

Synthesis and characterization of zirconium diboride precursor based on polycentric bridge bonds



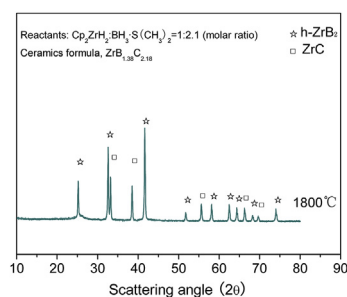
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HIGHLIGHTS

- ZrB₂ precursor based on Zr–H–B polycentric bridge bonds was synthesized.
- The ceramic yield of the precursor at 1000 °C was around 66% under N₂ atmosphere.
- After pyrolyzed at 1800 °C, the derived ceramics were composed of h-ZrB₂, ZrC and free carbon with a formula as ZrB_{1.38}C_{2.18}.

GRAPHICAL ABSTRACT



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ABSTRACT

Zirconium diboride (ZrB₂) is one of the most important ultrahigh temperature ceramics (UHTCs). ZrB₂ precursor was synthesized with bis(cyclopentadienyl)zirconium dihydride (Cp₂ZrH₂) and borane-dimethyl sulfide complex (BH₃·S(CH₃)₂). The influences of molar ratio of reactants and reaction temperature on the solubility of the as-synthesized precursors were investigated. The molecular structure of the precursor, pyrolysis behavior, and the composition of the derived ceramics were investigated by X-ray photoelectron spectroscopy (XPS), Fourier Transformed Infrared Spectroscopy (FT IR), Raman Spectroscopy (RMS), ¹H Nuclear Magnetic Resonance Spectroscopy (¹H NMR), ¹¹B Nuclear Magnetic Resonance Spectroscopy (¹¹B NMR), Thermogravimetric-Mass Spectroscopy (TG-MS), X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM), respectively. The results showed that, the precursor was an oligomer based on Zr–H–B polycentric bridge bonds with molecular weight of 750 and formula as (Cp₂Zr(BH₄)₂)₃. The precursor would probably further polymerize under vacuum or at high temperature and lead to an insoluble polymer. The ceramic yield of the precursor at 1000 °C was around 66% under N₂ atmosphere. After pyrolyzed at 1800 °C, the derived ceramics were composed of h-ZrB₂, ZrC, and free carbon with a formula as ZrB_{1.38}C_{2.18}.

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1. Introduction

Zirconium diboride (ZrB₂) is one of the most important ultrahigh temperature ceramics (UHTCs). The structure of ZrB₂ crystal-lite is a hexagon of the AB₂ type. The strong covalent bonding between boron–boron and zirconium–boron atoms, leads to its unique features of extremely high melting point (3250 °C), high

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hardness (22.1 GPa), high electrical conductivity ($9.2 \times 10^{-6} \Omega/\text{cm}$), high thermal conductivity (57.9 W/m K), low coefficient of thermal expansion ($5.9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), good chemical inertness against molten metals, good thermal shock resistance, and excellent mechanical properties even at elevated temperatures [1,2]. These outstanding properties enable ZrB₂ ceramics as a promising material for ultrahigh temperature applications in the field of the aerospace and advanced weapons, such as thermal structural/protection system in hypersonic re-entry vehicles, leading edges, rocket nozzles, propulsion system components, etc. [3,4].

The poor high-temperature oxidation/ablation resistance and intrinsic brittleness, however, limit the development of ZrB₂ ceramics. Researches on ZrB₂ ceramics are mainly focused on how to overcome the weakness. To improve the high-temperature oxidation/ablation resistance, some substances (e.g. SiC, ZrC) are introduced as anti-oxidizing inhibitors [5]. To increase the fracture toughness of ZrB₂-based ceramics, reinforcements such as whiskers, particles, or fibers are used. Among the reinforcements, continuous fibers (e.g. carbon fiber, SiC fiber, etc.) and the woven thereof are considered to be the most effective reinforcements [6].

ZrB₂ ceramics can be prepared by direct reaction between Zr and B, solid reduction reaction from ZrO₂ and/or B₂O₃, chemical vapor deposition, molten salt electrolysis, solution-based technique, polymer-derived technique, etc. [7–15]. Among them, solution-based technique and polymer-derived technique were developed in recent years. The inorganic-organic hybrid sources of zirconia, boron oxide and carbon were employed and heated at high temperature to obtain ZrB₂ ceramics in solution based technique. However, the precursor was synthesized by dispersing ZrO₂ powders in a boron carbide polymer and subsequent pyrolyzed at high temperature in polymer-derived technique. They are therefore the reduction reactions in nature.

Polymer infiltration pyrolysis (PIP) process is one of the conventional methods for the preparation of fiber and the woven reinforced ceramic matrix composites. Firstly, the fiber preform is infiltrated by molten polymer or polymer solution in vacuum. Secondly, the filled preform is cured if necessary. Finally, the cured preform is pyrolyzed at the designated temperature under a controlled atmosphere. Further densification is achieved by repetitive cycles of infiltration-curing-pyrolysis process [16]. Therefore, precursor with good solubility and high ceramic yield are necessarily required.

