

Synthesis and Characterization of a Boron-Containing Precursor for ZrB₂ Ceramic

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Abstract

A precursor for ZrB₂ ceramic was successfully synthesized in a chemical reaction between polyzirconoxanesal (PZS) and boric acid. The molecular structure of the precursor, thermal properties and the pyrolysis behavior of the precursor were investigated. The results showed that the as-synthesized precursor was a polymer based on Zr-O-C-B bonds. The precursor was stable in air atmosphere and soluble in common organic solvents. The ceramic yield of the precursor at 1200 °C was around 65.5 % under N₂ atmosphere. The derived ceramics obtained at 1200 °C were composed of B₂O₃, ZrO₂ and carbon. When the temperature was increased up to 1300 °C, peaks of ZrC emerged owing to carbothermal reduction. m-ZrO₂ and t-ZrO₂ disappeared when the pyrolysis temperature was increased to above 1400 °C. ZrB₂ became the predominant phase when the pyrolysis temperature was increased up to 1500 °C.

Keywords: Zirconium diboride, preceramic polymers, boric acid, precursor infiltration pyrolysis

1. Introduction

Carbon/carbon composites (C/C)^{1,2} have been widely used in aerospace and aircraft owing to their excellent high-temperature strength, high thermal conductivity, and low coefficient of thermal expansion (CTE). However, the use of C/C composites^{3,4} has been limited because C/C begins to oxidize over 673 K, restricting their applications at high temperature. Therefore, it is necessary to improve the oxidation resistance of C/C composites in oxidizing atmosphere for application in the temperature range above 673 K. It has proven effective to improve the oxidation resistance of C/C composites by doping them with ultra-high temperature ceramics (UHTCs), such as refractory carbides/borides. Among the family of UHTCs, zirconium diboride (ZrB₂) is a material of interest because of its excellent and unique combination of high melting point (3250 °C), high hardness (22 GPa), high thermal and electrical conductivity, high strength (565 MPa) and good thermal shock resistance^{5–10}. Addition of ZrB₂ can enhance the oxidation resistance of C/C composites for various ultra-high temperature applications.

Many methods^{11–13} have been explored for synthesizing ZrB₂, including solid-state reaction, electrochemical, mechanical alloying, and self-propagating high-temperature synthesis. However, some disadvantages are inevitable, such as high synthesis temperature, long production period, low purity, relatively large crystallite size and poor sinterability. The preceramic polymer method^{14,15} is an

effective method to prepare advanced ceramics based on the thermal decomposition of the polymers. This method has unique advantages: the applicability of polymer processing techniques; the good distribution of ZrB₂ phase in the matrix and relatively low processing temperatures. With this chemical approach, the chemistry and the polymerization of the starting molecular precursor can be tailored to adjust the composition and viscoelastic properties of the derived preceramic polymer and therefore prepare complex shapes (films, fibers, coatings) and ceramic matrix composites in a wide variety of non-oxide systems. Despite the numerous studies based on the precursor synthesis routes for the different classes of preceramic polymers, such as polysilanes, polysiloxanes, polysilazanes, etc., only a few papers have focused on the synthesis of preceramic polymer for ZrB₂ based on chemical reactions. Xie *et al.*¹⁶ prepared ZrB₂ polymeric precursors using [(C₄H₈O)Zr(acac)₂] and (NHCH₃)₃B₃N₃H₃ as raw materials and obtained ZrB₂ powders by means of pyrolysis at 1500 °C for 2 h. Li *et al.*¹⁷ synthesized pure ZrB₂ powders using Zr(OPr)₄, H₃BO₃, C₁₂H₂₂O₁₁ as raw materials and acac as chemical modifier at 1550 °C for 2 h. However, boric acid was only dissolved in solution, and did not participate in the build-up of the precursor structure. Thus, the uniformity of boron in the precursor was limited, which influenced the synthesized temperature and morphology of ZrB₂ powders.

