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One-pot syntheses and characterization of zirconium carbide microspheres by carbon microencapsulation

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Abstract

Due to the extremely harsh reaction conditions, it is very difficult to control the particle morphology during the synthesis of ZrC, a well-known ultra high temperature ceramic material. In this paper, carbon encapsulated zirconia microspheres (ZrO_2@C) are synthesized via two consecutive hydrothermal reactions in one pot. After carbothermal reduction, ZrC particles with controlled spherical morphology can be prepared. The spherical morphology suggests that carbon diffuses into zirconia during carbothermal reduction. The influences of reactant concentrations, reaction time and temperature on the microencapsulation process are also investigated. Meanwhile, as a comparison, zirconia coated carbon microspheres (C@ZrO_2) are also prepared, which results in ZrC particles with layered structure.

Keywords: Ultra high temperature ceramics (UHTCs); Microspheres; Carbon microencapsulation; Carbothermal reduction

1. Introduction

Zirconium carbide (ZrC) is a typical and important member of so-called ultra high temperature ceramic (UHTC) family. Due to its superior physical and chemical properties, ZrC is widely used in cutting tools and ultra high temperature applications [1–6]. ZrC is an important far-infrared ceramic material [7] and is considered to be one of the promising inert matrix materials in high temperature nuclear reactors [8–10] due to its small neutron absorption cross-section [11,12]. ZrC also shows potential applications as coating layer for nuclear reactor fuel particles [13,14].

ZrC can be synthesized by various methods: carbothermal reduction [15], self-propagating reaction [16], arc burning [17] and chemical vapour deposition [18] etc. Among all these methods, carbothermal reduction of zirconia and carbon [15] is the mostly used process, because of the simplicity of the reaction and the affordable cost of the raw materials. Typically, certain amounts of zirconia and carbon black are well mixed by high energy ball milling followed by carbothermal reduction at high temperatures [15]. More recently, the use of liquid zirconium- and carbon-containing precursors in carbothermal reduction becomes more popular due to the advantage of homogenous distributions of all reactants at molecular level [19–24]. However, regardless the precursors used, the carbothermal reduction reaction has to be performed at temperatures higher than 1400 °C. It is known that agglomeration and growth of oxide particles are significant at elevated temperatures [23–25]. Thus, the synthesized ZrC particles are usually much bigger than the precursor particles with irregular morphologies.

Particles with spherical morphology have attracted a lot of interests for the past decades and are still the focus of related researches. Microspheres based on carbon, polymers and metal oxides have been extensive studied and found numerous applications in separation, catalysis, drug delivery etc [26–29]. For ceramics, properties such as particle size, size distribution and morphology of the powder have strong effects on their sintering and densification processes and outcomes. But, due to the harsh synthetic conditions, the controlled syntheses of group IV B metal carbides such as ZrC, are fairly rare.

In this paper, carbon coated zirconia core–shell microspheres (ZrO_2@C) are synthesized via two consecutive hydrothermal

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reactions in one pot. The outer carbon layer functions both as the carbon source and the physical barrier to prevent particle growth. After carbothermal reduction, ZrC microspheres are obtained. To the best of our knowledge, this is the first report for preparation of spherical UHTC particles. As a comparison, zirconia coated carbon core–shell microspheres ($C@ZrO_2$) are also prepared and converted to ZrC after pyrolysis.

2. Experimental

2.1. Chemicals

$ZrOCl_2 \cdot 8H_2O$ (AR grade), urea ($\geq 99\%$), sucrose (AR grade), citric acid monohydrate ($\geq 99.8\%$), ethanol (190 proof) and acetonitrile (MeCN, $\geq 99\%$) were all obtained from Sinopharm Chemical Reagent Co. and used as received. Zirconium *n*-propoxide ethanol solution (ZNP, 70%) was purchased from Aladdin Reagent Co., used as received.

2.2. Syntheses

2.2.1. Preparation of ZrO_2@C microspheres

ZrO_2 nanoparticles were prepared according to the literature [30]. Typically, 8 g of $ZrOCl_2 \cdot 8H_2O$, 16 g of urea and 4 g of citric acid monohydrate were dissolved in 250 mL de-ionized water. The solution was stirred magnetically at room temperature for 30 min before being transferred into a Tefelon-lined autoclave. After 12 h reaction at 155 °C under mechanical stirring, the reactants were cooled to room temperature. Then, in the same autoclave, 10–42.78 g of sucrose was added and dissolved under stir. The mixture was further heated at 160 °C for several hours. ZrO_2@C particles were harvested after centrifuge and washed by de-ionized water for 5 times and ethanol for 3 times respectively before vacuum drying at 80 °C.

