REACTIVE SINTERING OF PLUTONIUM-BEARING TITANATES

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ABSTRACT

Titanate ceramics are being developed for the immobilization of weapons-grade plutonium. These multi-phase ceramics are intended to be both corrosion and proliferation resistant. Reactive sintering techniques were refined to reproducibly provide titanate ceramics for further characterization and testing. Plutonium-bearing pyrochlore-rich composites were consolidated to greater than 90% of their theoretical density.

INTRODUCTION

The Department of Energy (DOE) chose a titanate-based ceramic as the preferred waste form for the immobilization of surplus plutonium[1]. The baseline formulation being developed includes a pyrochlore matrix, (Ca,Gd,Pu,U,Hf)2Ti2O7, the primary site for plutonium and uranium, and several minor phases such as brannerite, (Pu,U)Ti2O6, and rutile, (Ti,Hf)O2. This baseline and ten other formulations were prepared to provide test specimens for corrosion studies. Several aspects of the processing techniques were refined in parallel.

The fabrication procedure initially employed to produce specimens was provided by Lawrence Livermore National Laboratory (LLNL). This paper will discuss how these techniques were refined to reproducibly provide ceramics appropriate for further characterization. To refine these techniques, various processing options were investigated to determine their effect on the structural
integrity and overall uniformity of the final ceramic. Nominal compositions and post-production data of select specimens are also included.

Nominal compositions representing three of the eleven formulations are shown in Table I. The baseline formulation (A0), represents a titanate ceramic for which the plutonium feed stream would be relatively free of impurity elements. The other formulations (B3-11 and A9) were designed to provide information about potential phase formations due to chemical variations in precursors, specifically the waste streams in which the surplus plutonium is contained.

Table I. Nominal Compositions of Select Titanate Formulations (wt%)

<table>
<thead>
<tr>
<th>Compound</th>
<th>A0</th>
<th>B3-13</th>
<th>B3-17</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>9.95</td>
<td>8.30</td>
<td>7.92</td>
</tr>
<tr>
<td>HfO₂</td>
<td>10.65</td>
<td>10.27</td>
<td>9.64</td>
</tr>
<tr>
<td>TiO₂</td>
<td>35.87</td>
<td>33.80</td>
<td>32.46</td>
</tr>
<tr>
<td>Gd₂O₃</td>
<td>7.95</td>
<td>7.52</td>
<td>7.20</td>
</tr>
<tr>
<td>UO₂</td>
<td>23.69</td>
<td>22.31</td>
<td>21.44</td>
</tr>
<tr>
<td>PuO₂</td>
<td>11.89</td>
<td>11.20</td>
<td>10.76</td>
</tr>
<tr>
<td>SiO₂</td>
<td>-</td>
<td>0.88</td>
<td>2.14</td>
</tr>
<tr>
<td>Other*</td>
<td>-</td>
<td>5.72</td>
<td>8.44</td>
</tr>
</tbody>
</table>

* Includes among other compounds CaCl₂, K₂O, Na₂O, Al₂O₃, and B₂O₃.

One concern in the non-baseline formulations is how the plutonium retention is affected. These formulations are designed to yield phases that may contain plutonium and subsequently may change the corrosion behavior of this critical element. Another concern arising from changes in precursor chemistry is how densification will be affected. Uniformly shaped and high bulk density products are desired in production of these ceramics. Impurities may affect these characteristics due to minor phase formations, not necessarily plutonium-bearing, or volatilizations that alter the kinetics and reactions involved in densification. For instance, the presence of a chemical species that evolves gas at or near the maximum sintering temperature can limit densification if the gas cannot escape the bulk of the sample. Another such possibility is the presence of a chemical species that causes the formation of a new phase that incorporates elements critical for the formation of a desired phase such as pyrochlore.
EXPERIMENTAL

Test specimens were made from powders representing the formulations described above. Raw materials were mixed by standardized wet-milling techniques. Powders were weighed and added to high-density polyethylene bottles along with an appropriate amount of deionized water and yttria-toughened zirconia grinding media. These slurries were rolled for ~16 hours to provide mixing and size reduction of any coarse particles.

The well-mixed slurries were then heated (typically at 110°C for 16 hours). The resulting powder cakes were pushed through a #20 mesh sieve to form granules.

Dried granules were placed in a platinum vessel and calcined at 750°C for 1 hour in either air or flowing argon. The calcined granules were then uniaxially pressed at ~69 MPa (10,000 psi) to form green, or unfired, pellets. A Carver Press, Model #3912, and a 1/2” or a 1-1/8” diameter die set was used to prepare all of these samples. Green densities were determined geometrically. The pellets were then placed on platinum setters coated with granules of similar or identical composition to avoid sticking.

