



Treatment techniques to prevent cracking of amorphous microspheres made by the internal gelation process

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ABSTRACT

The internal gelation process has been used to make plutonium gel spheres and zirconium gel spheres with stabilized yttrium. However, attempts to convert these amorphous gel spheres into kernels have failed due to cracking during the subsequent heat treatments. The porosity of the amorphous microspheres is typically not sufficient to permit the gases that are formed during subsequent heat treatments to escape. The microspheres will crack when the internal pressure becomes too great. In this study, several treatment techniques were applied to zirconium microspheres stabilized with yttrium in an effort to reduce or eliminate cracking. A combination of water washes, a pressurized water treatment at 473 K for 3 h, and a Dowanol PM treatment was shown to eliminate the cracking problem with the zirconium microspheres, which were heated to 1438 K.

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1. Introduction

The internal gelation process is an advanced production process for spheroid nuclear fuel particles. Its advantages include the following: (1) control of gelation time and microsphere size, (2) reproducible preparations, (3) homogeneous incorporation of fine particles of other materials into the microspheres, and (4) a large-scale engineering process [1–5]. In addition, 500 μm uranium dioxide (UO₂) fuel kernels that were produced using the internal gelation process [6] and the external gelation process with ammonia (NH₃) [7] had average sphericities of 1.02 and 1.05, respectively. Manufacturers of TRISO coated fuel particles would prefer sphericities as close to one as possible because the nonsphericity will increase as the coatings are added.

Zirconium dioxide (ZrO₂) has been considered for use in the cermet and inert matrix nuclear fuels. Recent research on ZrO₂ microspheres that were made by the internal gelation process [8–10] has revealed cracking, which is a common problem with amorphous microspheres. Another group has studied the cracking of heated microspheres that consisted of 76% zirconium, 14% yttrium, and 10% cerium [11]. Additional water washes or different heat treatments were considered as a means to eliminate or reduce these cracking and porosity problems [8,9]. In 1978, researchers at Oak Ridge National Laboratory encountered an extensive cracking problem when they tried to sinter plutonium dioxide (PuO₂) kernels made via the internal gelation process. It is speculated that the cracking problem of ZrO₂ and PuO₂ is due to their amorphous

nature. The porosity of the amorphous microspheres is typically not sufficient to permit the gases that are formed during subsequent heat treatments to escape. The microspheres will crack if the internal pressure becomes too great. Because of the interest of the Department of Energy (DOE) in the preparation of amorphous Pu–Np kernels, our current effort has focused on techniques that could significantly reduce or eliminate the cracking problem occurring in amorphous microspheres made by this process. If the problem could not be solved, then alternative production processes such as the external gelation processes would need to be explored. However, amorphous microspheres made via the external gelation process using ammonia will still have the potential for cracking because the gel spheres will contain ammonium nitrate (NH₄NO₃) and a thickener such as polyvinyl alcohol (at a minimum) [12]. This paper discusses the performance of various treatment techniques for stabilized ZrO₂ microspheres made by the internal gelation process.

2. Experimental

2.1. General

The preparation of the ZrO₂ kernels involved several steps. First, a solution of zirconium nitrate with yttrium nitrate and a solution of urea with hexamethylenetetramine (HMTA) were prepared. Zirconia must be stabilized because pure ZrO₂ normally crystallizes in the monoclinic form and changes into the tetragonal form at approximately 1273 K. The monoclinic-to-tetragonal transformation causes the microspheres to crack. A minimum of 7 mol% yttrium is needed to provide a stable cubic solid solution phase [13]. Next,

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the chilled stock solutions were combined and placed into the internal gelation apparatus [6]. The chilled broth or feed solution was dispersed as droplets into silicone oil at 368 K to cause gelation to occur. After the microspheres were collected and aged in the hot silicone oil, they were first washed with trichloroethylene (TCE) and then with 0.5 mol/L NH_4OH . The microspheres were then subjected to a variety of treatments. After the microspheres were air-dried, they were heated to 1438 K in flowing oxygen. The diameters of the kernels and percentage of cracking were determined using a Motic digital microscope. The crush strength of the intact microspheres was determined. A description of the preparation of the stabilized ZrO_2 kernels is provided below.

