

Synthesis and pyrolysis evolution of glucose-derived hydrothermal precursor for nanosized zirconium carbide

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ABSTRACT

Nanosized zirconium carbide (ZrC) was synthesized successfully by a novel hydrothermal precursor conversion method using chelation of polydentate glucose as the carbon source. During the pyrolysis, the core-matrix structure of intimate nanosized ZrO₂ and amorphous carbon mixture forms, resulting in short diffusion path and limit of grain growth. ZrC first appears at a much lower temperature of 1200 °C and completes conversion at 1400 °C in comparison with that of precursor without hydrothermal treatment. By raising the heating temperature to 1600 °C, oxygen content could be reduced (0.55 wt%) with a low residual carbon content (2.3 wt%), and the average size of the spherical crystallite increases from 100 nm to 200 nm. Based on above ZrC powders, the additive-free ceramic with 99.4% relative density by spark plasma sintering (SPS) at a low temperature of 1700 °C has been achieved.

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1. Introduction

Zirconium carbide (ZrC) as one of the most attractive transition metal carbides, presents promising thermomechanical properties, such as high melting point, hardness, good wear and corrosion resistance, which ensure the excellent performance in ultra-high temperature area [1–3]. Besides the use as thermal protection, field emitter and cutting tool [4,5], ZrC has great potential application in the new generation of nuclear reactors (Gen-IV project), for example, as the fission barrier, fuels shielding and inert matrix material, because of the good thermal conductivity, neutronic transparency, and weak damage sensitivity under irradiation [6–8].

ZrC can be simply prepared by carbothermal reduction of zirconia and carbon sourced from gas phase, resin, or carbon black [9–11]. However, because of the strong covalent bond nature and low self-diffusion coefficient, a high temperature and a long production period are required for the method, resulting in heterogeneous carbide particle size and serious agglomeration with poor sinterability [12]. It has been attested experimentally and theoretically that powder size from micrometer range down to the nanoscale may lower the sintering temperature and facilitate the

densification due to the larger surface area and higher reactivity [13,14]. Further, unusual mechanical properties such as superplasticity and toughening are expected in such nanosized grain ceramics, where grain boundaries increase and the fraction of atoms in the grain boundaries cannot be ignored [15,16]. Thus high quality ZrC nanopowder is in urgent need.

Hence alternative solution-based methods such as sol-gel or polymer-derived preceramic routes are proposed with the advantages of homogenous distribution of reactants at molecular level [17–21]. However, sol-gel method is usually low content of the product in the solution, needing concentration, and with other drawbacks such as high cost, complicated operation, toxic organic reagent, and poor stability of the sol. The magnesiothermic reaction and self-propagating high-temperature synthesis (SHS) are also studied. Nevertheless, the propagation and composition are uncontrollable and the combustion process is poorly understood [22,23].

Consequently, the manufacture of nanosized ZrC showing well-controlled composition by a simple process scalable at an industrial level remains a challenge. In recent decades, hydrothermal strategy, which relies on the chemical reaction and solubility change in a sealed heated solution above ambient temperature and pressure, is considered as a handy and green route to prepare nano-/micro-materials [24,25]. However, the example of such hydrothermal method brought into synthesis of carbide is rare, compared with that for oxides [26].

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Take above into account, a novel precursor route based on hydrothermal reaction for ZrC synthesis has been suggested. Glucose, as the most abundant monosaccharide on earth, which has high content of carbon and hydroxyl groups, was introduced as the carbon source and polydentate chelating to zirconium oxychloride without needing air or moisture sensitive precautions. After hydrothermal treatment, the occurrence of Zr–O–C bonding in the skeleton of homogeneous precursor could lower the diffusion distance during carbothermal reduction, so the faster reaction kinetics and nanosized carbide materials are then expected. In present work, the reaction process, character, and microstructure of gained precursor and ZrC powders were researched by FTIR, XRD, TG-DTA, SEM, and TEM analyses. Furthermore, the consolidation through spark plasma sintering (SPS), which allows enhancing the densification leading to finer microstructure by particle surface activation and local melting, has also been investigated.

2. Experimental procedure

2.1. Preparation of precursor and ZrC

In a typical synthesis process, zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, ZOC, 99%, Aladdin, China, 0.06 mol), was dissolved in 10 mL deionized water, and then appropriate amounts of Glucose (Glu, 99%, Aladdin, China) were added to the solution to give various Glu/Zr mole ratios (0.8:1, 1:1, 1.2:1) with continuous stirring by a magnetic stirrer. The clear solution mixture was sealed in a 25 mL Teflon-lined stainless steel autoclave under autogenous pressure at 180 °C for 12 h. After cooling to room temperature at a rate of 1 °C/min, the resulting brown compounds were filtrated, washed with deionized water until the pH value was 7, and dried under vacuum at 120 °C. These obtained precursors denoted as $(\text{Glu-Zr})_{\text{HT-0.8}}$, $(\text{Glu-Zr})_{\text{HT-1.0}}$, and $(\text{Glu-Zr})_{\text{HT-1.2}}$, respectively, were heated to the required temperatures in the range of 900–1600 °C for 1 h under flowing argon atmosphere in a tube furnace with a heating rate of 5 °C/min. The pyrolyzed products could be easily grounded into nice powder in a crucible. As comparison, ZrC was also prepared from the precursor by mixing/drying protocol without hydrothermal reaction (denoted as $(\text{Glu-Zr})_{\text{MIX}}$) as following: appropriate amount of Glu was dissolved in zirconium solution, removed by rotary evaporation to give out brown powder. The dried precursor powder was converted into ZrC by a similar carbothermal reduction process.

