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Use of boiled hexamethylenetetramine and urea to increase the porosity of cerium dioxide microspheres formed in the internal gelation process[☆]

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ABSTRACT

Cerium dioxide (CeO_2) is a commonly used simulant for plutonium dioxide and for plutonium (Pu) in uranium (U) and Pu oxide [(U, Pu) O_2] mixtures used in nuclear fuel development. This effort developed CeO_2 microspheres with various porosities and diameters. The internal gelation technique has only been used to produce CeO_2 microspheres with limited initial porosity. Previous studies have shown that the crystallite size and porosity of mixed U and thorium oxide microspheres and the (U, Pu) O_2 microspheres from the internal gelation process increased when an equal molar solution of hexamethylenetetramine (HMTA) and urea is gently boiled for 1 h prior to its use in the gelation process. In this study with cerium, the combination of ammonium cerium nitrate and 1-h boiled HMTA-urea failed to produce a stable feed broth. However, when the 1-h heated HMTA-urea was combined with unheated HMTA-urea in 1–3 vol ratio or the boiling time of the HMTA-urea was reduced to 15–20 min, a stable solution of HMTA, urea, and Ce was formed at 273 K. This new Ce solution produced very porous CeO_2 microspheres, which are suitable simulants for uranium microspheres.

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1. Introduction

At Oak Ridge National Laboratory (ORNL) in the early 1990s, cerium dioxide (CeO_2) microspheres were first prepared using the internal gelation process. In this research, various feed formulations of cerium ammonium nitrate ((NH_4) $_2\text{Ce}(\text{NO}_3)_6$), hexamethylenetetramine (HMTA), and urea were used to prepare hydrous cerium oxide gel spheres in the temperature range of 333–363 K [1,2]. Next, a Texas A&M University effort examined the effects of process variables such as reactant concentrations, gelation

temperature, gel aging time, and wash conditions on hydrous cerium oxide microspheres [3]. Both of these studies produced CeO_2 microspheres with relatively low porosity using unheated HMTA/urea. These microspheres were prone to cracking using typical washing, drying, and calcining techniques. Cerium was also added to yttrium-stabilized zirconium microspheres as part of a European effort on actinide co-conversion [4]. Very recently, studies at Idaho National Laboratory [5] and in China [6] have used CeO_2 microspheres as a simulant for plutonium dioxide (PuO_2) microspheres in CERMET nuclear fuel studies. These CeO_2 microspheres from unheated HMTA/urea and PuO_2 microspheres have low initial porosity, and they are both prone to crack during the calcination process. None of these internal gelation studies made an effort to increase the porosity of the CeO_2 microspheres at a given temperature.

During the development of uranium dioxide (UO_2) microspheres at ORNL, a number of process variables that can impact the porosity and crystal size were identified. As expected, an increase in the crystal size led to increase in porosity. These variables included (1) the HMTA/uranium mole ratio, (2) the nitrate/uranium mole ratio, (3) the concentration of uranium in the feed solution, and (4)

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the gel-forming temperature. Unfortunately, the initial studies on CeO₂ microspheres [1–3] did not demonstrate that any of these process variables would impact the porosity of the cerium microspheres.

Initially, when plutonium was added to uranium to prepare mixed oxide (MOX) fuel kernels using the internal gelation process at ORNL, the resulting microspheres had very small crystal sizes and were not very porous as indicated by a high tap density of 1790 kg/m³. Furthermore, the addition of plutonium required a higher gelation temperature of 353–368 K to provide a fast enough gelation time [7]. Fortunately, a number of crystal growth steps were discovered which helped increase the crystal size of the uranium and thus increased the porosity of the microspheres. After the gel spheres were aged in the hot silicone oil for 15–20 min, they underwent a wet heat treatment at 353 K. The two treatment steps lowered the tap density of the air-dried microspheres from 1790 to 1270 kg/m³. Transmission electron micrographs of the crystals for these microspheres revealed that only the uranium crystals grew while the plutonium crystals remained very small. After these uranium crystal growth steps became routinely utilized, another uranium crystal growth process was discovered for the (U, Pu)O₂ microspheres. Solutions of HMTA and urea were gently boiled at 377 K for 10 min to 1 h before they were mixed with the acidic actinide solution [7,8]. The time of boiling was critical. The tap density of air-dried (U, Pu)O₂ microspheres could be tailored to provide values from 1270 to 950 kg/m³. The lowest tap density was more ideal for pressing calcined microspheres into pellets of high theoretical densities with no sphere remnants and no dust. Without using the other two crystal growth steps, the tap densities for the air-dried microspheres were 1460 and 1790 kg/m³ with and without boiled HMTA-urea solution treatment, respectively.

