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Synthesis of zirconium carbide whiskers by a combination of microwave hydrothermal and carbothermal reduction

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ABSTRACT

Zirconium carbide (ZrC) whiskers were successfully synthesized by a combination of microwave hydrothermal (MH) and carbothermal reduction. The precursors of ZrC whiskers were produced by MH, subsequently carbothermally reduced to ZrC whiskers at 1100–1600 °C in an Ar atmosphere. Effects of the reduction temperature and precursors with various carbon/zirconium (C/Zr) molar ratios on the synthesis of ZrC whiskers were investigated. The results showed that the carbothermal reduction occurred at 1100 °C, and terminated at a relatively low temperature (1400 °C). When the reduction temperature was 1500 °C and the C/Zr molar ratio was 5:1, the ZrC whiskers with the largest aspect ratio and the most uniform distribution were produced. The whiskers exhibited the diameters of 0.1–2 μm and the lengths of 5–30 μm. The synthesized ZrC whiskers with a single crystalline phase displayed cylindrical and pagoda-like morphologies. The growth of ZrC whiskers was considered to be governed by the Ostwald ripening and S-L-S mechanism.

1. Introduction

Zirconium carbide (ZrC) ceramics have attracted great attention in the field of ultra-high temperature owing to their high melting point (3693 K), high hardness (25.5 GPa), good thermal conductivity and excellent wear resistance [1–3]. Therefore, they have been widely used as reinforcing phase of cutting tools, thermal protection materials and field emitters [4]. Besides, they are ideal materials in nuclear reactors because of their neutronic transparency and low damage sensitivity under irradiation [5–7]. As one of the most attractive transition metal carbides, ZrC combines the merits of ceramics and metals due to the coexistence of covalent, ionic and metallic bonding in its NaCl-type lattice structure [8].

Several methods have been employed to synthesize ZrC, such as carbothermal reduction [9], direct reaction method [10], electrospinning and annealing [11], chemical vapor deposition (CVD) [12], preceramic polymer method [13], sol-gel process [14], organic covalent grafting [15], solid-state reaction [16] and so on. Among them, carbothermal reduction of metal oxides mixed with amorphous carbon in controlled atmospheres is a conventional method for manufacturing metal carbides. However, it usually requires a high temperature (1700–2100 °C) and a long reaction time on account of ZrO_2 and C being in solid state [17,18]. Combination of Microwave hydrothermal (MH) with carbothermal reduction provides a novel and effective way to resolve the above problems. Compared with traditional hydrothermal, the MH has many advantages in synthesis nano-particles, such as rapid volumetric heating, increased reaction rates, good homogeneity and high reproducibility. The principle of microwave radiation on materials is based on the conversion of electromagnetic field energy to heat energy. When fabricated by MH, the polymeric precursor reactants are equally distributed at a molecular level that reduces the kinetic barriers between the formed metal oxides and carbon particles created in pyrolysis of a metal alkoxide polymer precursors. Increasing contact area of the particles enables the carbothermal reduction of metal oxide and carbon at lower temperature and shorter time as compared to conventional techniques of carbide synthesis [19–24].

As-synthesized ZrC is always in particle form together with a few one-dimensional nanostructures like whiskers [12,25], nanorods [26,27] and nanofibers [11,28,29]. Among the one-dimensional structures, ZrC whisker is one of the very important reinforcement in composite materials, which not only can improve the ablation resistance but also enhance mechanical properties of the materials by forming mechanical interlocking with the matrix [30]. Liu et al. [12] codeposited the ZrC and SiC hybrid whiskers by CVD using methyl trichlorosilane, zirconium chloride, methane and hydrogen as the precursors. Xu et al. [25] obtained ZrC whiskers from the mixture of ZrO_2, C, Ni and NaF by carbothermal reduction at 1500 °C in an Ar atmosphere. Nevertheless, above reports only focus on the synthesis and growth mechanism of ZrC whiskers. To the best of our knowledge, no systematic study has yet been carried out to establish the correlation

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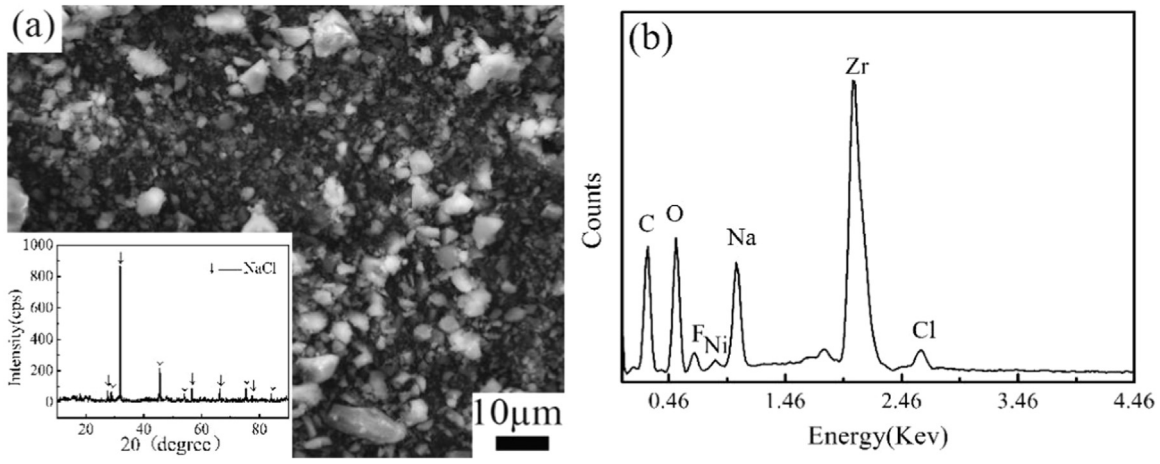

Fig. 1. Morphology and composition of the ZrC precursor: (a) SEM image with an inset of XRD pattern and (b) EDS pattern of the precursor corresponds to (a).

between the morphology of ZrC whiskers and preparation conditions.