2.2. Preparation of stock solutions and the feed solution

Zirconyl nitrate hydrate (Aldrich Chemical Company) was dissolved in deionized water. Concentrated nitric acid (HNO_3) was used to dissolve yttrium metal (Morton Thiokol Inc.). When these solutions were combined, the zirconium and yttrium concentrations were 1.063 and 0.093 mol/L, respectively, and the density of the Zr–Y mixture was 1.208 g/cm³. In the other stock solution, the standard concentrations for the HMTA (Fisher Scientific) and the urea (Fisher Scientific) were both 3.200 mol/L. After each stock solution was filtered, the density of the HMTA and urea mixture was measured to be 1.140 g/cm³.

In a typical experiment, 7.68 g of concentrated HNO_3 was added to 144.96 g of the Zr–Y solution. Another bottle contained 59.30 g of HMTA–urea solution. Both solutions were cooled to 273 K for a minimum of 1 h. Prior to a production run, the HMTA–urea mixture was added to the Zr–Y solution in stages, and this new solution was thoroughly mixed. The mole ratios of HMTA to metal and HMTA to acid in the broth or feed solution were 1.2 and 1.93, respectively. The broth was transferred into a stainless steel pot, which was chilled to about 278 K.

2.3. Experimental apparatus and conditions

The experimental system, which is described in detail elsewhere [6], is a modification of an apparatus used to produce uranium and plutonium microspheres in a glove box. The conditions were selected to generate sintered kernels that were less than 300 μm in diameter. The system had previously been used to generate microspheres that became 350 or 500 μm uranium fuel kernels. The smaller target diameter is needed to reduce self-shielding in the Pu–Np kernels and to increase reactivity and burnup. A 21 gage electropolished stainless steel needle (Popper & Sons) was used. The frequency of the accelerometer (Labworks Inc.) was set at 221 Hz, and the feed pump was set to deliver 9.2 cm³/min. These settings produced approximately 13,260 droplets per minute with an average diameter of 1100 μm . The droplets were directed into a veil of hot silicone oil at the top of the gel-forming column. The droplets then flowed down the column and gelled within 8–10 s. The exact gel time was difficult to measure because the droplets and spheres had similar colors.

2.4. Internal gelation chemistry

The pH of the chilled broth is ~0.8, which is close to the pH of precipitation for zirconium. Yttrium precipitates at a pH of 7.4. The pH of the gel is generally in the range of 3–6. Because of buffering action of the HMTA keeps the pH below 6, the yttrium will not precipitate during the gelation of the zirconium. However, yttrium will precipitate when the gel spheres are washed with the 0.5 mol/L NH_4OH solution. After the initial water washes, our DTA results indicate that the only residual components in the Zr–Y gel spheres are NH_4NO_3 , HMTA, and urea. Due to the variety

of products, several different washes may be required for complete removal.

2.5. Aging, washing, and drying

During an experiment, the microspheres were collected in the wire-mesh basket. At the end of a test, the basket was lowered into the reservoir with the hot silicone oil for 20 min. After the silicone oil was drained from the gel spheres, the basket was placed in a beaker with a magnetic stir bar, and the microspheres were washed with four successive batches of TCE (J.T. Baker). Each TCE wash lasted for a minimum of 15 min. The same equipment that had been used with TCE to remove residual silicone oil was used with 0.5 mol/L NH_4OH to remove the NH_4NO_3 , urea, and unreacted HMTA from the microspheres. Each NH_4OH wash lasted for a minimum of 30 min. The electrical conductivity of the spent NH_4OH solution was measured using a YSI 3100 conductivity instrument. The washings continued until the electrical conductivity of the spent washes was below 1000 $\mu\Omega$. (For comparison, the conductivity of fresh 0.5 mol/L NH_4OH was about 600 $\mu\Omega$.)

Next, treatment steps were varied to determine their effectiveness with respect to the cracking problem. First, no additional washes were performed because they were not needed to produce uranium fuel kernels without that did not crack [6]. Unlike the amorphous Zr–Y or Pu–Np gel spheres, the hydrous uranium oxide gel spheres can be highly porous. When the porous uranium gel spheres are heated, the gases from decomposition of the HMTA, urea, NH_4NO_3 , and NH_4OH can escape without damaging the microspheres. The degree of porosity is a function of the crystal morphology of the uranium [3,4]. Second, several washes with deionized water were performed until the electrical conductivity in the spent water became constant. The conductivity of the deionized water was 0.7 $\mu\Omega$. Third, the water washes in the second option were repeated. Then, the washed microspheres were placed in a small beaker and covered with deionized water. The microspheres were placed in a thick-walled Teflon container, and more water was added to ensure that the microspheres remained covered with water during the heat treatment. After the Teflon container was sealed, it was placed in a programmable oven (Barnstead–Thermolyne) and heated at 473 K for 3 h. All pressurized water treatments in this study were performed at 473 K for 3 h. Then, the treated microspheres were then washed with deionized water until the conductivity became constant. Fourth, the water washes in the second option were repeated. The microspheres were then treated five times with Dowanol PM (Aldrich Chemical Company). Each treatment with Dowanol PM ($\text{CH}_3\text{OCH}_2\text{-CH}(\text{OH})\text{CH}_3$) lasted 20 min. Dowanol PM is the fastest-evaporating solvent in the Dowanol glycol ether family, and its boiling point is 391–392 K. Fifth, the microspheres were washed with water until a constant conductivity was reached and then treated with pressurized water. The microspheres were next washed with deionized water until a constant conductivity was obtained. Finally, the microspheres were treated with Dowanol PM five times for 20 min each.