2.2.2. Preparation of $C@ZrO_2$ microspheres

Carbon microspheres were prepared according to the literature [31]. 250 mL 0.29 M sucrose aqueous solution was heated at 170 °C for 4 h in a Teflon-lined autoclave to yield carbon microspheres after centrifuge, water and ethanol washes. 0.18 g (0.015 mol) as-synthesized carbon microsopheres were dispersed in 300 mL ethanol/MeCN (v/v = 4/1) solution. 18 mL de-ionized water was added into above suspension. 2.09 g ZNP (0.005 mol) was dissolved in 200 mL ethanol/MeCN (v/v = 4/1) solution. Then the above ZNB solution was added into the carbon microsphere suspension dropwisely. Upon completing addition of ZNB, the whole mixture continued to react at 75 °C for 1 h. Powder was acquired after centrifuge, 3 times ethanol washes and vacuum drying at 80 °C.

2.2.3. Carbothermal reduction

The as-synthesized core–shell particles were heated at 1400 or 1500 °C for 2 h in graphite crucibles under Argon atmosphere. Major reaction can be described as:

$$ZrO_2 + 3C = ZrC + 2CO(g).$$

2.3. Instrumentation

XRD profiles were recorded on an X-ray diffractometer (Rigaku D/Max-2250V) using Cu $K\alpha$ radiation. The scanning electron microscopy (SEM) images were taken on a Magellan-400 scanning electron microscope. The high-resolution transmission electron microscopy (HR-TEM) images were taken on a JEM-2100F transmission electron microscope. Energy dispersive spectrometry (EDS) spectra were recorded on a JEOL JSM-7001F and JEM-2100F electron microscopes. The carbothermal reduction reactions were monitored by differential thermal analysis (DTA) and thermogravimetric (TG) analysis using a STA 449 F3 thermal analyzer (NETZSCH).

3. Results and discussions

3.1. Syntheses of ZrO_2@C microspheres

ZrO_2@C particles are synthesized by two consecutive hydrothermal reactions. First, the hydrothermal reaction of $ZrOCl_2$ is carried out in the presence of urea and citric acid to produce ZrO_2 nanospheres [30]. In the same reaction vessel, the second hydrothermal reaction of sucrose is performed to produce ZrO_2@C microspheres. It has been reported that carbonaceous microspheres can be made by hydrothermal reaction of saccharides, such as sucrose, glucose, starch and cellulose etc [32–34]. The formation of carbonaceous microspheres follows LaMer model. A critical supersaturation concentration has to be reached for material to precipitate out of the solution. The saccharide concentration, reaction temperature and time have strong effect on the formation of carbon sphere [31]. In our cases, carbonaceous material can precipitate from solution at a much lower concentration than the critical supersaturation concentration reported due to the existence of ZrO_2 nanospheres [31].

The reaction recipes are listed in Table 1, while the SEM and TEM images of the products are shown in Fig. 1. Similar to traditional hydrothermal reaction of sucrose, the reactant concentrations have strong effects on the product morphologies. When the sucrose concentration (sample 1 in Table 1) is far below the reported critical concentration (0.5 M), irregular-shaped agglomerates with obvious three-dimensional network are obtained at shorter reaction time (Fig. 1a). Prolonging the reaction time, the irregular-shaped agglomerates will grow into

Table 1
Recipes for syntheses of ZrO_2@C microspheres.

Sample	$ZrOCl_2 \cdot 8H_2O$ (g)	Urea (g)	Citric acid (g)	Sucrose (g)	[Sucrose] (M)	Reaction time (h)
1	8	16	4	10	0.12	3.5
1–1	8	16	4	10	0.12	5
1–2	8	16	4	10	0.12	6
1–3	8	16	4	10	0.12	10
2	8	16	4	25	0.29	3.5
3	8	16	4	42.78	0.50	3.5
4	16	32	8	25	0.29	3.5
5	16	32	8	42.78	0.50	3.5