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To cite this article: Bin Ye, Ji-Lang Miao, Jiao-Long Li, Zi-Chen Zhao, Zhenqi Chang & Christophe A. Serra (2013) Fabrication of size-controlled CeO$_2$ microparticles by a microfluidic sol–gel process as an analog preparation of ceramic nuclear fuel particles, Journal of Nuclear Science and Technology, 50:8, 774-780, DOI: 10.1080/00223131.2013.796897

To link to this article: http://dx.doi.org/10.1080/00223131.2013.796897

Published online: 28 May 2013.

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Fabrication of size-controlled CeO$_2$ microparticles by a microfluidic sol–gel process as an analog preparation of ceramic nuclear fuel particles

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(Received 13 March 2013; accepted final version for publication 9 April 2013)

In this study, microfluidics integrated with sol–gel processes are introduced in preparing monodisperse ceramic nuclear fuel microspheres using nonactive cerium as a surrogate for plutonium. Detailed information about microfluidic devices and sol–gel processes used in the research is also provided. The effects of the viscosity and flow rate of the continuous and dispersed phase on the size and size distribution of CeO$_2$ microspheres were investigated. A comprehensive characterization of the CeO$_2$ microspheres has been conducted, including the X-ray diffraction pattern, scanning electron microscopy, density, size, and size distribution. The size of prepared monodisperse particles can be controlled precisely in the range of tens of micrometers to a millimeter and the coefficient of variation of the size distribution is below 3%.

Keywords: microfluidics; sol–gel; ceramic nuclear fuel; surrogate; ceric dioxide; microparticles

1. Introduction

As an unavoidable by-product of the current uranium fuel cycle in thermal reactors, there is an excess of plutonium inventory around the world. Besides plutonium, the current fuel cycle in thermal reactors or fast reactors annually produces a great amount of long-lived minor actinides (MAs), including neptunium, americium, and curium. Because of their radiotoxicity, generation of decaying heat, very long half-life, and applicability for nuclear weapons, MA elements are a major concern for environmental safety [1].

There are many strategies for the disposal of Pu and MA elements, among which the approach of transmutation is considered as the most effective and economic solution [2]. The sub-critical accelerator-driven system (ADS) is being considered as a potential means of transmutation. Compared with other types of nuclear fuels, dispersed nuclear fuels are fit for the ADS. There are two kinds of promising nuclear fuels for the ADS: CERMET and CERCER composites [2]. The composite fuels or targets contain (Pu, MA)O$_2$ and inert matrix materials. The EUROPEANS Integrated Project has stated that the CERMET with the Mo-matrix is recommended as the reference fuel and CERCER with the MgO matrix as a back-up solution [3].

The fabrication of CERMET composite pellets is based on the fabrication of particles containing the actinide phase by a combination of external gelation [4] and infiltration methods [5], followed by mixing the particles and the matrix powder by conventional blending methods. The main advantage of such composite targets compared to a solid solution is that it potentially minimizes irradiation-induced property changes in the fuel pellets by localizing the fission damage in a limited geometric domain within the fuel [6]. The sol–gel process, which can directly convert plutonium and MA elements from solution to consolidated formulations, possesses the most brilliant future, since handling compounds of MA elements in powder form is very difficult because of their radiotoxicity [7]. Particularly, the sol–gel process steps are rather simple and no excessive liquid waste is produced, which is a major concern in the selection of the fabrication process.

However, the fabrication of composite fuels or targets is considerably more difficult than that of solid solution oxide pellets. This is a result of the specific requirements for the size distribution of the dispersed ceramic pellets. Thus, the volume of the ceramic phase and its distribution play a significant role in such fabrication [6].

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For the preparation of small-size microspheres, different methods have been reported. With the conventional external gelation method, Fernandez et al. [6] produced microspheres which had a polydisperse size distribution in the range of 40–150 μm; Ganatra et al. [8] have developed the so-called Jet Entrainment Technique for the preparation of UO$_2$ microspheres having a diameter of 100 ± 20 μm. However, both methods have limitations in controlling the size or size distribution of the ceramic microspheres. Recently, capillary-based microfluidic devices were adopted for the production of microspheres [9]. Because of a precise control over flows of fluids at small scales [10], they allow the production of size-controlled and monodisperse droplets. These devices exploit a shear-rupturing mechanism in which the size of the droplets generated is controlled by the capillary number (Ca = vμ/γ, where v is the velocity of the continuous liquid, μ its viscosity, and γ the interfacial tension) – i.e., by the interplay of the shear stress and surface tension. Thus, they have a practical applicability value in the fabrication of fuel microspheres [10].

