Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Synthesis and growth behavior of micron-sized rod-like ZrB_2 powders

Shaolei Song[a,b], Rong Li[b,*], Liangchao Gao[b], Chencen Sun[b], Pengfei Hu[c], Qiang Zhen[a,b,**]

[a] School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China
[b] Nano-Science & Technology Research Center, Shanghai University, Shanghai 200444, China
[c] Laboratory for Microstructures, Shanghai University, Shanghai 200444, China

ARTICLE INFO

Keywords:
Molten salt synthesis
Borides
Reduction
Anisotropy

ABSTRACT

Using $ZrOCl_2{\cdot}8H_2O$, $Na_2B_4O_7{\cdot}10H_2O$ and $C_{12}H_{22}O_{11}$ as raw materials, micron-sized rod-like ZrB_2 powders were prepared via a molten-salt-mediated carbothermal reduction from chemically homogenous precursors obtained by sol-gel method. The effects of Zr/B/C molar ratio, firing temperature, holding time and molten salt on the composition of products have been investigated, respectively. Pure micron-sized ZrB_2 powders with controllable rod-like morphology were obtained at 1400 °C for 4 h holding with Zr/B/C of 1/5/5 in presence of molten salt, which has a diameter of 1–2 μm and aspect ratios of 3–10. The investigation of growth behavior showed that at the first stage, nano-size ZrB_2 columns grew along the *c*-axis with ZrC_x thin film on their top as "active-site". Then, with consuming 'active sites', ZrB_2 columns started to grow in diameter direction, and finally small columns merged into a larger rod.

1. Introduction

As an important ultrahigh-temperature ceramics (UHTCs), ZrB_2 has unique properties of high melting point, high strength, high thermal and electrical conductivities [1–3]. It is considered as a potential material for various applications, such as reentry thermal protection systems, hypersonic vehicles, and high temperature electrodes [4–6]. Due to the primitive hexagonal structure, it is possible to obtain ZrB_2 with anisotropic morphology, such as platelet [7] or rod-like grains [8–10]. Recently, some researchers have studied the effect of morphology on the performances of ZrB_2 based ceramics [11–13]. For example, Ren et al. [14] reported that rod-like ZrB_2 grains in ZrB_2-SiC composites had improved the fracture resistance compared with the equiaxed ZrB_2 grains. Therefore, to fabricate high performance ZrB_2 based ceramic, it is necessary to use high purity ZrB_2 powders with controllable morphology and size.

Among variety of methods for ZrB_2 preparation, carbothermal reduction (CTR) is a potential method for production, due to their low preparation cost and better controllability [15]. Liu et al. [10] synthesized rod-like ZrB_2 powders from ZrO_2, B_4C and graphite at 1500 °C. ZrB_2 powders were also obtained using ZrO_2, HBO_2, and carbon as raw materials at 1600 °C [16]. However, the conventional CTR based on solid-state usually requires high temperature (1500 °C), and the products often have obvious agglomeration and unsatisfied purity. These disadvantages are mainly attributed to the large reactant particles, which slow the diffusion and limit complete reaction. In the present literatures [17–22], many liquid-systems, such as sol-gel, are applied before CTR to produce chemically homogenous precursors with fine particles. However, obvious agglomeration is still observed due to high reaction temperature. Molten-salt medium are usually used in high temperature solid reaction to facilitate the homogeneous mixing and diffusion of reactant species. As a result, the reaction temperature and dwell time for the complete reaction were reduced and homogeneous and well-defined products were obtained [23,24]. Liu et al. [8] prepared rod-like ZrB_2 powders via a molten-salt and microwave coassisted crabothermal reduction (MSM-CTR) method, the obtained powders had diameters of 40–80 nm and aspect ratios of > 10. Ding et al. [25] once obtained hexagonal columnar ZrB_2 powders from a glassy mixture of ZrO_2, B_2O_3 and C using microwave heating technique at low temperature. However, these reports are mainly focused on the composition and size of ZrB_2 powders and formation mechanism, the growth behavior of anisotropic ZrB_2 particles are rarely discussed.

In this paper, a sol-gel process was chosen to prepare a novel homogenous precursor containing molten salt, and rod-like ZrB_2 powders were synthesized using this precursor via a molten-salt-mediated carbothermal reaction. The effects of firing temperature, holding time and B/Zr molar ratio on products were investigated. For comparison, parallel experiments without molten-salts mediate were carried out to confirm its influence. The synthesis mechanisms and growth behavior of rod-like ZrB_2 particles were further discussed.

