

Synthesis, characterization and use of synthesized fine zirconium diboride as an additive for densification of commercial zirconium diboride powder

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ABSTRACT

Zirconium diboride (ZrB_2) was synthesized by a solution-based technique using zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$, ZOO), boric acid (H_3BO_3 , BA) and gum karaya (GK) as the sources of zirconium, boron and carbon, respectively. The initial formation temperature of ZrB_2 was 1200 °C and complete conversion was achieved by 1400 °C. Preceramic precursors and as-synthesized ZrB_2 powders were characterized by XRD, TG-DTA, SEM, TEM, EDX and compared with commercial ZrB_2 powder made by carbothermic reduction. FT-IR of as-synthesized dried preceramic precursor revealed the formation of Zr–O–C and Zr–O–B whereas SEM showed agglomerated spherical particles with mean diameter of $< 1 \mu m$. Commercial ZrB_2 and as-synthesized fine ZrB_2 powder were spark plasma sintered (SPS) at 1900 °C for 10 min. Addition of 10 wt% of synthesized fine powder improved the fired density from 87% to 93% of theoretical. A significant cost benefit arises from the utilization of cheap synthesized fine powder as an additive for the densification of the more expensive commercial powder.

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1. Introduction

Ultra-high-temperature ceramics (UHTCs) are materials (usually carbides, borides and nitrides) having extreme melting temperatures (> 3000 °C) along with excellent physical and chemical stability making them suitable for hypersonic flight leading edges, atmospheric re-entry and many aerospace and nuclear structural applications [1]. Transition metal diborides such as zirconium diboride (ZrB_2) show relatively good oxidation resistance leading to significant interest for the scientific community.

Methods used for the synthesis of metal diborides include i.e. reaction of a metal oxide with boron, borothermal reduction [2], carbothermic reduction of a metal oxide and boron oxide [3], mechanochemical synthesis in which the metal and boron are mixed by high energy milling [4] and wet chemical in which all components such as carbon, boron and the metal-containing sources are dissolved in a liquid medium and subject to condensation and hydrolysis to form a colloidal solution-based precursor [5].

Densification of diborides requires high temperatures and

external pressure because of the strong covalent bonding and low self-diffusion [6]. Methods of enhancing densification of borides include reactive hot pressing and spark plasma sintering (SPS) [7–9]. Sintering temperature can also be reduced by adding metal additives such as nickel [10]. However, metal additives lead to formation of nickel-rich phases at grain boundaries and triple junctions deteriorating the mechanical properties [10–11]. Preparation of highly pure and dense borides without any additives is desirable. Additionally, commercially available diboride powders made by carbothermic reduction of zirconia with boria have mostly coarse particles and poor sinterability [12]. SPS is commonly used to fabricate dense UHTCs mainly by concurrent application of high temperature, axial pressure and field-assisted sintering [13]. The field component is associated with an electric current which passes through the powder. SPS has advantages over conventional sintering or hot pressing, such as denser final materials, higher heating rates, shorter holding times, fine product grain size and cleaner grain boundaries [13–17].

The objective of this work was to synthesize ultrafine ZrB_2 particles by a solution-based polymer pyrolysis technique which gives the advantages of intimate mixing of the reactants at the atomic level and then to validate the applicability of using the as-synthesized submicron powder as an additive for densification of commercial ZrB_2 powder.

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2. Experimental

The starting materials were gum karaya (GK), zirconyl oxychloride octahydrate (ZOO) and boric acid (BO) obtained from Sigma-Aldrich Co (Dorset, UK). A flow chart for the synthesis of ZrB_2 is shown in Fig. 1. GK (3 M) was dissolved in distilled water with continuous stirring by a magnetic stirrer at 60 °C. Then, BO (3 M) and ZOO (1 M) were mixed and refluxed under continuous stirring with a magnetic stirrer for 2 h followed by drying at 110 °C for 24 h in an oven and crushed to powder in a mortar with a pestle to get ZrB_2 precursor powder. Finally, pyrolysis and subsequent heat treatment were carried out in a temperature range of 1000–1400 °C, dwelling for 1 h in a horizontal alumina tube furnace (Lenton furnaces and ovens, Derbyshire, UK) under controlled flow of argon (99.99% purity, 100 mL min⁻¹) to avoid oxidation.

Commercial ZrB_2 powder (Grade B) prepared by carbothermic reduction with an average particle size of $\sim 2.4 \mu\text{m}$ (H.C. Starck GmbH, Goslar, Germany) was used as a comparison with the laboratory synthesized ZrB_2 powder of this work. Sintering of commercial ZrB_2 alone and with laboratory synthesized ZrB_2 as an additive was carried out using SPS (FCT HPD 25; FCT Systeme GmbH, Rauenstein, Germany) under vacuum (5 Pa).

For compositions with laboratory synthesized ZrB_2 addition, commercial ZrB_2 (90 wt%) with 10 wt% lab synthesized ZrB_2 were mixed in acetone followed by ultrasonication for 30 min. A rotary evaporator (Rotavapour R-124, Buchi, Flawil, Germany) was used to remove the acetone and the powder was then grind in a glass mortar and sieved.

For the sintering, 6 g of ZrB_2 powder was poured into a 20 mm diameter graphite die containing a graphite paper used on the inner wall of the mold to prevent sticking. The sample was pressed between two graphite punches of 3 cm diameter. The temperature was probed by the top pyrometer focused on the inner graphite wall of the pressing punch at a distance of 4 mm from the sample. Graphite felt was wrapped around the sintering mold during sintering to prevent heat loss by radiation from the sample. For comparison, the commercial samples with and without additive were sintered at 1900 °C under a uniaxial pressure of 50 MPa with a dwell time of 10 min. The heating and cooling rates were 100 °C and 50 °C min⁻¹, respectively.

