp-up and ramp-down time. Temperature, time at temperature, sample mass, and gas flow velocity were varied in an effort to determine the rate limiting step and thus optimize Ga removal.

Figure 2 - Picture of furnace setup with Ga collector.

C. Analysis Techniques

The extent of Ga removal is best determined by chemical analysis following sample exposure. However, weight loss measurements also can be used to infer Ga removal. This technique is used to yield inside into the reduction of the PuO_2 . Figure 3 shows that weight loss measurements correlate well with the Ga loss. Thus, weight loss may be used as a predictor of Ga loss. Note that weight losses of greater than 2% are observed even though Ga_2O_3 only comprises 1.2 wt% of the starting material. This indicates that significant reduction of the PuO_2 occurs concurrently with Ga_2O_3 reduction / Ga_2O evolution.

Figure 3 - Correlation of weight loss to remaining gallium concentration following exposure. Data are from tests incorporating various sample masses, exposure temperatures, durations, and gas flow rates.

D. Reproducibility

Weight loss measurements yielded superior reproducibility as compared to Ga concentration analyses. Weight loss measurements on four replicate tests (1200°C , 4 h, 1.5 cm/s gas flow velocity) had standard deviations of 7.0%, 12%, and 7.6% for 0.3 g, 0.9 g, and 2.5 g samples respectively. Ga measurements were less reproducible. Three replicate tests (1200°C , 4 h, 1.5 cm/s gas flow velocity) yielded standard deviations of 29%, 8.9%, and 4.2% for 0.3 g, 0.9 g, and 2.5 g samples respectively.

III. RESULTS

A. Effect of Temperature

RECEIVED

DEC 13 2000

OSTI

The Ga concentration and weight loss following exposure to different temperatures are shown in Figure 4. 0.5 h exposures at 600°C and 800°C resulted in essentially no Ga removal and exposures at 900°C results in only slight Ga removal. Figure 4 indicates that a temperature of at least 1000°C is required to obtain significant Ga removal. At 1200°C, the Ga concentration was reduced to approximately 150 ppm.

Figure 4 - Remaining Ga concentration and weight loss as a function of exposure temperature. Test duration: 0.5 h. Sample mass: 2.5 g. Flow velocity: 1.5 cm/s.

of the weight loss attributable to Ga removal (Figure 5) increases with increasing exposure temperature.

B. Effect of Time

The effect of test duration on Ga removal is plotted in Figure 6. It is seen that increasing exposure time produces diminishing returns in Ga removal. For the 8 h exposure, the Ga concentration is reduced by over two orders of magnitude (from 8700 ppm to 34 ppm). However, the majority of this is removed during the first 0.5 h (remaining Ga concentration = 150 ppm). The asymptotic limit under these conditions has not been determined.

Figure 6 - Remaining Ga concentration and weight loss as a function of test duration. Temperature: 1200°C. Sample mass: 2.5 g. Flow velocity: 1.5 cm/s.

C. Effect of Sample Mass

Figure 4 shows that there is significant weight loss at 800°C even though there is little Ga evolution at this temperature. Thus, the majority of the weight loss at the lower temperatures is attributable to something other than Ga evolution, i.e., PuO_2 reduction. At higher temperatures, a significant fraction of the weight loss is attributable to Ga removal. The fraction

Figure 5 - Percentage of total weight loss attributable to Ga_2O_3 loss as a function of temperature.

It is important to understand the effect of sample mass for two reasons. First, during pit disassembly and conversion, it will be desirable to perform Ga removal using kilogram size batches. Because the tests-to-date use gram quantities, it is imperative to understand any potential effects of scale-up. Moreover, an observed dependency on sample size may suggest mass transport limitation through the powder interstices. Enhanced mass transport during processing of kilogram batches may then be necessary to reduce the Ga to a desired level in a reasonable time. Enhancement means may take the form of vessel rotation, fluidized bed, etc. Thus, understanding the effect of sample mass (or, more generally, the rate limiting step)

is necessary in order to design a Ga removal system.

The effect of sample mass on Ga removal is unclear. Weight loss measurements suggest that increasing sample mass decreases percent weight loss with a confidence of greater than 99% based on linear regression of the 0.3, 0.9, and 2.5 g data. However, one test using 25 g of PuO_2 yielded a weight loss similar to the smaller samples (Figure 7). Further, Ga concentration measurements suggest that sample mass has no statistically significant effect on Ga removal. In summary, the effect of sample size cannot be determined at this time.

D. Effect of Flow Rate

As with sample size, understanding the effect of flow rate is critical for the determination of the rate limiting step. Analogous to the effect of sample mass, the effect of gas flow rate cannot be unambiguously determined at this time. Initial experiments involved Ga removal using gas flow rates of 1.5 cm/s and 3.0 cm/s. Weight loss results from tests incorporating identical temperature, time, and sample mass but different flow rate are compared in Figure 8. There is no apparent difference in weight loss when the flow rate is doubled. That is, for every test condition where mass loss is larger for the faster flow rate, there is a different test where mass loss is larger for the slower flow rate. The same is observed when comparing Ga concentration data. Linear regression of the weight loss and Ga concentration data confirms this observation.

Thus Ga evolution does not appear to be limited by mass transport of Ga_2O_3 away from the boat to its deposition point downstream.

Additional tests were run using much higher flow rates - 13 cm/s and 26 cm/s. Although it appeared that these much higher flow rates may enhance Ga removal, the effect of flow rate cannot be unambiguously concluded at this time due to significant scatter in the data.

The effect of flow rate on pure Ga_2O_3 has been determined (Figure 9). For pure Ga_2O_3 , doubling the flow rate from 1.5 cm/s to 3.0 cm/s increases the rate of Ga evolution. This indicates that Ga evolution is not reaction rate limited but rather is limited by mass transport. Moreover, calculations indicate that in the event of gas mass transport limitation, Ga_2O will be the limiting specie, as opposed to H_2 or H_2O . Given that Ga_2O evolution is not reaction rate limited for pure Ga_2O_3 , evolution will not be reaction rate limited for PuO_2 . Since Ga evolution does not appear to be either kinetically limited or mass transport limited by transport away from the boat, there are only two other potential rate limiting steps - mass transport within the PuO_2 particles themselves, or mass transport within the interstices between the powder particles.

E. Acceptability of Ga Concentration

Although the process for Ga removal has not been optimized (higher temperatures have yet to be examined), it is of interest to compare the remaining Ga concentration following TIGR to particular Ga levels that may correlate to particular levels of cladding damage. Figure 1 shows a comparison of remaining Ga concentration as a function of temperature (data points) to four particular levels. The highest level, level A, appears to be unacceptable based on examination of Zr clad material microstructure following Ga implantation. Level B appears to be an acceptable concentration based on embrittlement testing. Level C appears to be an acceptable concentration based on examination of Zr clad material microstructure following Ga implantation. Level D is known to be an acceptable concentration based on levels that are observed in existing MOX fuel as a result of fission. The lowest concentration that we have obtained, 34 ppm in PuO₂, was observed following an 8 h exposure at 1200°C. 34 ppm approximately corresponds to 2 ppm in MOX fuel assuming that the MOX fuel is composed of 95% UO₂ and 5% PuO₂. Although the research that determined the suitability of levels A - C is not definitive, it appears at this time that the Ga removal may be sufficient to avoid clad failure. However, given that the exact concentration to cause clad failure is not known (and may never be known), it is prudent to optimize Ga removal to obtain levels that are as low as reasonably achievable. Higher temperatures (>1200°C)

should readily produce sub-ppm Ga concentrations in the fuel.