Finally, the pressed pellets were reactively sintered at 1350°C for 4 hours; the heating and cooling rates were 2.5°C/min. A bottom-loading Deltec furnace, Model #DT-31-RS-B, was used for the sintering process. Most specimens were sintered under an argon purge (1L/min). Some pellets were sintered in stagnant air for comparison.

RESULTS AND DISCUSSION

Many baseline specimens were initially produced to test various processing parameters. Processing refinements described below, such as initial mixing and uranium oxide stock, were then employed in making representative specimens of all formulations. These final specimens were fully characterized to provide a database describing the resulting ceramics.

Green densities of pressed pellets showed little variation. All were ~40% (±5%) of their final theoretical density. The granules created after drying, by pushing the dried cakes through a #20 mesh sieve, provided an appropriate level of flow for loading into pressing dies. Since these granules were made up of agglomerated fine powders, it was necessary to limit applied uniaxial loads to ~69
MPa and pellet height to diameter ratios to ~0.25 to avoid pressing flaws such as lateral cracking. Cracking was consistently observed when these limits were exceeded.

Raw mixing proved to be a critical processing step. Insufficient mixing and milling resulted in relatively less-reactive powders. Since the desired phases are formed during densification by reactive sintering mechanisms, it is extremely important that the materials be in intimate contact [2]. As mentioned previously, we adopted a 16-hour milling cycle time to ensure sufficient mixing and particle size reduction. Powders mixed less aggressively, say, for only one hour, yielded poorly reacted products, which was evident by limited densification. For instance, baseline specimens prepared from powders that were ball milled only one hour had an average bulk density of 4.91 g/cm³, while those milled for 16 hours consistently yielded ceramics with average bulk densities of 5.55 g/cm³ (theoretical density ~5.6 g/cm³, sample standard deviation < 0.1 g/cm³). Figure 1 illustrates this difference. The A0-1, baseline specimens were made from powders milled for only one hour. All other specimens represented in Figure 1 were made from powders milled for 16 hours.

Uranium purity also proved critical. The initial two batches of baseline ceramic, A0-1 and A0-2, were prepared using UO₂ that contained approximately 0.7 wt% carbon contamination. The final densities of these two batches were 4.91 and 5.21 g/cm³ (both ± 0.10 g/cm³). Three other batches of baseline material were prepared, labeled A0-3, 4, and 5, that did not contain any detectable carbon in the UO₂. The densities of specimens made from these powder batches averaged 5.56, 5.61, 5.48 g/cm³ (all ± 0.01 g/cm³). As illustrated in Figure 1, the purer UO₂ stock consistently attained denser final products.
Figure 1. Average Bulk Densities of Baseline Specimens Containing Carbon Impurity (A0-1, 2) and Without This Impurity (A0-3, 4, 5)

Processing techniques initially recommended by LLNL called for powders to be calcined in an inert atmosphere. It was later thought that calcining the powders in an oxidizing atmosphere, such as air, may actually improve the reactivity of the relatively refractory uranium oxide by changing its oxidation state from +4 to +5. To test this hypothesis specimens were made from two different powders that used cerium as a chemical surrogate for plutonium. The calcined powders differed in that two were calcined in air and the others under flowing argon (99.999% purity level). Resulting specimens showed no discernable difference in degree of densification as illustrated in Figure 2. This result supports using air in the calcination of all subsequent materials. Although air calcination did not seem to improve densification of these baseline samples, it
may be of great benefit for efficient removal of potential carbon contaminants in non-baseline formulations.

Figure 2. Comparison of Calcination Atmospheres for Specimens Made from Two Different Baseline Formulations That Use Cerium as a Chemical Surrogate for Plutonium

Sintering in air was also investigated. As shown in Figure 3, side-by-side experiments showed that regardless of overall composition sintering in stagnant air yielded comparable products in terms of bulk density to those made under an argon purge. This is encouraging for scaling up the processing techniques. Being able to process in air greatly simplifies equipment design and control.
By use of the processing techniques discussed above, final specimens of each formulation were prepared. Full cross-sectional samples of each type of specimen were mounted for SEM analysis.

Figure 4 is a SEM photomicrograph representing typical phase assemblages observed in baseline samples. These specimens contain brannerite, rutile, and pores evenly distributed within a pyrochlore matrix. The minor, actinide oxide phase is always located within brannerite grains. The impurity specimens made from formulations such as B3-13 and B3-17 (see Table I) contain these phases along with zirconolite and silicate phases, which are more prominent with increasing impurity levels.
CONCLUSIONS

Processing techniques were refined such that uniform ceramics of high bulk density could be produced routinely. Raw materials and their subsequent mixing proved the most critical processing steps. The viability of calcining and sintering in air, instead of an inert atmosphere, was tested and appears feasible.

Most of the specimens were consolidated to greater than 90% of their theoretical density by use of reactive sintering techniques. Major phases identified by SEM/EDS and XRD were pyrochlore, brannerite, and rutile.

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REFERENCES
