Synthesis of nanosized zirconium carbide powders by a combinational method of sol–gel and pulse current heating

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Abstract

Zirconium carbide nanopowders were synthesized by a novel method combining the advantages of sol–gel method and rapid synthesis using pulse current heating. The core-shelled structure of ZrO_2/C mixture was obtained during the sol–gel process, and further heat treatment in SPS led to the fast formation of ZrC. The particle size of ZrO_2 played an important role in the synthesis of nanosized ZrC powders. In addition, the coalescence and grain growth of ZrC particles could be also limited due to the fast heating rate. As a result, the reactions were thoroughly completed at a relatively low temperature and ZrC nanopowders of 60–100 nm were obtained. The corresponding powders also had low oxygen content ($\sim$0.64 wt%) and residual carbon content ($\sim$0.27 wt%). Additive-free ZrC powders could be sintered to $\sim$99% relative density with an average grain size of 0.8 μm at low temperature of 1750 °C.
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Keywords: Core-shelled structure; Zirconia; Grain growth; Pulse current heating; Nanopowder

1. Introduction

Zirconium carbide (ZrC) is one of the most attractive transition metal carbides with wide applications for its unique properties, such as high refractarity, high hardness, good wear resistance and chemical stability.[1,2] In addition, due to the low neuron absorption and weak damage sensitivity under irradiation,[3] it has great potential applications in the new generation of nuclear reactors (Gen-IV project). However, for the strong covalent bonding, ZrC sintering usually requires high applied load and temperature and or the use of sintering aids.[4,5] Recent studies[6,7] suggested that the sintering kinetics of ZrC powder was highly marked when the refinement of crystallite size was from submicrometer range (<0.5 μm) down to the nanoscale. Hence, finding a synthesis route for high purity ZrC nanopowder is desirable.

A variety of synthesis routes have been developed to prepare ZrC powders.[8–12] Among these methods, the sol–gel process is proved to be an effective way to obtain ultra-fine ZrC powders for the high intimacy and low synthesis temperature. Sacks et al.[9] used metal alkoxide and phenolic resin to form ZrC powders at 1475 °C, but the products still contained some oxygen ($\sim$3.3%) and residual carbon (>1.8%). Consequently, during the traditional heat treatment, higher temperature and longer reaction time were required to further complete the reactions by a progressive removing of oxygen impurity. Unfortunately, it also induced undesirable grain size increase.[10,13] It has been reported that the grain growth of zirconia (ZrO_2) usually occur especially at the temperature higher than 1300 °C, at which the carbothermal reaction is just initiated.[9,14] The grain growth of ZrO_2 would induce the degradation of high intimacy, lower the activity of reactant and have a negative effect on the particle size of final product. Thus, suppressing the ZrO_2 growth is of primary importance in the preparation of ZrC nanopowders. A great excess carbon in the starting materials could retard the growth of ZrO_2 particles,[15] but the residual carbon in final ZrC powders would be responsible for the poor powders densification and low mechanical properties.[10] Earlier reports focused mainly on the composition of starting materials and provided little information on how to control the ZrO_2 particle size during the reaction process.

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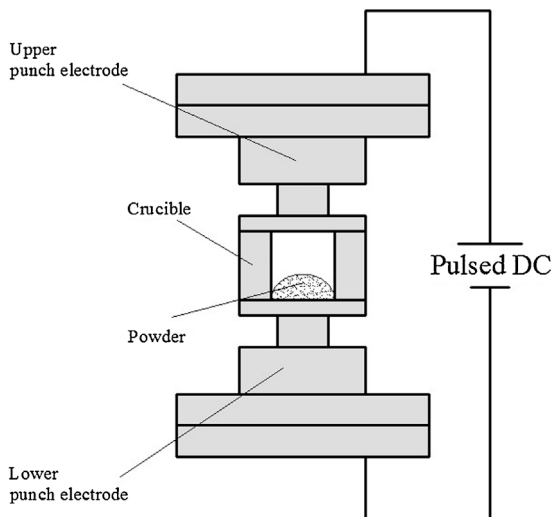 *E-mail address:* zyfu@whut.edu.cn (Z. Fu).

Fig. 1. The schematic diagram of graphite crucible for powder synthesis in spark plasma sintering.

