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A top-down approach to densify ZrB_2–SiC–BN composites with deeper homogeneity and improved reliability

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HIGHLIGHTS

- Fine grained ZrB_2–SiC–hBN composite were reactively densified from coarse precursors.
- Employ the SHS ignited in ZrN–Si–B_4C systems to improve microstructure homogeneity.
- Strength reliability and strain tolerance of obtained ceramics were much improved.

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ABSTRACT

A novel top down approach was developed to fabricate dense ZrB_2–SiC–BN (ZSN) composites with a fine-grained (<1 μm) microstructure using coarse-grained (~10 μm) ZrN and Si precursors that reacted with fine (~0.5 μm) B_4C powders at 1850 °C. The results show that the "reaction" and "densification" mechanisms acting during sintering could be separated or happen simultaneously by changing the pressure loading strategy. Loading cycles not only have a substantial influence on the microstructure homogeneity and the strength reliability of as sintered composites, but might alter the electric current path during the Spark Plasma Sintering process as well. A residual compressive stress of 361 MPa, generated upon the SiC grains in the ZSN composites, was measured by Raman spectroscopy. The fine SiC grains tended to form larger clusters in the dense microstructure if the loading cycle is inappropriate, which was further employed to interpret the observed scattering of strength values in one batch of ZSN. The $48ZrB_2$–24SiC–28BN (number in vol%) composite has an average strength of 473 MPa, which was 94% of that of *in situ* densified ZrB_2–SiC ceramics (ZS). Considering the corresponding Younǵs modulus was only half of that for ZS, the *in situ* ZSN composite owns a better mechanical strain tolerance.

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1. Introduction

In ceramic particle reinforced composites, according to the Hall–Petch relationship, the particle size of individual grains has a substantial influence on the achieved mechanical properties like strength and hardness. Therefore, the properties of a composite can be significantly improved if there is a way to retain nano/submicron-sized grains in the densely sintered ceramics [1–3]. However, it is almost impossible to homogeneously disperse such fine particles into a ceramic matrix and, furthermore, there is no accessible source of high purity nano-sized raw powders in the market. Another difficulty is that the finer powders available always contain relatively much more of oxygen impurity than coarse grained precursors. Ceramic composite containing refractory boride is such a representative case, since it is difficult to purchase boride powder with an average particle size smaller than 1 μm, e.g. ZrB_2 powder with low oxygen content.

Recent worldwide interest in ZrB_2–SiC based Ultra-high Temperature Ceramics is strongly driven by an advanced concept of making the next generation of hypersonic re-entry vehicles with sharp geometries [4–7]. Such a special design aims to improve the flight performances by increasing the lift-drag ratio and enhancing the manoeuvrability. As a result, the hypersonic vehicle is able to operate at very high speeds of 7–10 Mach, and at their critical thermal protection parts, e.g. leading edges and nose cones,

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the temperature must be allowed to reach up to 2400 °C during a shorter time [8,9]. Benefiting from the excellent high temperature stability and high thermal conductivity, ZrB_2–SiC composites can in theory transfer sufficient heat away from the hottest areas and redistribute it to cooler parts. However, ZrB_2, SiC, as typical brittle ceramics, are very sensitive to the mechanical and thermal stress created by the mentioned extreme environment. Thus, the engineering applications of ZrB_2–SiC composites were restricted. The incorporation of fine hexagonal BN grains, with high thermal conductivity and low elastic modulus, into a stiff ceramic matrix has been proved to be an effective way to improve the mechanical reliability and the thermal shock resistance of prepared ceramic composites [10–12]. In light of this, several attempts have been prepared to densify ZrB_2–SiC–hBN (ZSN) composites targeted for ultra-high temperature applications [13–15]. Nevertheless, all the results so far showed a significant decrease in strength and hardness of ZSN compared to the original ZrB_2–SiC ceramics, mainly due to the cleavage feature, instinct low strength of hBN and the coarse grains inside the ZSN composites.

Reactive sintering provides another possibility to obtain an *in situ* grain refinement of ceramics even using coarse precursors [16–21]. Current *in situ* reactive routes, however, to prepare boride containing ceramics are less useful as they either start from pure metals (like Ti, Zr) [16–19], metal hydride (e.g. TiH_2, ZrH_2) [13,14,20] or oxides (e.g. TiO_2, ZrO_2) [21]. The route starting from pure metals is quite expensive and difficult to control, as metallic powders are ductile during milling and newly exposed surfaces will be partially oxidized even at trace amounts of oxygen or water present. When metal hydride is a precursor, special attention should be required, because any release of hydrogen and an uncontrolled reaction can crack the die or even set off an explosion. The most economical approach is starting from oxides, but volatilization of B_2O_3 will be a problem inevitably, as it contaminates the furnace and the vacuum pumping system. In addition, the use of oxide precursors might result in inhomogeneous composition, porosity and poor properties of the sintered composites.