X-ray diffraction (XRD) (PANalytical Xpert³ diffractometer, Cambridge, UK) with Cu K α 1 radiation ($\lambda = 1.540598 \text{ \AA}$) and a

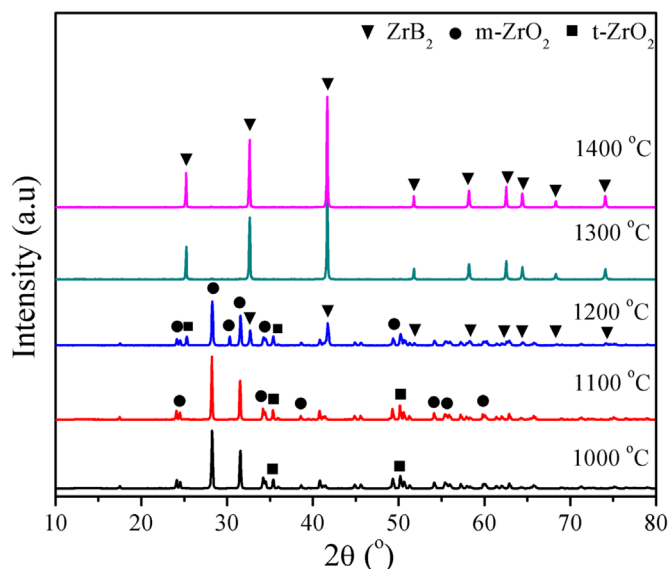


Fig. 2. XRD of synthesized ZrB_2 powders heat treated 1 h at 1000, 1100, 1200, 1300 and 1400 °C under Ar.

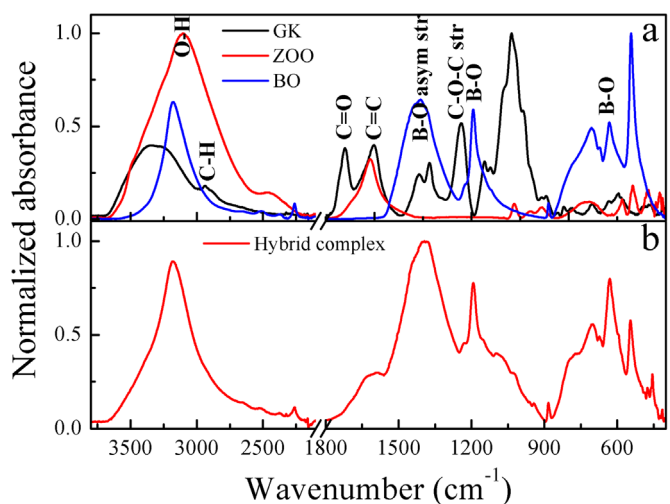


Fig. 3. FT-IR of (a) starting materials (b) as-synthesized sample dried at 110 °C.

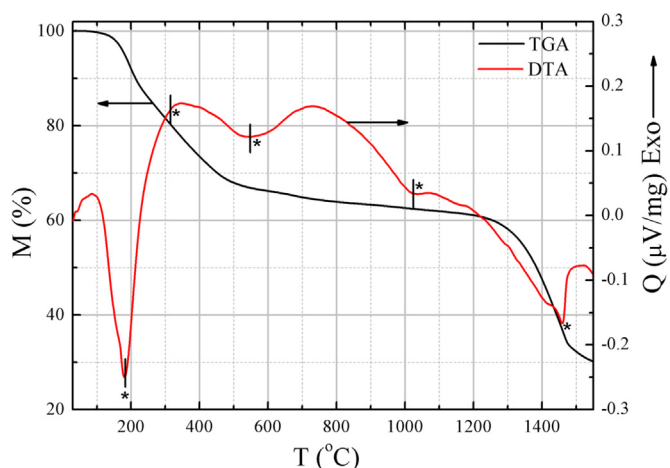


Fig. 4. TG (M represents mass) and DTA (Q represents heatflow) of as-synthesized hybrid precursor in argon.

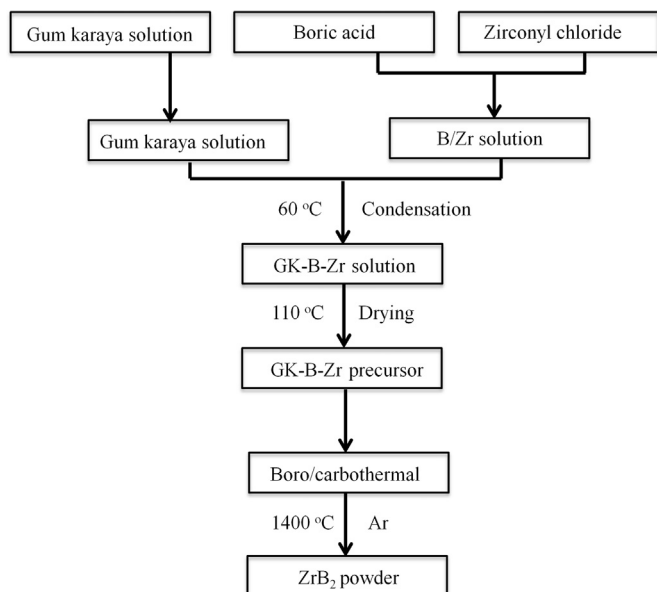


Fig. 1. Flow chart for the synthesis of ZrB_2 from solution based process.

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