Recently, we¹⁸ have developed a new precursor (PZS) that could yield nanosized ZrC at 1300 °C. Poly(zirconoxanesal (PZS) is a soluble polymer for preparing nanosized

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zirconium carbide, with linear Zr-O-Zr as the main chain and acetylacetone and salicyl alcohol as ligands. PZS is air-stable and exhibits excellent rheological properties for the processing of ceramic matrix composites. Thus, in this paper, we use PZS as the source of zirconium and carbon (acetylacetone and salicyl alcohol ligands), and H_3BO_3 as the source of boron to synthesize a boron- and zirconium-containing precursor (PZSB). The PZSB synthesis process was described and its characterization, thermal properties and pyrolytic conversion to ZrB_2 were investigated.

II. Experimental

(1) Synthesis of PZS

The synthesis of PZS was based on our previous study¹⁸. Acetylacetone (Hacac), salicyl alcohol (SA) and (4.10 g, 0.04 mol) triethylamine were added dropwise below 5 °C into 100 mL of methanol containing (6.44 g, 0.02 mol) zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$). The reaction mixture was stirred at room temperature for 4 h and then the solution was concentrated in a rotary evaporator to give a white solid. THF 50 mL was added, the precipitate was filtrated, and the filtrate was concentrated to a highly viscous solution. Reprecipitation of the solution with hexane, followed by drying *in vacuo* for 3 h, gave PZS as a yellow powder. PZS might be a linear Zr-O-Zr chain polymer, with acetylacetone and salicyl alcohol as ligands and the molecular weight is about 700–1000. FT-IR (ν , cm^{-1}): 3062, 2923, 2862, 1590, 1529, 1483, 1452, 1278, 757, 543.

(2) Synthesis of PZSB

PZSB was prepared based on the reaction of PZS and boric acid. 1.25 g boric acid was added to a solution of 1.1 g PZS in 50 mL ethanol at room temperature and stirred. Then the reaction mixture was stirred at reflux temperature for 8 h and a transparent brown solution was obtained. Removal of the ethanol with a rotary evaporator and drying *in vacuo* at 50 °C for 2 h yielded a brown solid PZSB. FT-IR (ν , cm^{-1}): 3062, 2923, 2862, 1590, 1529, 1483, 1452, 1362, 1278, 1188, 1033, 757, 543.

The dried powders were weighted in alumina boats and placed into the tubular furnace. The samples were then heated slowly (2 K/min) in a sequence at 120 °C (2 h), 150 °C (2 h), 170 °C (2 h), 200 °C (2 h), 250 °C (2 h) in flowing argon; hard and brown thermoset polymers were obtained.

The obtained thermoset polymers were pyrolyzed in Ar up to set temperatures. A typical heating program was as follows: 1) from room temperature to set temperatures at 3 K/min; 2) set temperatures for 2 h; 3) set temperatures to room temperature at 5 K/min.

(3) Measurements and characterizations

The precursors and the samples pyrolyzed at different temperatures were rubbed into powders for FTIR, TG/DTA, XRD and SEM measurements. FT-IR spectra were recorded between 4000 and 400 cm^{-1} on a Bruker Tensor 27 spectrometer. TGA was performed on a TGA instrument (Netzsch STA 409 PC, Germany) at a heating rate of 10 K/min in Ar atmosphere. XRD measurements were

performed with a powder diffractometer (Rigaku D/M4X 2500, Rigaku Co., Japan) using $\text{Cu}/\text{K}\alpha$ radiation. The morphology of the samples was examined using SEM (S-4800, Hitachi, Japan)

III. Results and Discussion

(1) Advantages of the process used compared with other methods

Fig. 1 shows the synthetic route for the precursor investigated in this study. The PZSB precursor was prepared in a reaction of PZS and boric acid according to a new and simple chemical route. When boric acid was added to the solution of PZS, the mixture changed into a homogeneous solution right after stirring at reflux temperature and the product was isolated as an air-stable brown solid. The synthesis of PZSB was based on the condensation reaction between PZS and boric acid to form B-containing organozirconium polymers.