ZrB₂ could be introduced by slurry infiltration of ZrB₂ powders. For example, Tang et al. reported that C/SiC–ZrB₂ composite was fabricated by ZrB₂ powder infiltration and chemical vapor infiltration (CVI) process. The fracture toughness and ablation property of the composite were greatly improved [17]. Hu et al. prepared carbon fiber cloth reinforced SiC–ZrB₂ composites (2D C/SiC–ZrB₂) by slurry infiltration of ZrB₂ powders and subsequent PIP process. The oxidation and ablation resistance of the composite increased [18]. ZrB₂ powders, however, are difficult to be dispersed uniformly in the composite by slurry infiltration. It is hard to increase the content of ZrB₂ in the composite.

The above-mentioned synthesis methods of ZrB₂ do not completely meet the requirements of PIP process. The usual ZrB₂ precursors are the mixtures source compounds of Zr, B, and C, respectively. The pyrolysis temperature is usually higher than 1500 °C. The oxygen in the precursor is also harmful to the reinforcement, such as carbon fibers, under high temperature. The composition and microstructure of the derived ceramics are usually inhomogeneous due to solid–solid reaction under high temperature.

In the present paper, ZrB₂ precursor was synthesized with bis(cyclopentadienyl)zirconium dihydride (Cp₂ZrH₂) and borane-dimethyl sulfide complex (BH₃·S(CH₃)₂). The molecular structure of the precursor, pyrolysis behavior, and the composition of the

derived ZrB₂ ceramics were investigated.

2. Experimental procedure

2.1. Materials

Bis(cyclopentadienyl)zirconium dihydride (Cp₂ZrH₂), borane-dimethyl sulfide complex (BH₃·S(CH₃)₂) solution (2 M in tetrahydrofuran, THF), and THF were purchased from J & K Chemical (China). THF was freshly distilled under argon from sodium and benzophenone prior to use. Argon (>99.999%) and nitrogen (>99.999%) were purified by passing through phosphorus pentoxide.

2.2. Synthesis of ZrB₂ precursor

ZrB₂ precursor was synthesized in an argon atmosphere, using standard Schlenk techniques. Firstly, Cp₂ZrH₂ was introduced into a three-necked flask in a glove-box. Then the three-necked flask was equipped with a water-cooled reflux condenser under argon. Some THF was introduced by syringe. The reaction temperature was holding at –25, –15, 0, 12, and 25 °C, respectively. A certain amount of BH₃·S(CH₃)₂ solution was dropwisely introduced into the flask under vigorous stirring. Finally, the solvent was removed under vacuum (10^{–2} mbar). Colorless solid product was therefore obtained. The yield of product was almost 100%, based on the weight of raw materials.

2.3. Pyrolysis

Bulk pyrolysis of the precursor was carried out with a heating rate of 5 °C/min in a furnace up to 1200, 1400, 1600, and 1800 °C with a dwell time of 1 h under an argon atmosphere, respectively.

2.4. Characterization

The precursor was characterized by X-ray Photoelectric Spectrum (XPS) on a K-Alpha 1063 of Thermo Fisher Scientific Ltd. The molecular weight of precursor was measured by Gel Permeation Chromatograms (GPC, Dawn Heleos II, Wyatt Technology Corporation). The precursor was investigated by Fourier Transformed Infrared (FT IR) Spectroscopy using a Nicolet-360 spectrometer in KBr pellets over a range of 4000 to 400 cm^{–1}. Raman spectroscopy was measured in the range from 3200 to 400 cm^{–1} on a SPEX1403 spectrometer with the wavelength 785 nm. ¹H and ¹¹B Nuclear Magnetic Resonance (¹H NMR, ¹¹B NMR) spectra were taken on Bruker Avance 500 spectrometer with dimethyl sulfoxide, DMSO-d₆, as solvent. Si(CH₃)₄ and BF₃·OEt₂ were used as chemical shift references for ¹H NMR and ¹¹B NMR data, respectively. Thermogravimetric-Mass Spectroscopy (TG-MS) was carried out up to 1000 °C with a heating rate of 10 °C/min in a nitrogen flow using a SETARAM SETSYS Evolution 16/18 and PFEIFFER VACUUM OMNI Star instrument. X-ray diffraction (XRD) patterns of the derived ceramics were obtained on a Bruker ADVANCED diffractometer using Cu K α radiation. The obtained ceramics were ground simply in a WC mortar. The morphologies of the derived ceramics were observed by scanning electron microscopy (SEM) with field emission equipment, Hitachi S-4800. Energy-dispersive X-ray microanalysis (EDS) were also performed.

Zr and B elemental analysis were made by Inductively Coupled Plasma-Atomic Emission Spectrometer, ICP-AES, at Perkinelmer 5300. C content was measured by a combustion volumetric method at Horiba EMIA-320V2.

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