After each treatment option, the microspheres were permitted to dry under ambient conditions. The targeted gel spheres shrank from ~1100 to ~510 μm . The microspheres were rolled across a stainless steel pan positioned with a slight slope so that any non-spherical microsphere could be identified and removed. A slit was cut along one of the pan walls to permit the defective microspheres to be pushed into a second pan.

2.6. Heat treatment and subsequent analysis

Small samples of the microspheres from the various treatments were placed in a Harrop model ST-736 differential thermal

analyzer (DTA)/thermogravimetric analyzer (TGA). The samples were heated to 1438 K at various ramp rates under flowing oxygen. The standard ramp rate was 100 K/h until 663 K was reached and then 200 K/h until 1438 K. Slower ramp rates and low-temperature dwell periods did not appear to reduce the cracking problem when it was present.

The partially sintered microspheres were then inspected using the digital microscope to determine the relative amount of cracking. The diameters of several intact microspheres were measured. Finally, the crush strength of individual microspheres was measured using a custom-designed apparatus that could apply up to 1.200 kg of pressure to an individual microsphere.

3. Results and discussion

Trace amounts of NH_4NO_3 , urea, and HMTA are the most likely cause of cracking in amorphous microspheres. The NH_4NO_3 , HMTA, and urea will completely decompose by 553, 513, and 723 K, respectively. The amounts of the trace components will be dependent on the effectiveness and number of the treatments. The gel spheres will contain a considerable amount of the final treatment solution even after the microspheres are air-dried. As the microspheres are heated, the trace components and the remains of the final treatment solution will generate a considerable amount of gas. The heating also causes the diameter of the microspheres to decrease. With the broth formulation used in this study, the shrink

factor from the initial gel sphere to the sintered kernel is four. As the amorphous microsphere shrinks, it becomes harder for the gases to escape. The microsphere will crack if sufficient pressure builds up. When cracking is observed, the three potential corrective actions include additional washes or treatments, an improved heating profile, and the use of a pore-forming agent. A recent study [11] used excess urea to form porous gel spheres that did not crack. In this effort, the use of pore-forming agents was not considered because these agents should make it very difficult to meet the requirement of near-theoretical density for the sintered Pu-Np kernels.

A series of treatment techniques was evaluated in an effort to prevent cracking. Key results from the various treatments are shown in Table 1. With the first treatment, the stabilized zirconium gel spheres were washed with TCE and then with 0.5 mol/L NH_4OH . After the spheres were air-dried, they were heated to 483 K, which should cause a significant fraction of the NH_4NO_3 , HMTA, and urea to begin to decompose. After 1 h at 483 K, the microspheres were heated to 748 K, which is slightly above the temperatures for complete decomposition of the NH_4NO_3 , HMTA, and urea. Under these conditions, approximately 50% of the microspheres cracked.

The next option considered was the addition of numerous water washes. Six water washes were needed to lower the conductivity of the spent water from 715 to 22 $\mu\Omega$. The conductivities from additional water washes ranged from 9 to 21 $\mu\Omega$. A sample was heated to 663 K at 100 K/h and to 1438 K at 200 K/h. The DTA results (Fig. 1) showed a strong exothermic reaction, which began at 703 K and was completed by 727 K. The TGA results did not show any noticeable weight loss during the exothermic reaction. Therefore, the strong exothermic reaction is probably caused by a phase change that produced a more-crystalline structure. Nearly all of the weight loss for the sample occurred before 473 K. Additional DTA/TGA tests demonstrated that essentially all of the cracking occurred below 653 K; therefore, the phase change did not play a noticeable role in cracking. A visual inspection of the microspheres with the digital microscope indicated that the cracking problem was less than 5%. Another internal gelation study [11] reported that cracking of amorphous microspheres could occur

Table 1
Performances of the washes after the microspheres were heated to 1438 K.