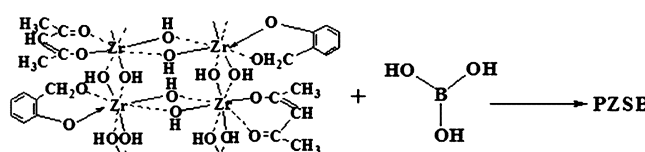


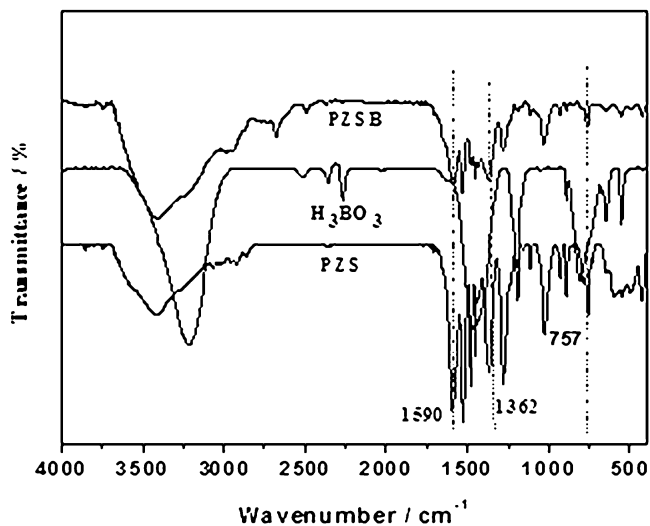
Fig. 1: Synthetic route of the ZrB_2 precursor.

The advantages¹⁵ of the used process compared with other methods were as follows. First, the materials employed in the synthesis were low-cost and easily obtained. The polymer PZS and boric acid were used as the zirconium source and boron source respectively, which were cheap and less toxic than zirconium alkoxides. Second, the polymer PZSB was prepared based on the chemical reaction of PZS and boric acid, in which zirconium, boron and carbon elements are distributed uniformly at an atomic level in the polymer, not just by blending of the source of zirconium and boron. Last, the precursor exhibits good solubility in common organic solvents, such as ethanol, acetone, etc., and the viscosity of the solution can be tailored to the desired level by diluting it, which is useful in preparing ZrB_2 -based composites via the PIP process, especially C/C- ZrB_2 composites. Moreover, the precursor is stable in air and can be preserved for a long time without hydrolysis, so it was safe and convenient for use and storage.

The structure of PZSB was investigated by means of FTIR, as shown in Fig. 2. The corresponding characteristic absorption peaks are shown in Table 1. The strong bands at 1590 cm^{-1} ($\text{C}=\text{O}$), 1529 cm^{-1} ($\text{C}=\text{C}$) and 1278 cm^{-1} ($\text{C}-\text{CH}_3$) show the existence of acetylacetone ligand. The absorption at 1483 cm^{-1} , 1452 cm^{-1} and 757 cm^{-1} is attributed to $\text{C}=\text{C}$ stretching and $\text{C}-\text{H}$ stretching of the phenolic ring, the band at 1022 cm^{-1} is due to the $\text{C}-\text{O}$ of methylol, absorption at 2923 cm^{-1} , 2862 cm^{-1} due to bridging $-\text{CH}_2-$ in the salicyl alcohol ligand. The absorption at 543 cm^{-1} , 1033 cm^{-1} and 1188 cm^{-1} was assigned to the $\text{Zr}-\text{O}-\text{Zr}$, $\text{Zr}-\text{O}-\text{C}$ and $\text{Zr}-\text{O}-\text{C}-\text{B}$ bond¹⁹, respectively. The occurrence of chemical reactions was confirmed by the appearance of the $\text{B}-\text{O}-\text{C}$ ²⁰ absorption peak at 1362 cm^{-1} . This indicates that boron and zirconium atoms have been successfully introduced into the PZSB polymer.

Table 1: Characteristic absorption peaks of the ZrB₂ precursor.