* Corresponding author.
** Corresponding author at: Nano-Science & Technology Research Center, Shanghai University, Shanghai 200444, China.
E-mail addresses: li-rong@shu.edu.cn (R. Li), qzhen@staff.shu.edu.cn (Q. Zhen).

https://doi.org/10.1016/j.ceramint.2017.12.026
Received 10 November 2017; Received in revised form 1 December 2017; Accepted 4 December 2017

2. Experimental procedure

2.1. Precursor materials

$ZrOCl_2{\cdot}8H_2O$ (≥ 99%, Guoyao Chem. Co. Ltd., Shanghai, China), $Na_2B_4O_7{\cdot}10H_2O$ (≥ 99%, Sigma-Aldrich. Co. Ltd., Shanghai, China), and $C_{12}H_{22}O_{11}$ (≥ 99%, Guoyao Chem. Co. Ltd., Shanghai China) were used as starting raw materials.

$ZrOCl_2{\cdot}8H_2O$, $C_{12}H_{22}O_{11}$ and $Na_2B_4O_7{\cdot}10H_2O$ were dissolved in alcohol-water mixture (v_a/v_w, 1:4, solution Z) and distilled water (solution B), respectively. A certain amounts solution B were dropped into solution Z at 80 °C (water bath) with continuous magnetic stirring to obtain a sol, which translate into gel quickly. The obtained gel was aged at 25 °C for 24 h and dried at 80 °C for 24 h to obtain the precursors. Precursors were labeled as ZB_xC which x was B/Zr molar ratio.

2.2. Synthesis of ZrB_2 powders

In order to optimize the synthesis condition of ZrB_2, the obtained precursors were treated at different temperature from 1200 °C to 1500 °C with 1–4 h holding under flowing Ar. The heating rate was kept at 3 °C/min from room temperature to 300 °C then change to 5 °C/min above 300 °C. The obtained powders were washed by hot water and ethyl alcohol for three times to remove the salt medium, and finally dried at 60 °C for SEM characterization.

2.3. Characterization

The ZB_5C precursor was characterized using Fourier transform infrared spectroscopy (FT-IR, AVATAR370). Thermal decomposition behavior of ZB_5C precursor was investigated using TG (F1 Jupiter, Netzch TG/DTA) from room temperature to 1500 °C in a flowing argon atmosphere with a heating rate of 10 °C/min.

Phases of precursors and the as-prepared powders were analyzed by X-ray diffraction (XRD) using Cu Kα radiation (λ = 0.15406 nm) (XRD, D/max 2550 V). Morphologies of as-prepared powders were examined using scanning electronic microscopy (SEM, JSM-7500) equipped with an energy dispersive spectroscopy (EDS) system. High resolution transmission electron microscopy (HRTEM, JEM2100F) was also used to determine the phase composition.

3. Result and discussion

3.1. Characterization of ZB_xC precursor

FT-IR of the ZB_5C precursor dried at 110 °C for 24 h is shown in Fig. 1a. The absorption at 929 cm^{-1} is assigned to the characteristic peak of Zr–O–B bond, which is attribute to the reaction between B-OH and Zr-OH [22,26,27]. The absorption peaks at 532 cm^{-1}, 740 cm^{-1}, 1075 cm^{-1} are assigned to Zr–O, Zr–O–Zr and Zr–O–C–O–B bond, respectively [26,27].

When dissolved in water, under magnetic stirring, $ZrOCl_2{\cdot}8H_2O$ hydrolysed to form soluble metal hydroxides as shown in Eq. (1) and converted into $[Zr_4(OH)_8]^{8+}$ [28], then Zr-O-Zr bonding are formed after further hydrolyzation. While in solution B dissolved $Na_2B_4O_7{\cdot}10H_2O$ converted into to $B_4O_5(OH)_4^{2-}$ and Na^+ as shown in Eq. (2).

$$ZrOCl_2(cr) + H_2O(l) \rightarrow Zr(OH)_4(aq) + 2H^+(aq) + 2Cl^-(aq) \quad (1)$$

$$Na_2B_4O_7(cr) + 2H_2O(l) \rightarrow B_4O_5(OH)_4^{2-}(aq) + 2Na^+(aq) \quad (2)$$

When solution Z dropped into solution B, the original acid environment of the solution B was damaged. Because of electron-deficient, $B_4O_5(OH)_4^{2-}$ radical reacts with OH^- from $Zr(OH)_4$ through coordination reaction to form metal oxide nanoparticles network. With dropping solution Z into solution B, the nanoparticles network reaches the percolation concentration limit of the solution B, and solution B transforms into a transparent gel.