Treatment	Cracking (%)	Crush strength (kg/sphere)	Failure rate (%)
TCE and NH_4OH	50	–	–
TCE, NH_4OH , and H_2O	5	1.030	25
TCE, NH_4OH , H_2O , pressurized H_2O , and H_2O	2	1.090	50
TCE, NH_4OH , H_2O , and Dowanol PM	2	1.140	30
TCE, NH_4OH , H_2O , pressurized H_2O , H_2O , and Dowanol PM	0	>1.200	0

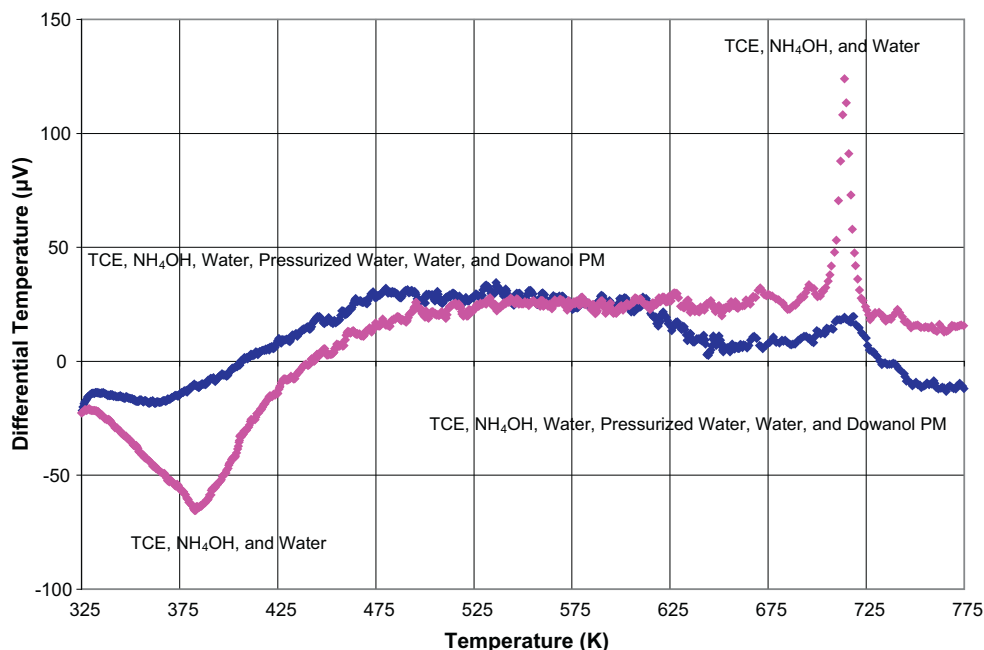


Fig. 1. DTA results for zirconium–yttrium microspheres from two treatment.

before 383 K so changes to the heating profile are unlikely to reduce cracking.

As individual compounds, urea, HMTA, and NH_4NO_3 do not have any exothermic reactions. However, a 1:1 mixture of HMTA and urea has a strong exothermic reaction, which is slightly above 573 K [11]. When the DTA/TGA experiment on microspheres that were washed with TCE, NH_4OH , and water was repeated with flowing nitrogen, a large percentage of the microspheres became black, which suggested the presence of the carbon from an organic contaminant. A visual inspection indicated that about 5% of the microspheres cracked. External cracks or fault lines were present in a significant fraction of the intact microspheres. During the crush strength tests, 25% of the tested microspheres failed before the 1.200 kg/sphere limit. It is likely that the microspheres with the fault lines failed during these tests. Even with the failures, the average crush strength was 1.030 kg/sphere. For most applications, this level of crush strength is probably acceptable. However, higher crush strengths would be beneficial during the coating of TRISO fuel kernels.