The peak of absorption band/cm ⁻¹	Chemical bond
2923,2862	-CH ₂ - vibration of salicyl alcohol
1590	C=O stretching of acetylacetone
1529	C=C stretching of acetylacetone
1483,1452	C=C stretching of phenolic ring
1362	stretching vibration of B-O
1278	C-CH ₃ stretching of acetylacetone
1022	C-O stretching of methylol of phenolic ring
757	C-H flexural vibration of phenolic ring
543	vibration of Zr-O-Zr

**Fig. 2:** FT-IR spectra of PZS, H₃BO₃ and PZSB.

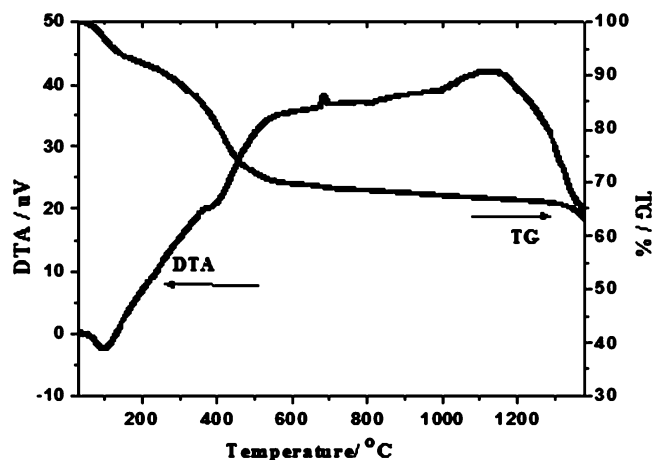
(2) Thermal behavior

A series of TG and tube furnace experiments was conducted to study the conversion process of the polymer to ceramic. Fig. 3 shows a typical TG/DTA plot for the precursor sample dried at 100 °C. The TGA curve shows a four-step mass loss: room temperature to 200 °C, 200 ~ 500 °C, 500 ~ 1200 °C and from 1200 ~ 1375 °C. The first stage is from room temperature to 200 °C, during which the weight loss is mainly due to the evaporation of residual solvent, water and cross-linked by-products. The second stage is between 200 °C to 500 °C, during which a considerable weight loss is observed. The weight loss in this stage is caused mainly by the decomposition of organic groups during the ceramization of the precursor. The third stage is between 600 °C and 1200 °C, which exhibits a small weight loss. The fourth stage between 1200 °C and 1375 °C²¹ is apparently due to the carbothermal reduction reaction between ZrO₂, B₂O₃ and carbon derived from the polymer precursor. The residue at 1375 °C was black, and the ceramic yield was 63.5 %.



(3) XRD investigations

XRD patterns of the precursor powders at different heat treatment temperatures for 2 h from 1200 °C to 1600 °C are shown in Fig. 4. The peaks due to ZrO₂ and B₂O₃ are detected from the 1200 °C sample. This indicates that the pyrolysis products of PBZS are ZrO₂, B₂O₃ and undetected amorphous carbon. At 1300 °C, the phase of ZrC and ZrB₂ appears and the intensity of ZrO₂ and B₂O₃ decreases. Up to 1400 °C, the phase of ZrO₂ disappears and ZrC-ZrB₂ composites are the dominant phase. At 1500 °C, ZrB₂ is the only crystalline phase in the samples, which means that the formed ZrC will further react with B₂O₃ and carbon to form ZrB₂. This corresponds with the thermodynamic calculation results that the Gibbs energies of ZrB₂ are lower than those of ZrC in the range of 0–1730 °C¹⁹. This shows that carbothermal reduction reaction is completed at 1500 °C after 2 h. With further increase of the temperature to 1600 °C, the phase composition basically would not change. Therefore, the optimal pyrolysis temperature is 1500 °C.

**Fig. 3:** TG/DTA curve of ZrB₂ precursor in Ar with a heating ratio of 10 K/min.

(4) Microstructural investigation

Usually, the morphology of particles is a comprehensive reflection of the synthesis methods and processes.

