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PREPARATION OF THORIA-BASED POWDERS VIA DECOMPOSITION FROM NITRATE SOLUTION

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Abstract - The behaviour of wet ground thorium-based powders produced by hydrothermal, microwave, and "pot" denitration are compared. Crystallite size controls sintered density, but the minimum crystallite size required to produce high-density pellets depends on the method of preparation. It is also demonstrated that very rapid sintering kinetics can be achieved by utilizing the inherently small crystallites provided by denitration.

I - INTRODUCTION

Thorium fuel cycles are being developed for CANDU 

/1/. This entails the conversion of nitrate solutions into oxide powders suitable for pellet fabrication. Due to high gamma radiation fields, all processing must be carried out remotely /2/. This implies that the process employed must be as simple and reliable as possible.

The most direct and probably simplest method of converting a nitrate solution into an oxide powder is denitration (thermal decomposition). Only heat is required and no waste products are formed /1/. Denitration produces coarse particles made up of very fine crystallites. It has been shown that high-density pellets can be fabricated from such powders by heat treating and wet grinding /3,4/. This paper examines the influence of denitration method on powder properties. Because denitration produces a coarse powder that must be

/1/ Water and NOx vapors generated during denitration would be converted back to nitric acid and recycled.
modified by grinding, it is reasonable to expect that the powder properties should not be sensitive to the heating method. If this were the case, it would allow for considerable flexibility in the manner in which heat was applied in an industrial setting.

In the previous work /3,4/, heat treatment was used to increase the mean crystallite size. When the crystallites were too small, the cakes dried from the ground slurries produced hard granules that led to inhomogeneous sintering. The second part of this paper describes work aimed at packaging the small crystallites into suitable granules, so that the rapid sintering kinetics offered by the small crystallites can be exploited in fast, low-temperature sintering.

II - EFFECT OF DENITRATION METHOD

Hydrothermal and microwave denitration were studied earlier. Hydrothermal denitration involved heating hydrated thorium nitrate crystals in the presence of steam in a rotary tube furnace /4/. Microwave denitration involved heating mixed-nitrate solutions with microwaves /3/. Despite the very different conditions, both of these methods produced similar powders. The as-denitrated powders were made up of large, hard particles (Fig. 1a) consisting of small crystallites (Fig. 1b). Heat treating the powders did not change the particle morphology (Fig. 1c), but did result in crystallite growth (Fig. 1d). Wet grinding produced near-colloidal slurries which were dried into cakes. Crushing these cakes created powders like those shown in Fig. 2. Powders treated at low temperatures (small crystallites) and ground produced hard cakes that yielded dense, brittle granules (Fig. 2a). Powders treated at high temperatures (large crystallites) and ground produced cakes that yielded large, soft granules (Fig. 2c). The hard granules making up small-crystallite powders did not deform during pressing, resulting in inhomogeneous green structures. During sintering, each granule sintered rapidly, shrinking away from its neighbours and resulting in fissures, such as those shown in Fig. 2b. The soft granules making up the large-crystallite powders consolidated into homogeneous green structures, which sintered into high-density pellets with normal microstructures (Fig. 2d).

Although the hydrothermal and microwave denitrated powders behaved in a similar fashion, the crystallite size necessary for fabrication of high-density pellets and the heat-treatment temperature required to achieve the required crystallite size differed for each preparation. For example, a thoria powder hydrothermally denitrated at 600°C and ground, which had a crystallite size of only 6.5 nm, sintered to 97% of theoretical density (TD). With microwave denitrated thoria/
3% urania, a heat treatment temperature of 1300°C and 48 nm crystallites were required before a sintered density of 97%TD was achieved. This difference in behaviour might also have been caused by the uranium in the latter material.

Fig. 2 - Microwave denitratated powders and corresponding sintered pellets. Shown are a powder heat treated at 600°C and ground (a), a polished section through the 82% TD pellet sintered from this powder (b), a powder heat treated first at 900°C and at 1300°C and ground (c) and an etched section through the 97%TD pellet sintered from it (d).

Recently we have examined a third method of denitration and taken a closer look at this apparent anomaly. Powders were prepared by "pot" denitration, which involves heating a vessel containing nitrate solution in a resistance furnace. 2.3 M thorium nitrate and 2.2 M mixed thorium/uranyl nitrate (U:Th = 0.03) solutions were placed in a Pyrex vessel and heated to 400°C at a rate of 10°C/h. These powders were then heat treated for 2.0 h, ground for 1.0 h, fabricated into pellets and examined using the same techniques and conditions employed in the earlier work /3, 4/.

