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Preparation of UC ceramic nuclear fuel microspheres by combination of an improved microwave-assisted rapid internal gelation with carbothermic reduction process

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ABSTRACT

Uranium carbide (UC) ceramic microspheres filled into a cladding are a potential nuclear fuel format for nuclear reactors. Uniform sized ceramic UC microspheres with a diameter of 675 ± 10 μm were successfully prepared by an improved microwave-assisted rapid internal gelation process combined with carbothermic reduction. First of all, the nanoparticle carbon was dispersed into the HMUR stock solution, and the C-UO_3·$2H_2O$ gelled microspheres were prepared using an improved microwave-assisted internal gelation process without cooling the initial stock solutions. Next, the gelled microspheres were subjected to a carbothermic reduction process to obtain ceramic UC microspheres. TG and XRD investigations indicated that the C-UO_3·$2H_2O$ microspheres were firstly reduced into UO_2 at a temperature of 700 °C, and were further converted into UC at 1500 °C in argon atmosphere. Crack-free ceramic UC microspheres with a smooth and metallic shiny surface were obtained at a sintering temperature of 1500 °C for 5 h with an initial C/U molar ratio of 3.5.

1. Introduction

Nuclear power is considered as one of the cleanest and most efficient energy sources and nuclear power plant designs have been improved over the recent years. Many of these systems are foreseen to be installed in the coming decades, especially in China. Considering the increasing usage of this energy source, the amount of spent nuclear (SNF) will also grow to a considerable amount. The traditional disposal method of the SNF is the placement in a geological repository, this however requires further research on the durability of these repositories for an increasing amount of waste on one hand, and greatly limits the utilization of the uranium to its fissionable fraction on the other hand. Therefore, the closure of the nuclear fuel cycle would greatly enhance the sustainability of nuclear power.

Because of the high radioactivity and radiotoxicity, the conventional pellet process is inapplicable for the reproduction of nuclear fuels from the SNF. The innovative Sphere-Pac concept was then proposed as a new potential fuel format for the Accelerator Driven System (ADS) reactors and fast reactors owing to its convenient production process [1]. The reusable nuclides, such as U, Pu and minor actinides (MAs) recycled from the SNF are reproduced into ceramic microspheres instead of classical fuel pellets, and then these ceramic microspheres are directly filled in the cylindrical cladding tubes to fabricate nuclear fuel elements. Therefore, an important and practical issue is the fabrication of ceramic nuclear fuel microspheres.

Currently, uranium monocarbide (UC) ceramic fuel has been considered as a potential nuclear fuel because of its high thermal conductivity, high melting point, good mechanical property and high uranium atom density [2]. Many theoretical and experimental studies on the preparation of UC have been carried out since its discovery [3,4]. Traditionally, UC was prepared by the carbothermic reduction of UO_2 via the solid-state mixing of UO_2 powder with carbon black [5,6]. However, for the solid-state mixing method, a high temperature above 1700 °C was required because of the inadequate contact between the carbon and UO_2, and thus it was very difficult to get pure UC products. Recently, Guo et al. [7] reported a low-temperature synthesis of UC powder using a Pechini-type in-situ polymerization complex method, some previous works suggested using the wet-route process to prepare

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ceramic U-C-O and ZrO-ZrC$_2$ microspheres [8–18], and Bart et al. [19] reported the preparation of carbide microspheres using the conventional internal gelation process, but little investigations were conducted to prepare pure ceramic UC microspheres via the microwave-assisted internal gelation process combined with carbothermic reduction.

The internal gelation process is an advanced and experienced technology for the fabrication of ceramic microspheres with the chemical forms of metal oxides, carbides and nitrides. Our previous work [20] reported a self-developed microwave-assisted rapid internal gelation process to produce ceramic cerium oxide and it revealed that the temperature had great effect on the gelation time of the internal gelation process and the gelation process became faster with increasing temperature. Furthermore, due to the decay heat of the MAs and Pu, the mixed solutions were very difficult to keep at low temperature (0–5 °C) for a long time. Therefore, in-situ instant mixing method was used in our experiments. The stock solutions were directly transferred through two separate pumps and mixed in a T-joint mixer. The T-joint mixer had an inner volume of 0.5 μL, and the mixed solutions just stayed for several milliseconds in the capillary and remained ungelled before they left the needle. In this case, it was unnecessary to cool down the initial solutions anymore, and room-temperature initial solutions were used directly for the experiment, which greatly simplified the internal gelation process.

This work, we devoted to prepare ceramic UC microspheres by combination of the as-developed microwave-assisted rapid internal gelation process with the carbothermic reduction. Firstly, carbon containing gelled microspheres (C-UO_3·2H_2O) were prepared via an improved microwave-assisted internal gelation process, which combined the in-situ instant mixing of room-temperature precursor solutions with the microwave-assisted internal gelation. Secondly, pure ceramic UC microspheres were obtained by carbothermic reduction of the C-UO_3·2H_2O microspheres. TG, XRD and SEM were used to investigate the effects of C/U molar ratios, temperature and reaction time on the phase and microstructure evolution of the whole process. Crack-free ceramic UC microspheres with a density of 92% TD and smooth metallic luster surface were obtained at a sintering temperature of 1500 °C for 5 h with an initial C/U molar ratio of 3.5.