In India, researchers at the Bhabha Atomic Research Centre used the 1-h boiled HMTA-urea solution and were able to prepare a more crystalline and porous thorium dioxide microsphere. The use of these more porous microspheres allowed the researchers to impregnate uranium into the microspheres to produce a (Th,U)O₂ microspheres which could be pressed into pellets [9]. More recently, the Bhabha Atomic Research Centre researchers have used pre-heated HMTA and urea to make (U, Pu)O₂ microspheres [10] via the internal gelation process. These sintered microspheres were ideal starting material for the production of tristructural-isotropic (TRISO) fuel particles, which are designed for use in advanced gas reactor.

An ORNL research effort to make porous CeO₂ microspheres was recently launched. The initial fabrication results, which include the first pathway to make more porous CeO₂ microspheres, are presented below. When the 1-h heated HMTA-urea was combined with unheated HMTA-urea in 1–3 vol ratio or the boiling time of the HMTA-urea was reduced to 15–20 min, a stable solution of HMTA, urea, and Ce was formed at 273 K. These feeds were then used to make more porous Ce microspheres using the internal gelation process.

The precise chemistry that occurs during the boiling of the HMTA-urea solution is not yet known [11,12]. However, two important factors appear evident. During boiling, a constant rate of ammonia (NH₃) is evolved due to the partial decomposition of the urea. Decomposition of the HMTA does not occur even though the compound is likely to be modified in some manner such as a rearrangement of the HMTA molecule or formation of an HMTA-urea addition product. For uranium and MOX, the feed stability drops dramatically if the HMTA-urea is boiled for longer than 1 h because sufficient urea is no longer present to complex with all of the actinides. Normally, a molar ratio of urea to actinide must be equal to or greater than 1 for a stable feed [13].

2. Experimental

2.1. Preparation of stock solutions and the feed solution

A stock solution was prepared at room temperature where the concentrations of HMTA (Fisher Scientific) and urea (Fisher Scientific) were each 3.2 M, and the density was 1141 kg/m³. Based on the technique in the earlier work [8], 1 L of this stock solution was transferred to a beaker, covered with a watch glass, and gently boiled at 377 K for 15, 20 or 60 min with stirring. A strong odor of NH₃ was noted during the boiling process. The heated beaker of HMTA-urea was then quickly cooled in a water bath and then in an ice bath. The density of each heat treated HMTA-urea solution was approximately 1140 kg/m³. All of the urea-HMTA solutions were kept in sealed containers.

Due to the buffering action of HMTA in the internal gelation process, the pH of precipitation of targeted metal must be less than 6 [13]. Most of the rare earth elements are precipitated in nitric acid in the pH range of 6.3–8.4 with ammonium hydroxide (NH₄OH) [14]. Only Ce⁺⁴ has a pH of precipitation less than 6 in a nitric acid solution and precipitates with NH₄OH at a pH of 2.7 while Ce⁺³ precipitates at pH of 8.1.

The preparation of the stock solution with (NH₄)₂Ce(NO₃)₆ (Acros Organics) required more steps. First, the actual concentration of NH₄OH (EMD) was determined to be 12.7 M using a standard titration technique. Next, the (NH₄)₂Ce(NO₃)₆ was dissolved in distilled water. For most tests in this study, this solution had an (NH₄)₂Ce(NO₃)₆ concentration of 1.675 M and a density of 1550 kg/m³. Predetermined volumes of the NH₄OH solution and the (NH₄)₂Ce(NO₃)₆ solution were both chilled to 273 K, and then they were combined to produce a Ce⁺⁴ feed stock with a hydroxide to Ce molar ratio of 0.50–0.75. This NH₄OH addition was a crystal growth parameter for uranium microspheres [7]. Less of the HMTA-urea solution is required when NH₄OH is used with the Ce solution.

2.2. Experimental apparatus and conditions for the internal gelation

The experimental system, which is described in detail elsewhere [15,16], is a modification of an apparatus used to produce uranium and plutonium microspheres in a glove box using silicone oil as the gelation medium. For most tests, the conditions were selected to generate partially sintered CeO₂ microspheres that were 300–425 μm in diameter. A 23 gage electropolished stainless steel needle (Cadence Inc.) was used to form droplets. The temperature of the silicone oil was 353 K. The frequency of the accelerometer (Labworks Inc.) was set at 700 Hz, and the feed pump was set to deliver 4.6 mL/min. The droplets were directed into a veil of silicone oil at the top of the gel-forming column. The droplets then flowed down the column and gelled in approximately 10 s. The microspheres were then transported from the bottom of the column to a stainless steel mesh basket via a Tygon tube. Unlike previous studies on uranium microspheres performed at ORNL [15,16], a considerable amount of water from the gelation process was transferred into the silicone oil, which can be problematic for the gelation process. Therefore, the water was periodically removed from the bottom of the silicone oil reservoir.

2.3. Aging, washing, and drying

At the end of a test, the basket remained in the reservoir with the hot silicone oil, and the gel spheres were permitted to age for 15 min. After the silicone oil was drained from the microspheres, the basket with the microspheres was placed in a tall beaker with a magnetic stir bar and washed with four successive batches of

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