Spark plasma sintering (SPS) has been demonstrated to prepare nanocrystalline ceramics with a minimal grain growth.[16] Due to the fast heating/cooling rate, long heat treatment period is significantly reduced and the grain growth is strongly suppressed.[17] Although SPS is a developed sintering technique and enables the ceramic powders to be fully densified at a relatively low temperature, few reports focus on the pulse current heating for the powder synthesis. Just recently, ultra-fine HfB_2 powder was prepared by using SPS apparatus through a solid-state reaction of HfO_2, B_4C and C.[18] But the as-synthesized powders had an inhomogeneous particle size and seriously agglomerated because the staring powders were physically mixed on a relatively coarsen scale.

In the present work, a novel method of combining sol–gel and pulse current heating was proposed. For SPS, a mold was specially designed for the powder synthesis (as shown in Fig. 1). The core-shelled structure of precursors, the chemical state, microstructure and sinterability of ZrC powders were investigated. Furthermore, the reaction process during pulse current heat treatment was also experimentally studied.

2. Experimental procedure

ZrC precursor was prepared using zirconium n-propoxide $Zr(OPr)_4$ (70 wt% in n-propanol, Alfa), n-propanol (99.9 wt%, Alfa), acetic acid (99.8 wt%, Sigma) and sucrose (99.5 wt%, Sigma) as the starting materials. Briefly, 7.5 g sucrose was dissolved in 50 ml acetic acid kept at 80 °C with stirring, and then cooled down to room temperature, followed by diluting with 64 ml n-propanol. Then sucrose solution was added drop by drop to 16 ml $Zr(OPr)_4$ solution under vigorous stirring, and the amounts of sucrose solution were determined by the C/Zr ratio (the atomic ratio of C in the sucrose to Zr). The gel formed after 48 h at room temperature and then was dried at 110 °C for 24 h. This dried powder was ground for 1 h before being pyrolyzed to 700 °C in a tube furnace at 5 °C/min under argon atmosphere for 30 min.

For SPS (Model 1050, Sumitomo Coal Mining Co. Ltd., Kanagawa, Japan), 3 g precursors were directly placed into the graphite crucible without being pressed. The graphite crucible was specially designed for powder synthesis, and the surface of that was coated with BN to prevent the reactions between the die and reactants. The reduction was conducted in argon atmosphere at a heating rate of 100 °C/min and the temperature was monitored by an optical pyrometer focusing on the surface of graphite crucible.

The sintering of ZrC nanopowder was performed in the same SPS apparatus in an argon atmosphere. As-synthesized ZrC powders without further treatment were poured into a traditional graphite die of 20 mm inner diameter. The temperature was increased to 600 °C in first 3 min, from where the temperature was regulated at a heating rate of 100 °C/min by an optical pyrometer focusing on the surface of graphite die. A uniaxial pressure of 65 MPa was loaded within first 3 min and kept to the end of sintering cycles.

The phase of ZrC powder was examined by X-ray diffraction (XRD). The field emission scanning electron microscopy (FESEM, Hitachi S-4800) and high-resolution transmission electron microscope (HRTEM, JEM-2010F) were used to observe the structure and morphology of sample. The particle size was determined with a particle size analyzer (ZetaPALs) and oxygen content was detected by an oxygen analyzer (TC-600, Leco). Total carbon content was analyzed using the Carbon/Sulfur Determinator (CS-444, Leco) and free carbon content was detected by chemical separation in hydrofluoric and nitric acid followed by filtration and successive combustion in the Carbon/Sulfur Determinator. The apparent density of the sintered specimen was measured using the Archimedes method in water and the average grain size was observed from the fractured section.

3. Results and discussion

3.1. Sol–gel process

XRD patterns for ZrC precursors indicate that all diffraction peaks are in agreement with the XRD date of a crystalline tetragonal ZrO_2 (Fig. 2). The broad peaks are assigned to the presence of nano-sized ZrO_2 particles with an average size about 10 nm. The formation of such fine powders is proposed to be related with the sol–gel route. Fig. 3a shows the image of ZrO_2/carbon nanocomposite precursors. Most of ZrO_2 particles are homogeneously distributed in carbon matrix. High-resolution transmission electron microscopy (HRTEM) and EDS examination of some isolated particles find that they all possess core-shelled structures,[19,20] with ZrO_2 core and carbon shell (Fig. 3b–d). Compared with the ball-milled state of reactants,[18] the primary advantage provided by coated precursors is the intimate contact between reactants.[19] The high-surface contact between ZrO_2 and C has a decisive advantage in carbothermal reduction process by shortening the diffusion path of carbon, oxygen and zirconium atoms, thus ZrO_2 can be easily carburized.[21] In light of this, the core-shelled structure is also preferable for the subsequent rapid synthesis using