2. Experimental procedure

2.1. Materials

Hexamethylenetetramine (HMTA) and urea were purchased from Sinopharm Chemical Reagent Co., Ltd. Uranium dioxide (UO_2) powder of nuclear grade was obtained from China North Nuclear Fuel Co., Ltd. Nitric acid (AR) and ammonium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used as the solvent for all the experiments. The dispersing agent Tamol SN and Cabot Black Peal L (10 nm) using as the carbon source were obtained from Cabot Corporation.

2.2. Preparation of room-temperature stock solutions

The preparation of acid-deficient uranyl nitrate (ADUN) stock solution was elaborated in detail. Nuclear grade UO_2 powder was firstly oxidized at 500 °C for 5 h to obtain pure U_3O_8 in a muffle furnace under air atmosphere. For 100 mL ADUN solution, 85 g U_3O_8 was added into a round-bottom flask and wetted with 2 mL deionized water to form slurry. Then 48 g concentrated nitric acid was slowly added to the slurry over several hours. Next, the blend was heated up to 60 °C under continuous stirring to speed up the dissolution process. The volume was increased by adding deionized water and kept at 100 mL. Finally, the sample was cooled to room temperature and filtered to obtain a clear ADUN solution. The concentration of NO_3^- in the ADUN solution was determined to be 4.71 mol/L using an ion chromatography (IC). The density of the as-prepared ADUN stock solution was measured to be 1.89 g/mL and the concentration of uranium in the ADUN solution was 2.86 mol/L according to the following equation (Eq. (1)) [16]. The concentration of uranium was also determined to be 2.85 mol/L using the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and was almost the same with the result from the empirical equation (Eq. (1)). Therefore, the molar ratio of NO_3^-/U in the ADUN solution was 1.65.

$$\text{density(g/mL)} = 1.006 + 0.3092*[U]\text{(mol/L)} \quad (1)$$

1 L Stock solution of 3.18 mol/L HMTA and 3.18 mol/L urea was prepared by dissolving 445.77 g HMTA and 190.99 g urea into 505.24 g deionized water (hereafter noted as HMUR solution). Next, a predetermined amount of Tamol SN (mass weight ratio of Tamol SN to carbon was 0.11) was dissolved into the HMUR solution. Then a certain amount of carbon black was added to the above HMUR solution (hereafter noted as C/HMUR solution), molar ratios of C/HMUR were 0.38, 1.92, 2.30 and 2.70 respectively. To make sure the well dispersion of carbon black, the above slurry was dispersed using an ultrasonic probe for 2 h [13].

2.3. Preparation of C-UO_3·2H_2O gelled microspheres and UC ceramic microspheres

The apparatus used in this work is the same as what we have developed in our previous work [20] and the flow scheme of the whole process is displayed in Fig. 1. The room-temperature C/HMUR and ADUN stock solutions were directly transferred to the T-joint (SSI Company) through two separate High Performance Liquid Chromatography (HPLC) pumps (flowrate accuracy: 0.001 mL/min, series III, SSI Company). The flowrates of the C/HMUR and ADUN solutions were 1.756 and 1.500 mL/min respectively. Therefore, the molar ratio of HMTA/U was 1.3 (the molar ratio of C/U changed accordingly when C/HMUR solutions with different C/HMUR ratios were used). The stock solutions were mixed in-situ in a T-joint mixer. A 20 Gauge flat capped needle was used to disperse the mixed solution into separate droplets. The droplets fell through an implemented microwave cavity.

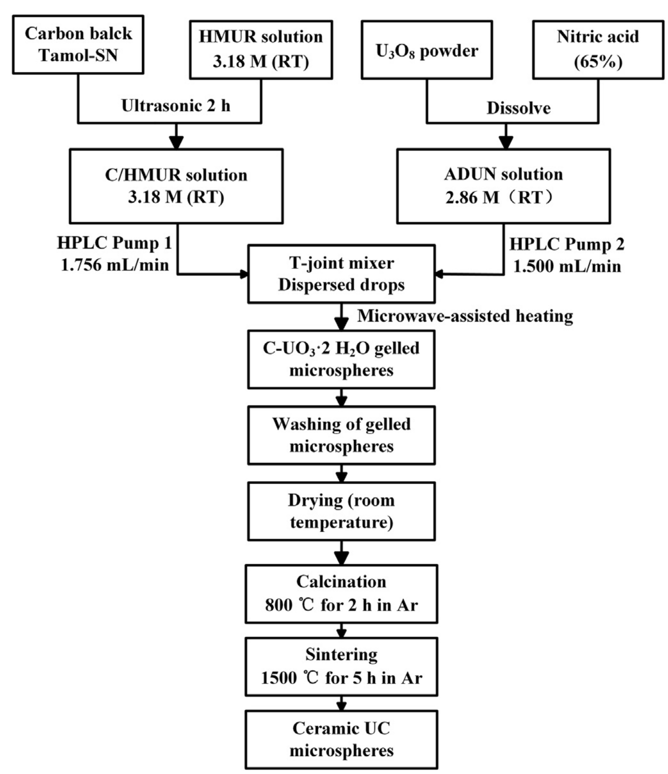

Fig. 1. Flow scheme of the preparation of ceramic UC microspheres.