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Preparation of zirconium diboride powders by co-pyrolysis of a zirconium-containing organic precursor and polyborazine using a solution based method

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Abstract

Zirconium diboride (ZrB_2) powders were prepared from a mixture of a zirconium-containing organic precursor and polyborazine by a solution based method. The soluble zirconium-containing organic precursor was firstly synthesized by using zirconium tetrachloride and phenol as a zirconium and a carbon source, respectively. The synthetic soluble zirconium-containing organic precursor was directly used both as a zirconium source and also as a carbon source for the preparation of zirconium carbide powders. Following this, a mixture of the zirconium-containing organic precursor and polyborazine in toluene solution was used as a precursor for the preparation of ZrB_2. The formation mechanism of various ceramic products derived from relevant organic precursors and the influence of heat treatment temperature on the formation of these ceramic products were discussed. When using the zirconium-containing organic precursor both as a zirconium and carbon source as well as polyborazine as a boron source, hexagonal ZrB_2 powders are formed.

Keywords: Polyborazine; Zirconium diboride; Zirconium carbide; Boron nitride; Carbo/borothermal reduction

1. Introduction

Zirconium diboride (ZrB_2), as one of the most important members of the family of ultra-high temperature ceramics, has attracted much attention in recent years [1–3]. Its stable Zr–Zr metallic bond, B–B covalent bond and Zr–B ionic covalent bond that impart various unique physical and chemical properties, such as a high melting-point (3245 °C), high modulus, high hardness (22 GPa), low density, no phase transformation, excellent electrical conductivity ($9.2 \times 10^{-6}\ \Omega$) and thermal conductivity, resistance to high-temperature oxidation, ablation and thermal shock [4–9], chemical inertness against acid and alkali corrosion and outstanding neutron capture cross-section [10,11] etc. The unique chemical stability and excellent physical properties of ZrB_2 impart great potential as thermal protection materials for extreme chemical and thermal environment application related to hypersonic flight, space shuttle, rocket propulsion and other extreme environments [12]. In addition, as an important anti-oxidation component, ZrB_2 ceramic possesses low saturated vapor pressure and a low coefficient of thermal expansion at high temperatures [13]. However, there are still a number of barriers to overcome for ZrB_2 to be used as an anti-oxidation component in C/C composites. Firstly, ZrB_2 or its precursor must be easily impregnated into C/C composites. Secondly, the ZrB_2 precursor should contain elements carbon, boron and oxygen

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according to the following reactions involved in a carbo/borothermal reduction method [14].

$$2ZrO_2+B_4C+3C=2ZrB_2+4CO \quad (1)$$

$$ZrO_2+B_2O_3+5C=ZrB_2+5CO \quad (2)$$

Currently, ZrB_2 powder can be prepared mainly by the following methods: (i) solid-state method; (ii) vapor-state method; (iii) liquid-state method or solution based method; (iv) mechanochemical method. The first two ways are usually used in industrial manufacturing. Since the raw materials are micron-scale powders with low sintering activity, the synthetic powder products usually have a relatively coarse particle and a low purity. The solid-state or vapor-state synthesis is also difficult since both require a higher temperature and a longer production period.

In contrast to those traditional methods, the liquid-state method is usually applied to synthesize ultrafine powder at a lower temperature. As the metastable amorphous phase in the preparation process can be formed using a sol–gel method, the liquid-state method promotes effective contact between reactants, thus increasing their reactivity. In particular, the liquid organic precursor conversion method with the advantages as mentioned above has in recent years been widely used for the synthesis of ultrafine ZrB_2 powders. This technology only requires simple equipment and a short processing cycle. The organic precursors, with high ceramic yield and good solubility in organic solvent, are very suitable for impregnating carbon fiber preform to introduce the ceramic precursors into C/C composites.

The preparation of ZrB_2 precursor via a sol–gel process uses zirconium n-propoxide/zirconium oxychloride, sucrose/phenolic resin and boric acid as zirconium, carbon and boron sources, respectively [15–17]. On this basis, the ZrB_2 precursor was successfully synthesized by adopting zirconium diketonate as a source of zirconium [18] or boron-containing polymer as a source of boron [19].

However, the precursors prepared by the methods cited above are not soluble in organic solvent to form a homogenous ceramic precursor solution, and thus it is difficult for them to impregnate the carbon fiber preforms via molecular diffusion. Cheng [20] synthesized a kind of soluble zirconium-containing organic precursor via the condensation polymerization of zirconium oxychloride, salicylol and acetylacetone. Then a ZrB_2 organic precursor was produced by mixing the zirconium-containing organic precursor with boric acid in organic solution. The improvement in solubility of the precursor in organic solvent using this method was limited because of the poor solubility of boric acid in the organic solvent.

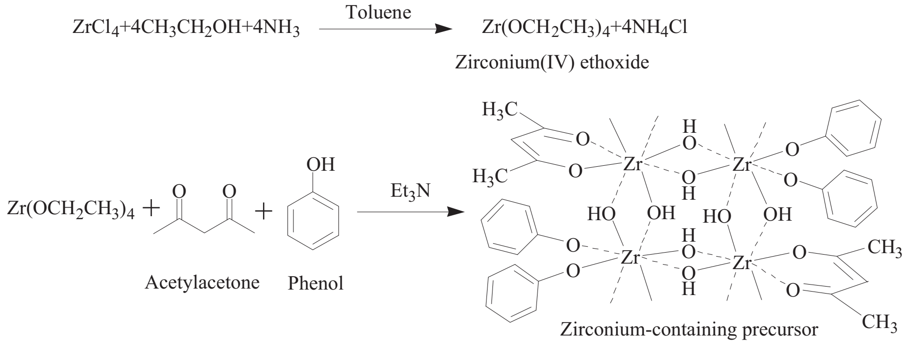
This paper presents a method for the synthesis of soluble ZrB_2 precursor, which can effectively solve the problem of poor solubility of both zirconium and boron sources. Furthermore, ZrB_2 ceramic powders were prepared through liquid organic precursors by the following steps. Firstly, a zirconium-containing organic precursor was prepared by reacting zirconium ethoxide, obtained by the alcoholysis of zirconium tetrachloride in ethanol, along with acetylacetone and phenol. Then a liquid organic zirconium diboride precursor was prepared by blending the polyborazine with the zirconium-containing organic precursor. The ceramic transformation behavior and mechanism of the precursors were also investigated.

2. Experimental procedures

All chemical reagents were commercially available and were used as received. $ZrCl_4$ (99.9%) was purchased from Yi County Jincheng Zirconium Co., Ltd. BCl_3 (99.9%) was purchased from Tianjin Summit Specialty Gases Co., Ltd. ZrO_2 powder (99.99%) with the granularity of 300 mesh was purchased from China New Metal Technology Co., Ltd. The other chemical reagents were purchased from Sinopharm.

2.1. Synthesis of zirconium-containing organic precursor

Stoichiometric amount of zirconium tetrachloride (48 g, about 0.2 mol) was dissolved in a mixture of 60 ml ethanol and 300 ml toluene. The solution was cooled down to 0 °C and the ammonia was bubbled into the solution to neutralize hydrogen chloride. The reaction mixture was stirred at 0 °C for 1 h and then separated in a closed plastic cup by a centrifuge at 3000 r/min for 5 min to get a clear transparent liquid. The obtained transparent liquid was poured into a mixed solution of acetylacetone (41 ml, about 0.4 mol) and phenol (36 ml, about 0.4 mol) and reacted at 140 °C for 5 h. Then the reddish brown liquid zirconium-containing precursor



Scheme 1. Synthetic route of the zirconium-containing organic precursor.