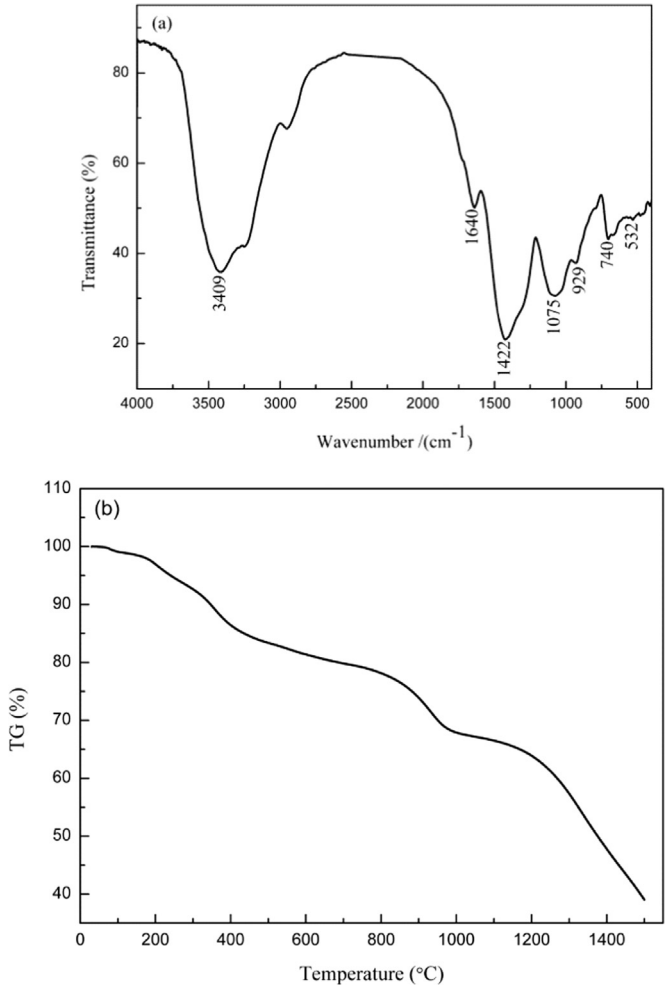

Fig. 1. FT-IR (a) and TG (b) of ZB_5C precursor.

Fig. 1b shows the TG curve of ZB_5C precursor under argon flowing with a heating rate of 10 °C/min. The weight loss occurred in the temperature range of 50–450 °C was attributed to the evaporation of physically absorbed water and dehydration of the ZB_5C precursor [29]. The slight weight loss between 450 °C and 850 °C was related to the decomposition of the network of Zr-O-Zr and Zr-O-C-O-B [30]. The weight loss from 850 °C to 1000 °C was caused by the evaporation of molten salt (NaCl and B_2O_3) and carbonization of sucrose. Fast weight loss above 1200 °C was corresponding to carbothermal reaction [31].

Fig. 2 shows the XRD patterns of as-prepared powders treated at different temperature using ZB_5C precursor. Different from previous literatures [9,17–22], in this sol-gel process, a novel precursor contained NaCl were obtained. Only NaCl was identified in precursors treated at 110 °C for 24 h and 400 °C for 1 h [Fig. 2a and b]. After treated at 800 °C for 2 h , monoclinic phase ZrO_2 (m-ZrO_2) was observed as main phase with NaCl, while at 1000 °C, the peaks of NaCl almost disappeared due to its evaporation with rising temperature under following argon. NaCl crystals were found on the tube inter surface after firing.

3.2. Synthesis of ZrB_2 powders

3.2.1. Effect of reaction temperature

Fig. 3 shows XRD patterns of as-prepared powders obtained at different temperature using ZB_2C precursor. ZrB_2 peaks were firstly observed at 1300 °C (Fig. 3b), but accompanied with strong peaks of m-