In general, refractory metal nitrides are considered as chemical inertness, e.g. ZrN and TiN. They are prone, however, to react with some boron compounds at high temperatures, as displayed by the Reaction (I):

$$4ZrN + 3B_4C + 3Si = 4ZrB_2 + 3SiC + 4BN \tag{I}$$

In the present study, Reaction (I) will be used to prepare a fine-grained ZrB_2–SiC–hBN composite from available precursors with low-oxygen and coarse particle size. The heat released during the reaction will be utilized in order to achieve an intimate or deeper homogeneity and thereby a subsequent property improvement of the ZSN composite. Further details and results will be presented below.

2. Experimental procedure

Commercial powders of zirconium nitride (ZrN > 99.8%, d_{50} = 10 μm, ZR-301, Atlantic equipment engineers, Bergenfield, NJ), boron carbide (B_4C, d_{50} = 0.5 μm, Grade HD 20, H.C. Starck, Germany), and silicon (Si, >99.9%, typical less than 10 μm, H.C. Starck, Germany) were mixed in a molar ratio of 1 ZrN:2 B_4C:1 Si using a shaker mixer (Turbula T2C, 50 rad/min) in acetone for 12 h to obtain a homogeneous mixture. Yttria stabilized tetragonal zirconia (3Y–ZrO_2) milling media (balls) were used, but any contamination of blended powders was found negligible since the low energy method adopted. The acetone solvent was removed by a rotary evaporator at 70 °C to minimize segregation. As-sieved powder mixtures were sintered in a Spark Plasma Sintering apparatus (SPS Type HP D 25/1, FCT System, Rauenstein, Germany) under vacuum. A cylinder shaped graphite die with inner diameter of 40 mm was chosen and the die was further lined inside with graphite foil and surrounded outside by a layer of porous carbon felt insulation. Above 450 °C, the sintering temperature was measured by a vertical placed pyrometer focused near the center of the sample [22].

Powder compacts were heated under vacuum (~5 Pa) to 800, 1200, 1300, 1700 and 1850 °C with a fixed heating rate of 100 °C/min. For all the cycles, the final soaking time and the starting loading pressure were set as 5 min and 4 MPa, respectively. In the initial experiments, a uniaxial loading of 60 MPa was applied slowly as soon as the temperature reached 1600 °C, as sintered specimens were called ZN-ND. For the followings, the temperature for applying the pressure moved to 700 °C and the corresponding specimens were marked as ZN-D. In order to increase the loading in a steady state, a short holding either at 700 °C (ZN-D) or 1600 °C (ZN-ND) was added in the program, the completed sintering schedules are shown in Fig. 1.

After sintering, the dense billets were removed from the die and their surfaces were ground before density measurement through the Archimedes method. The microstructure and the phase assemblage of the samples were examined using Scanning Electron Microscopy (SEM, XL30-FEG, FEI, Eindhoven, Netherlands) and X-Ray Diffraction (XRD, Seifert, Ahrensburg, Germany). Image analysis software (Image-Pro) was chosen to calculate the grain size as well as the phase proportions in some randomly collected SEM images with different magnifications.

For the mechanical test, Vickers hardness (H_V) was measured using a load of 9.8 N (1 kg) with a 15 s dwell time on the polished surface of ZN-ND and ZN-D samples sintered at 1850 °C. The flexure strength at room temperature was measured in three-point bending (3-pt) configuration with a fixed span width of 20 mm and a cross-head speed of 0.5 mm/min. The test bars were cut from as-sintered samples, they were further ground and polished into 2 mm × 2.5 mm × 25 mm. For each sample, 25 bars were loaded to failure and the achieved strength data were further analyzed by a two parameter Weibull distribution. Elastic constants were determined at room temperature through the impulse excitation method on cylindrical discs with diameter of ~40 mm and thickness of ~3 mm (Grindo-Sonic, Lemmens N.V., Heverlee, Belgium).

Residual stress measurements were made by a micro-Raman spectrometer (LabRAM HR 800) with a spectral resolution of 0.5 cm^{-1} using a 50 mW, 532 nm Nd:YAG laser. Before the measurement, the apparatus was calibrated by the line at 520.7 cm^{-1} from a silicon wafer. Raman patterns were acquired from at least five random areas upon the flat surfaces of ZN-ND samples sintered at 1300 °C and 1700 °C and the polished surfaces of the dense ZN-ND and ZN-D samples sintered at 1850 °C. Each area contains about 1000 individual SiC particles, as estimated by optical microscopy observations, and the Raman measurement of an area was repeated at least ten times for getting a highly reliable curve.

3. Results

3.1. Powder characterization

The morphologies of the three starting powders, namely Si, ZrN and B_4C, for preparing ZSN composites are shown in Fig. 2a–c, respectively. The particle size of Si powder is between 5 and 10 μm as shown in Fig. 2a. The ZrN powder has an average size of 10 μm, but some finer particles ~2 μm and a few coarser >20 μm could be observed, see Fig. 2b. With regard to B_4C powder, the mean particle size is small (~0.5 μm) and its distribution is relatively narrow, but a few larger particles (>2 μm) could be found occasionally.

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