Fig. 5 shows SEM images of the samples heat-treated at 1400 °C and 1500 °C. In the case of the 1400 °C-heat-treatment sample, the particles have equiaxed morphology. Furthermore, the size distribution of the particles was uniform and the particle size was around 100–200 nm, with some amorphous carbon around the particles. With the increased heat treatment temperature, the equiaxed particles become unobvious. At 1500 °C, many granular ZrB₂ particles appeared and the amorphous carbon disappeared. The obtained ZrB₂ particle sizes are distributed over 10–300 nm, but a few agglomerations appear. At 1500 °C, the Zr/B molar ratio is about 0.502, which indicates that the synthesized ZrB₂ powders had a high purity.

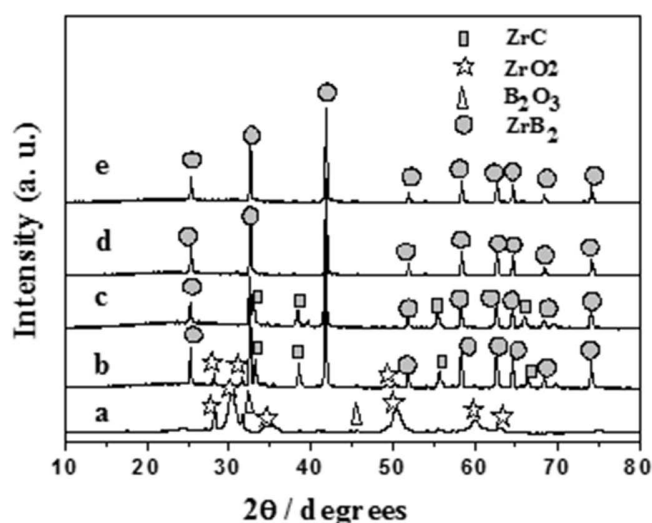


Fig. 4: XRD patterns of the ceramic products obtained at various temperatures: (a) 1200 °C; (b) 1300 °C; (c) 1400 °C; (d) 1500 °C; (e) 1600 °C.

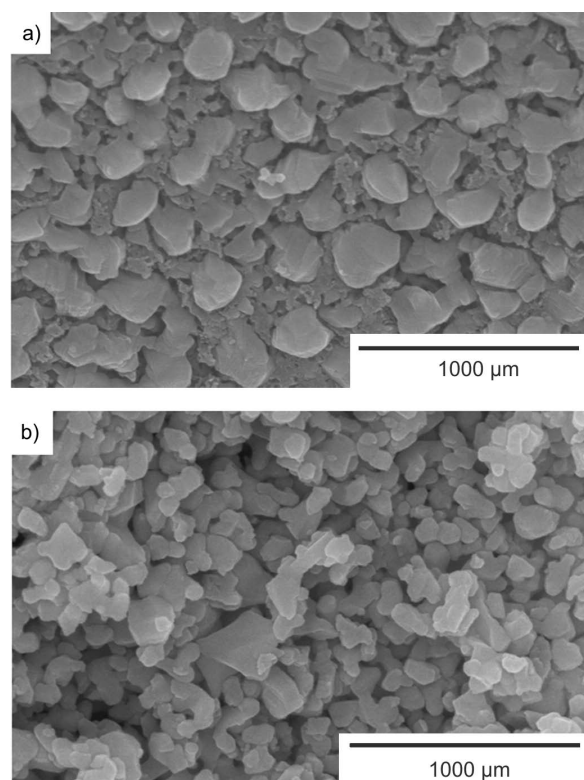


Fig. 5: Scanning electron microscopy image of the pyrolyzed ceramics: (a) sample pyrolyzed at 1400 °C; (b), sample pyrolyzed at 1500 °C.

IV. Conclusions

In this work, a novel preceramic polymer for ZrB₂ was facilely synthesized based on the chemical reaction of PZS and boric acid. The structure of the precursor was a kind of polymer based on Zr-O-C-B bridge bonds. The ZrB₂ precursor was air-stable and soluble in common solvents. The precursor decomposed at 400–500 °C and changed into ZrB₂ at 1500 °C, with the ceramic yields at about 60.5 % at 1500 °C. This simple synthesis method can be expected to have more applications in the preparation of UHTCs precursors and further in ZrB₂-based ceramic composites via the PIP process.

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