2.2. Spark plasma sintering of powders

The sintering was performed in SPS equipment (SPS-211Lx, Fujidempa, Japan) in an argon atmosphere. As-synthesized ZrC powder was poured into a 10 mm diameter graphite die lined with graphite paper. Graphite felt was used around the cylindrical graphite mold to prevent heat loss. The temperature, measured by a vertically located optical pyrometer through a hole in the upper graphite punch, was increased to 600 °C in the first 6 min, and regulated at a heating rate of 100 °C/min until 1700 °C for 5 min henceforth. A uniaxial pressure of 50 MPa was loaded within the first 6 min and kept constant until the end of the dwell period.

2.3. Characterization

Fourier transformation infrared spectra (FTIR, Spectrum One, PerkinElmer, USA) of starting reagents and precursors were recorded in the range of 4000–400 cm^{-1} . The phase compositions were examined by X-ray diffraction (XRD, Miniflex 600, Rigaku, Japan) using $\text{Cu K}\alpha$ radiation. Then the lattice parameters of ZrC phase were determined

by indexing and least-squares refinement with the MDI Jade 5 software [27]. The morphology and structure of the products were characterized by field emission scanning electron microscope (FESEM, SU-8010, Hitachi, Japan), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, Tecnai F20, FEI, USA). Thermogravimetric analysis (TGA, STA 449F3, Netzsch, Germany) was performed in argon or air atmosphere at a heating rate of 10 °C/min. Oxygen content was detected by an oxygen analyzer (ONH836, LECO, USA). The bulk density of the sample was measured by the Archimedes method using water as the immersion medium. The SPS sample was ground and polished with diamond paste to 0.5 μm and chemically etched using a mixed acid ($\text{HF}:\text{HNO}_3:\text{H}_2\text{O}$, volume ratio=1:1:48) for microstructure investigation.

3. Results and discussion

3.1. Hydrothermal process

Under the hydrothermal condition which results in the subcritical internal environment, the polydentate ligand Glu with hydroxyl (–OH) groups, can coordinate to Zr(IV) spontaneously, forming suitable precursor. We have adjusted the synthetic conditions, where deviation of the optimal parameters can lead to a low yield (short time or low temperature) and nonuniformity (high temperature), respectively.

As shown in Fig. 1, FTIR was used to monitor the structural change and the interaction between Glu and the metal ion. For Glu (Fig. 1(a)), the major bands observed correspond to 3410 cm^{-1} (ν (O–H)), 2913 cm^{-1} (ν (C–H)), and 1460 cm^{-1} (ν (C–C)) cm^{-1} , respectively [28]. While the band at 1622 cm^{-1} can be assigned to the “scissor” bending mode of coordinated water of ZOC (Fig. 1(b)) [29]. Obvious differences between the precursor ($(\text{Glu-Zr})_{\text{HT-1.2}}$) and the raw materials appear when the ligand coordinates to zirconium (Fig. 1(c)). The wide peak assigned to the stretching vibration of –OH shifts to the lower wave number at 3385 cm^{-1} , suggesting the –OH group is involved in the complexation. A new angular absorption band at 1580 cm^{-1} appears, which is considered as a characteristic peak of the association of ligand with zirconyl [30]. In addition, absorption peaks at 1004 cm^{-1} , 933 cm^{-1} and 653 cm^{-1} could be assigned to C–O and Zr–O vibrations in the Zr–O–C chains, respectively [30,31]. So the appearance of these peaks demonstrates zirconium and Glu has been successfully

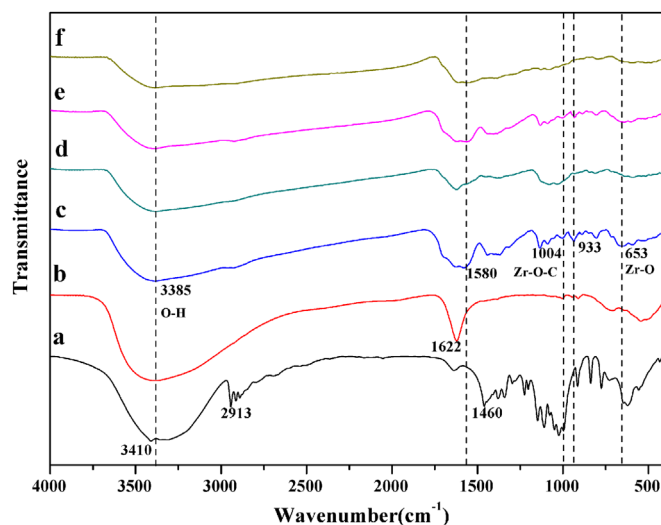


Fig. 1. FTIR spectra of starting reagents and precursors: (a), (b) as-received Glu, and ZOC, (c) $(\text{Glu-Zr})_{\text{HT-1.2}}$, (d) $(\text{Glu-Zr})_{\text{MIX}}$, (e) and (f) $(\text{Glu-Zr})_{\text{HT-1.2}}$ and $(\text{Glu-Zr})_{\text{MIX}}$ heated at 350 °C (in Ar).

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