In this study, we focus on the preparation of microparticles for CERMET composite fuels. These particles were supposed to be PuO$_2$, followed by MA infiltration, but due to the radioactivity of Pu, we have used Ce as a surrogate for Pu. Related research has proved that CeO$_2$ has a similar sintering behavior, pore former effect and thermal properties similar to PuO$_2$ [11]. A flexible microfluidic device was designed and used for synthesizing monodisperse porous beads of CeO$_2$. The diameter of the microparticles can be precisely controlled in the range of tens of micrometers to a millimeter by simply adjusting experimental parameters [12]. To the dispersion-type nuclear fuel, the monodispersity and precise size controllability of the microspheres is beneficial to form a uniform nuclear element distribution in the composite fuels or targets.

2. Experiments

2.1. Microfluidic device

A schematic drawing of the microfluidic system is shown in Figure 1 [13]. A capillary was inserted inside a T-junction (P-728-01, Upchurch Scientific) along its main axis. Two syringe pumps (LSP01-1A, Longer Pump) were used to deliver the continuous and dispersed phases at a specific flow rate. The dispersed phase flows through the left junction, the continuous phase through the top junction, and both phases exit through the right junction. Upon contact with the continuous phase, the dispersed phase spontaneously formed a droplet. Due to the shear stress imposed by the flow of the continuous phase, the droplet detached from the capillary tip to form a free-flowing droplet conveyed by the continuous phase flow. Experiments reported here were run using capillaries with an outer-to-inner diameter ratio of 358:251 (μm) and polytetrafluorethylene tubing with an outer-to-inner diameter ratio of 1.6:1.06 (mm). The direct observation of droplet formation was made by coupling a CCD camera (uEye UI-2220SE, IDS) with a microscope (XSP-30E, Shanghai halibur instrument limited company). The camera captures up to 52 frames per second at a full resolution of 768 × 576 pixels.

2.2. Materials

Continuous phase: Dimethyl silicone oil of different viscosity (AR, Sinopharm Chemical Reagent Co., Ltd). Dispersed phase: Urea CO(NH$_2$)$_2$ (AR, Shanghai Suyi Chemical Reagent Co., Ltd); HMTA (CH$_2$)$_6$N$_4$ (AR, Tianjin Guangfu Science and Technology Development Co., Ltd); (NH$_4$)$_2$Ce(NO$_3$)$_6$ (AR, Sinopharm Chemical Reagent Co., Ltd); and distilled water. Washing chemicals: CCl$_4$ (AR, Sinopharm Chemical Reagent Co., Ltd) and ammonia (AR, Sinopharm Chemical Reagent Co., Ltd).

As can be derived from Table 1, the mole ratio (R) of HMTA, urea and Ce is 2.3:2.3:1, and the solution was close to being a saturated solution so as to avoid unwanted precipitation of the coordination compound. The saturated solution, having the lowest amount of water in the gels, ensures droplet stability and good sphericity.

2.3. Fabrication process

In our experiment, ammonium ceric nitrate [(NH$_4$)$_2$Ce(NO$_3$)$_6$] was mixed with urea and an HMTA solution under cooled conditions (5°C). The transparent mixture, i.e. the dispersed phase, was injected
through the capillary, while the silicone oil, i.e. at the continuous phase, was pumped through the upper T-junction inlet as shown in Figure 1.

In Figure 2(a), the dispersed phase droplet is clearly seen to be formed at the capillary tip upon contact with the silicone oil. Downstream, the droplets are collected and transformed into gel microspheres after being heated in a 90°C water bath (Figure 2b) [4].