Results from this work on pot denitration are plotted with those obtained in the earlier studies in Fig. 3.

Fig. 3 - Plot of geometric sintered density versus crystallite size for denitratated powders prepared by three different methods.

Each preparation results in pellets whose densities follow crystallite size in a similar manner, which is consistent with the fact that crystallite size controls sintered density through the same mechanism.
in all cases. For a single preparation method (pot denitration), thoria yields a higher density pellet than thoria/3%urania for a given crystallite size. However, each preparation has its own crystallite size/sintered density curve. More importantly, the curves approach full density asymptotically and this translates into a large range of crystallite sizes for any specified density greater than about 95%TD. The associated span of heat treatment temperatures is also wide and this has serious implications from a processing point of view. Further experimental work is required to explain this unexpected sensitivity to preparatory method.

III - EFFECT OF CRYSTALLITE SIZE ON SINTERING KINETICS

We are now trying to package the inherently small crystallites provided by denitration into granules that can be pressed and sintered into homogeneous bodies. There are a large number of possible ways of achieving the required packaging. The first one that we examined was spray drying the ground slurries with the aim of getting the granule size into the micrometre size range, in the hope that this would reduce the scale of inhomogeneity to the point were inhomogeneous sintering did not occur.

Powder was prepared by denitrating thorium nitrate solution in the rotary hydrothermal denitrator at 500°C. A portion of this powder was heat treated in air for 1.0 h at 1500°C and then ground as a 20 vol% aqueous slurry in a stirred-ball mill (2). Grinding was carried out for 2.0 h at 330 r/min using 4.76 mm diameter spheres as the grinding media. A proprietary additive was used to increase the fluidity of the slurry. The as-denitrated powder was ground in the same way. The ground slurries were then spray dried in a small, co-current flow spray dryer (3). Some of the characteristics of these powders are summarized in Table 1. Crystallite size was measured in the usual manner /3/, particle size was measured by diluting the ground slurries with distilled water containing 0.5 wt% sodium hexametaphosphate and then analysing in the normal way /4/.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Crystallite Size (nm)</th>
<th>Particle Size (μm)</th>
<th>Green Density (% TD)</th>
<th>Sintered Density (% TD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-denitrated</td>
<td>7.0</td>
<td>0.26</td>
<td>51.6</td>
<td>90.7</td>
</tr>
<tr>
<td>heat-treated</td>
<td>96</td>
<td>1.25</td>
<td>64.1</td>
<td>96.2</td>
</tr>
</tbody>
</table>

Table 1 - Characteristics of spray-dried powders and pellets sintered from them in high-temperature dilatometer.

Crystallite size had a dramatic effect on the morphology of the spray-dried granules, as can be seen in Fig. 4. The particles making up the granules of the heat-treated powder are large enough to create rough surfaces. The as-denitrated powder, which was determined to have a smaller particle size (Table 1), produced smooth spray-dried granules.

Pellets were pressed from these powders and then vacuum sintered in a high-temperature dilatometer. Fig. 5 shows the heating cycle and change in pellet length during sintering. The large-crystallite

(2) 01 Attritor, Union Process Inc., Akron OH, USA.

(3) 130 Mini Spray Dryer, Büchi Laboratoriums-Technik AG, Flawil, Switzerland.
material did not undergo significant sintering until it was above 1500°C, which is the temperature that it was heat treated at. Contrast this behaviour to that of the small-crystallite material, which began to shrink almost immediately.

**Fig. 4** - Morphology of spray dried denitrated thoria powders with crystallite sizes of 7.0 nm (a) and 96 nm (b).

Although the small-crystallite material sintered rapidly and at a low temperature, a high-density pellet did not result (Table 1). In addition to increasing the sintering kinetics, small crystallites also cause lower green densities. Thus, even though the small-crystallite material shrunk the most, it did not produce a higher density pellet. Ceramography revealed granule remnants in the pellet sintered from the small-crystallite material.

**Fig. 5** - Change in length during sintering of pellets fabricated from spray dried powders with two different crystallite sizes. Shrinkage has been corrected for thermal expansion and temperature was measured close to furnace heating elements, several centimetres from the pellets.

These results demonstrate that there is tremendous scope for reducing sintering temperatures and times, if we can learn to package small crystallite powders into homogeneous green pellets. Spray drying might be capable of providing the required packaging, but only if the resulting granules can be made more plastic, for example by utilizing organic additives. Although high densities were not achieved in this work, it has demonstrated that sintering begins at just a few hundred degrees Celsius in small-crystallite thoria pellets.
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