In this work, a novel and highly efficient method for synthesizing ZrC whiskers was proposed. It consisted of (1) synthesizing precursors of ZrC whiskers by MH and (2) subsequently reducing them by carbothermal reduction. The effects of preparation conditions (reduction temperature and C/Zr molar ratio) on the composition and morphology of ZrC whiskers were investigated, and the growth mechanism was also discussed.

2. Materials and methods

2.1. Raw materials

Zirconium oxychloride octahydrate ($ZrOCl_2{\cdot}8H_2O$, 99 wt%, Tianjin Fengyue Chemical Reagent Co., Ltd., China) as the source of zirconium, sucrose ($C_{12}H_{22}O_{11}$, carbon yield of 17%, Shanghai Aladdin Industrial Co., China) as the source of carbon, sodium hydroxide (NaOH, ≥ 96 wt %, Tianjin Tianli Chemical Reagent Co., Ltd., China) as the source of sodium ions, nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$, ≥ 99 wt%, Tianjin Tianli Chemical Reagent Co., Ltd., China) as catalyst and sodium fluoride (NaF, ≥ 99 wt%, Tianjin Tianli Chemical Reagent Co., Ltd., China) as mineralizer were used for the experimental work. All the chemicals with analytical grade were used as received without further purification.

2.2. Preparation of ZrC precursors and ZrC whiskers

The preparation of ZrC whiskers can be divided into two steps; (1) synthesis of precursors and (2) conversion of precursors to whiskers. After dissolving 6 g $ZrOCl_2{\cdot}8H_2O$ into 30 mL deionized water, 1.6 g NaOH was added and stirred. Subsequently, appropriate amounts of sucrose were added into this solution to get various C/Zr molar ratios (1:1, 2:1, 3:1, 4:1, 5:1 and 6:1) in 6 batches. Then, 0.24 g $NiCl_2{\cdot}6H_2O$ and 0.8 g NaF were added orderly into each batch and mixed under a magnetic stirrer until a homogenous suspension was formed. The suspension was sealed in a 100 mL teflon-lined autoclave and heated (10 °C/min) by a microwave accelerated reaction system (MARS-10) to 180 °C for 40 min. The pressure in the autoclave was maintained in the range of 1.2–2.5 MPa. After cooling to room temperature, light brownish solution was formed and dried in a vacuum oven at 70 °C for 24 h. The resulted batches of precursors were denoted as C/Zrn (n = 1–6), corresponding to solution with the C/Zr ratio of 1:1, 2:1, 3:1, 4:1, 5:1 and 6:1. Finally, these batches were put in a tube furnace and heated in the temperature range of 1100–1600 °C under Ar atmosphere. The heating rate was 4 °C/min with a holding period of 2 h at the maximum temperature.

2.3. Characterization

Thermogravimetric analysis (TGA, STA429CD/3/7, Netzsch, Germany) was performed under Ar atmosphere at a heating rate of 4 °C/min from room temperature to 1400 °C. Fourier transformation infrared spectra (FT-IR, Vector-22, Bruker, Germany) of the starting reagents and precursors were recorded in the range of 4000–250 cm^{-1}. The morphologies of ZrC whiskers were observed using scanning electron microscope (SEM, FEI NANOSEM450) equipped with an energy dispersive X-ray spectroscope (EDS). The microstructure was examined under a transmission electron microscope (TEM, FEI TECNAI G20) with selected area electron diffraction (SAED) patterns. The phase composition was evaluated by X-ray diffraction (XRD, Philips X'Pert PRO, Cu Kα radiation, 0.15406 nm).

3. Results and discussion

3.1. Synthesis of ZrC precursors

The MH provides a subcritical internal environment where the polydentate ligand sucrose with hydroxyl (-OH) groups can coordinate to Zr spontaneously, forming appropriate precursor [31]. The morphology and phase composition of ZrC precursor were characterized by SEM and XRD, respectively. According to the SEM image (Fig. 1(a)), many irregular particles are generated and disperse relatively uniformly, with major particle sizes in the range of 0.5–10 μm. The XRD pattern reveals that only NaCl peaks are detected (left bottom inset in Fig. 1(a)). The probable reason is that the Zr was introduced into the formed complex backbone [32]. The related EDS pattern (Fig. 1(b)) demonstrates the existence of Zr, Cl, C, Na, O, Ni, and F elements, implying the raw materials were merged into the complex.

FT-IR was employed to monitor the structural changes and interaction between the sucrose and metal ions, as shown in Fig. 2. For sucrose (Fig. 2(a)), the major bands correspond to 3663 cm^{-1} (ν(O-H)), 2913 cm^{-1} (ν(C-H) and 1460 cm^{-1} (ν(C-C)), respectively [33]. The peak at 1622 cm^{-1} can be assigned to the "scissor" bending mode of hydrate water in $ZrOCl_2{\cdot}8H_2O$ (Fig. 2(b)) [18]. After the reaction of