These gel microspheres were first washed with CCl₄ to remove the silicone oil and then with an NH₄OH solution to remove the excess gelation agents HMTA, urea, and ammonium nitrate. The washed microspheres were dried at 150°C in air and then calcined up to 500°C for 4 hours to remove residual organic matter and ammonium nitrate. The resulting CeO₂ microparticles were then sintered at 900°C for 2 hours [4]. A flowchart for the above fabrication process is shown in Figure 3.

2.4. Characterization

The crystallographic phase analysis was conducted with X-ray diffraction (MXPAHF, MacScience Co., Ltd, Japan) at room temperature using Cu Kα radiation. The microstructure of the CeO₂ microparticles was observed with a scanning electron microscope (SEM; KYKY-AMRAY 1000B, Scientific instrument factory of the Chinese Academy of Sciences, China). The pore size distribution of the sintered microparticles was measured by a surface area and porosimetry analyzer (V-sorb 2800, Gold APP Instruments Corporation, China).

3. Results and discussion

3.1. Preparation of the dispersed phase by a sol–gel process

A sol–gel process provides an alternative route for the fabrication of ceramic nuclear fuels. In comparison with the conventional powder pellet fabrication process, the sol–gel process possesses several advantages, among which one is the elimination handling of radioactive powders. The sol–gel process uses only fluids or fluid-like materials, thus becoming amenable to remote handling [4].

Vaidya [4] has described the principle of reaction among urea, HMTA and heavy metal ions in the sol–gel process. Following his method, we prepared the dispersed phase by mixing an (NH₄)₂Ce(NO₃)₆ solution with an equimolar mixture of urea (CO(NH₂)₂) and HMTA ((CH₂)₆N₄) under cooled conditions (5°C) in a beaker. HMTA underwent hydrolytic decomposition, releasing ammonia (Equations (1) and (2)), which caused the gelation of cerium hydrated oxide under heating processes.

\[
(CH₂)_₆N₄ + H^+ = ((CH₂)_₆N₄)H^+ \quad (1)
\]

\[
(CH₂)_₆N₄H^+ + 9H₂O = 6HCHO + NH₄^+ + NH₄OH \quad (2)
\]
In such processes, urea plays an important role by preventing premature gelation and consuming formaldehyde to form methylol urea derivatives that enhance the hydrolytic reaction [14]. The reaction was driven forward by scavenging of $\text{H}^+$ ions with HMTA (reaction (1)) [7].

Then, the obtained dispersed phase was proceeded as described in Section 2.3. Finally, CeO$_2$ microparticles were obtained by sintering the gel microspheres. As shown in Figure 4, the sintered particles have been identified as cubic-phase CeO$_2$. Therefore, it is proved that the fabrication process given in Figure 3 results in successful CeO$_2$ microparticle preparation.

3.2. Controllable size of CeO$_2$ microparticles in a microfluidic device

The process of preparing gelation particles in a microsystem is that the dispersed phase droplets are first produced in the microfluidic device and then solidified downstream by gelation. The uniform droplet formation is the basis of synthesizing uniform nuclear fuel microparticles.

The droplet size can be controlled by varying operating parameters. With a given capillary (i.e. for a fixed inner diameter), the droplet size can be controlled by tuning experiment parameters, such as the phase flow rates and viscosity of the continuous phase, as shown in Figure 5.

As seen from the $d$ vs. $Q_c/Q_d$ curve in Figure 5, the gel microspheres’ size decreases when the continuous to dispersed phase flow rate ratio is increased. High continuous phase flow rates $Q_c$ make the droplet breakup time shorter since the high continuous phase velocity raises the drag force and makes the equilibrium between the interfacial tension force and hydrodynamic force to be reached earlier. In addition, a high dispersed phase flow rate $Q_d$ results in a larger microsphere size in a more direct way. Under ordinary experimental conditions, the breakup time is mainly determined by the continuous flow rate but remains approximately constant for varied dispersed phase velocity [15]. Therefore, the increase in the dispersed phase flow rate leads to more dispersed phase fluid to accumulate in the capillary tip under the same droplet breakup time, which results in a larger droplet size.

