

Pellet Fabrication Characteristics of TRU-Oxides Produced by Modified Direct Denitration

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INTRODUCTION

Modified Direct Denitration (MDD) was a process developed at the Oak Ridge National Laboratory in the 1980s [1,2] to produce fuel-grade UO_2 from uranyl nitrate solutions and fuel-grade mixed oxide (MOX) powder from the coprocessed U-Pu nitrate solution product. MDD is being reexamined on a glove box scale for coconversion of the mixed actinide nitrate solution (U+TRU) into MOXs suitable for use in fuel fabrication or as a storage or disposal form. In MDD, ammonium nitrate is added to a metal nitrate solution and the double salt that forms [e.g., $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4$, $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$, $(\text{NH}_4)_2\text{Np}(\text{NO}_3)_6$, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$] is decomposed inside a sloped and rotating heated pipe. The double salt directly and continuously decomposes, thus eliminating the problems associated with blending individual oxides and the difficulties associated with transition through a molten-nitrate “mastic” phase encountered in conventional denitration operations.

The current work [3] is being done in support of the Advanced Fuel Cycle Initiative and, after initial testing with cerium (used as a nonradioactive surrogate for plutonium), has produced plutonium dioxide; uranium trioxide; and MOXs of uranium, plutonium, neptunium, and americium. The focus is now on working with the products produced to date. This includes characterizing the products to the extent possible, examination of varying calcination/reduction conditions, and examination of pellet pressing parameters. Most of the effort thus far has been with MDD-produced cerium oxide, with the results to be used as a starting point for similar work with MOXs. Some pellets have been pressed with the calcined/reduced MOX.

BACKGROUND

The pellet fabrication properties of the first MDD-produced UO_3 were studied by Haas [1] and also by Davis and Griffin [4]. Both studies concluded that excellent quality UO_2 pellets could be made with the material. Uranium trioxide produced by Kitts [2] was examined by Slagle, et al. [5] who found that UO_2 powders could be “processed/sintered using standard powder preparation and pellet

fabrication techniques to yield pellets with densities greater than 96% TD.” Mailen, et al. [6] produced MOXs, $\text{UO}_3\text{-PuO}_2$ (~22 wt % Pu), which were reduced, pressed into pellets, and sintered. The sintered pellets had “densities of 95% of theoretical, good external appearances, and good microstructures [6],” and were completely soluble in refluxed 7M nitric acid. The current work has found the MOX directly out of the kiln to also be completely soluble in nitric acid. A sinterable PuO_2 product was also made by Mailen but found to have poor flowability. Plutonium dioxide produced in the current work, however, was found to flow and pour without difficulty.

CURRENT DEVELOPMENT EFFORT

Cold-testing, initially done with cerium, produced improvements in equipment performance and generated the initial operating conditions for the first glove box runs, which were plutonium nitrate solutions. Subsequent runs were with uranyl nitrate and produced UO_3 . Coconversion tests were then performed using the following actinide mixtures: (a) 90%U/10%Pu, (b) 90.4%U/9.1%Pu/0.5%Np, and (c) 90.4%U/9.0%Pu/0.3%Np/0.3%Am feed solutions.

The MOX product has been calcined/reduced under varying conditions, including the use of moist reduction/inert gases. Pellets have been pressed using an existing uniaxial press located in a glove box. Sintering was conducted at the maximum temperature of the existing glove-box furnace (1350°C) using a 4% H_2/Ar gas mixture, both with and without water vapor. This sintering temperature is significantly less than the typical sintering temperature of 1700°C for MOXs.

Recent work has been carried out with the MDD--produced cerium oxide to determine methods for the characterization of the powders and pressing of pellets. The “cold” pellet-pressing equipment is almost identical to that in the glove box. Green pellet variables have been investigated, including the calcination temperature of the powder, the binder/lubricant used, and the pressing pressure. Sintering temperatures and the time at temperature have also been examined.

RESULTS

The B.E.T. surface area of the cerium oxide made during cold testing is $\sim 50 \text{ m}^2/\text{g}$. This is well outside of the range preferred for UO_2 (5 to $15 \text{ m}^2/\text{g}$); however, surface area can be reduced by calcining at a higher temperature. High surface area can hinder pellet sintering. The typical shortcoming of thermal denitration processes is the production of oxides with surface areas that are too low.

The cerium oxide powder was calcined before being pressed into pellets to remove residual/adsorbed water and nitrates. Higher calcination temperatures produced higher-density powders before pressing, which resulted in somewhat higher density green pellets. However, the resulting higher pressed pellet densities did not necessarily correspond to higher density sintered pellets (for pellets pressed at the same pressure). The higher green densities did, however, lead to less shrinkage during sintering and thus a lower possibility of cracking or hour-glassing during heating.

While the majority of the pellets were pressed to 45,000 psi, some were pressed at lower pressures. Lower pressures ($\sim 28,000$ psi) resulted in lower density green pellets and these pellets also had lower densities after sintering (all other variables constant). Up to a certain applied pressure, the green density increases logarithmically with the increasing force and then it only increases slightly [7]. Pellets pressed at or above 37,000 psi had very similar sintered densities.

The decomposition temperatures of various pellet binders and/or lubricants were determined in order to develop a temperature profile for use during pellet sintering. Stearic acid and polyethylene glycol were found to decompose completely in air by $\sim 425^\circ\text{C}$, while zinc stearate left residual zinc upon decomposition of the organics at $\sim 450^\circ\text{C}$. Decomposition of the organic in the pressed pellets was found to be very rapid. Therefore, during sintering of the pellets, a slow ramp of the temperature is used up to 450°C allow the binder/lubricant to completely decompose.

Increased time at the final sintering temperature increases the final density of the pellet. One set of cerium oxide pellets was sintered to 950°C for 6 hours and then for another 12 hours. An increase in the theoretical density of 6–8% was noted after the longer sintering time. Higher sintering temperatures also increase the density of the final pellet.

Characterization of the transuranic-containing powder for particle size distribution and surface area has not yet been done because of limitations in the availability of equipment to analyze powders containing plutonium. The calcined/reduced

U/Pu/Np/Am powder flows well into the press die and the resulting pellets had good structural integrity and achieve $\sim 50\%$ TD. Sintering of the green pellets to 1350°C increased the density by $\sim 35\%$ to $\sim 85\%$ TD. Past experience has shown that green pellets pressed from MDD powder with densities of $\sim 50\%$ TD densify to greater than 95% at sintering temperatures between 1450 and 1700°C [1, 4–6]. Pellets have been pressed both with and without various binders.

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