The third option added a pressurized water treatment after the initial water washes. The spheres were then washed again with deionized water. The conductivities of the spent water washes immediately before and after the steam treatment were 21 and 982 $\mu\Omega$, respectively. It appeared that the pressurized water treatment destroyed part of the residual contaminants in the gel microspheres. Four water washes were needed to lower the conductivity of the spent wash to 23 $\mu\Omega$. After these microspheres were air-dried, they were heated to 1438 K in flowing oxygen. Surprisingly, the DTA results indicated that the size of the exothermic peak on a mass-adjusted basis was reduced by 20%. A visual inspection of the microspheres indicated that the cracking problem was on the order of 2%, which was a noticeable improvement. Because the microspheres were much more opaque than their water only counterparts, it was difficult to detect fault lines. The crush strength results were mixed. Approximately 50% of the pressurized water-treated microspheres failed before 1.200 kg; however, the average crush strength was 1.090 kg/sphere. The percentage of failures during the crush strength tests may be a better indicator of potential cracking problems than the visual inspections.

The next treatment option added rinses with several commercially available liquids after the initial water washes. Our tests indicated that Dowanol PM was the best option of those liquids tested. It was originally thought that the Dowanol PM could possibly remove water-insoluble reaction products from the microspheres. The DTA results indicated that most of the exothermic peak was eliminated by the Dowanol PM washes. However, the exact amount of the decrease could not be determined because a broad, weak endothermic peak appeared at approximately 613 K. A visual inspection of the microspheres indicated that the cracking problem (2%) and opaqueness were comparable to the findings with pressurized water-treated microspheres. Approximately 30% of the Dowanol PM-treated microspheres failed before 1.200 kg, and the average crush strength was 1.140 kg/sphere. Therefore, the Dowanol PM results were slightly better than the results after the pressurized water treatment.

The final treatment technique included TCE, NH_4OH , water, pressurized water, water, and Dowanol PM. In comparison with the Dowanol PM results without a pressurized water treatment, the DTA results, shown in Fig. 1, indicate that the pressurized water treatment slightly reduced the endothermic peak at 613 K and the exothermic peak at 703 K. No cracking was observed in any of the microspheres that were treated with pressurized water and Dowanol PM. Fig. 2 shows the zirconium–yttrium microspheres after this series of treatments had been completed and the microspheres were annealed to 1438 K. In addition, all of the tested microspheres had crush strengths in excess of 1.200 kg/

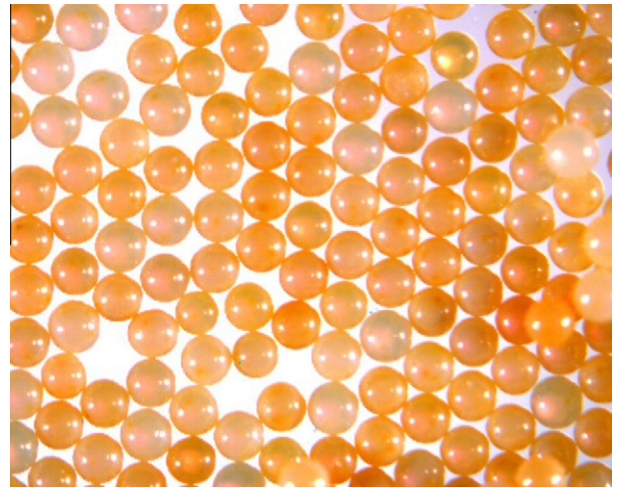


Fig. 2. Microspheres (average diameter of 300 μm) after the best wash treatments and heating to 1438 K.

sphere, and the density of the heated treated microspheres was 5300 kg/m^3 . Therefore, high-quality amorphous kernels can be produced by the internal gelation process.

4. Conclusions

Amorphous microspheres from the internal gelation process tend to crack during subsequent heat treatment. Zirconium microspheres stabilized with yttrium were evaluated because zirconium and Pu microspheres are both amorphous and suffer the same cracking problems. The porosity of the amorphous microspheres is typically not sufficient to permit the gases that are formed during subsequent heat treatments to escape. The microspheres will crack if the internal pressure becomes too great. Several treatment techniques were evaluated in an effort to reduce or eliminate cracking for amorphous microspheres. Performing water washes until the conductivity of the spent washes became constant lowered the percentage of cracked microspheres from 50% to 5%. Water washes that included a pressurized water treatment or Dowanol PM treatment lowered the cracking problem to 2%, based on visual inspections. As the cracking problem was reduced, the average crush strength of the intact microspheres increased. A combination of water washes, a pressurized water treatment, and a Dowanol PM treatment was shown to eliminate the cracking problem with the zirconium microspheres that were heated to 1438 K. These treatment procedures may be directly applicable to all amorphous microspheres that are produced by the internal gelation process, and they will be tested within the next year during the preparation of amorphous Pu–Np fuel kernels by the DOE's Deep-Burn Development Project.

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