Besides flow rates, the fluid viscosity also strongly affects the droplet formation. The relationship can be seen
from the \( d \) vs. \( \mu \) curve in Figure 5. The higher the viscosity of the continuous phase, the smaller is the droplet diameter. The reasons lie in the shorter droplet breakup time induced by the increasing shear force exerted by the continuous phase when the viscosity is getting higher [9]. These results show the size-controlled preparation of the feed droplets for which the subsequent gel microsphere diameter can be obtained by varying the experimental parameters.

3.3. Characterization of microparticles

As described in Section 3.2, the size of the fabricated particles can be controlled with selected material properties and procedure parameters. The microparticles after being sintered are shown in Figure 6. The mean diameter given in Figure 6 is 200 \( \mu \)m. Particles with size of about 200 \( \mu \)m suffice to realize the aim of localizing damages within a small volume for fuel pins in the scale of 1–10 mm. Pellets containing small microparticles avoid large temperature gradients in large microspheres and thus distribute the heat to the inert matrix faster [16].

The density of the microparticles is calculated to be 5.56 g/cm\(^3\) (78.0% of the theoretical density) using Archimedes’ method as the theoretical density of CeO\(_2\) is 7.13 g/cm\(^3\). The difference between the real and theoretical density can be attributed to the formation of pores during the sintering process.

In addition, a narrow microparticle size distribution is achieved with the microfluidic device. The narrow distribution is validated with the small coefficient of variance value, less than 3%. A narrow microsphere size distribution contributes to a better in-core behavior in two ways. First, a wide size distribution makes it difficult to blend the fuel particles and inert matrix powders sufficiently. The potential large pores and cracks in the pellets undermine the mechanical properties of fuel elements. Second, a homogenous fuel particle distribution leads to a similarly well-distributed reaction rate, and consequently uniform heat deposition and radiation damage.

An SEM was used to investigate the morphology of microparticles. The two surface features deserving notification, sphericity and porosity, are shown in the SEM images in Figure 7.

From Figure 7(a), the sintered microparticles seem to possess a spherical shape. Specific measurements were carried out to evaluate the sphericity factor which was found to be as low as 1.05. Among all the possible shapes, the sphere encloses the greatest volume for the same surface area. Therefore, microparticles with a good sphericity will transfer more heat through the same surface area from the enclosed volume.

The surface of a microparticle is magnified in Figure 7(b). The surface is not smooth and it can be attributed to the pores formed for further infiltration. The microparticles exhibit homogenous microstructure with a relatively narrow grain size distribution in the range of 0.5–3 \( \mu \)m and the mean grain size was less than 1 \( \mu \)m. In fact, the grain-formed surface implies sufficient inter-spaces in the microparticle.

Figure 7(c) and 7(d) shows the cross-sectional view of particles: it is smoother and has a smaller grain size than the surface, which illustrates that there are fewer pores in the microparticle’s interior.

The pore size distribution of the sintered pellets was measured by a surface area and porosimetry analyzer. Results are given in Figure 8. The Brunauer-Emmett-Teller specific surface area is 0.070704 m\(^2\)/g. The pore size ranges from 8 to 110 nm and the distribution is peaked at about 20 nm. Porosity is needed for the further MA infiltration step, which will be investigated later.
4. Summary and conclusion

Applying microfluidic technology to synthesize size-controlled CeO$_2$ microparticles that were used for a surrogate of PuO$_2$ has been developed in this study. Narrow size distributed cerium gel microspheres were first fabricated by sol–gel processes in a capillary-based microfluidic device. Then, the high uniform CeO$_2$ microparticles were obtained after sintering the gel microspheres. The size of CeO$_2$ microparticles can be controlled precisely by adjusting the flow rates of the continuous and dispersed phases as well as the continuous phase viscosity in the size range from tens of micrometers to hundreds of micrometers. The fabricated microparticles possess a good sphericity factor as low as 1.05% and 78.0% of the theoretical density, respectively. The microstructure analysis reveals that as-prepared CeO$_2$ microparticles have the pore size peaked at about 20 nm and the mean grain size less than 1 $\mu$m.

Acknowledgements

Authors are grateful to the National Natural Science Foundation of China for having funded this work through the grant nos 91226109 and 21076203. Authors thank the National Cooperation Program of Anhui Province for financially supporting this research.

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