



Enhanced mechanical properties, thermal shock resistance and oxidation resistance of Si₂BC₃N ceramics with Zr-Al addition

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ABSTRACT

Highly densified Si₂BC₃N ceramics were prepared through SPS sintering the Zirconium (Zr) and aluminum (Al) incorporated amorphous Si₂BC₃N powder obtained from mechanical alloying. The phase compositions, microstructures, mechanical properties, and thermal shock resistance, as well as the oxidation resistance were investigated. The results show that the nano ZrO₂ and Al₂O₃ could enhance the solid diffusion and therefore induce the development of larger turbostratic BN(C) plates and SiC particles. The addition of only 1 mol% composite additive could enhance the properties of composites significantly. Therefore, the flexural strengths and fracture toughness can reach up to 590.2 MPa and 4.93 MPa m^{1/2}, respectively. Furthermore, the additive containing composites have much better crack initiation and propagation resistance. The residual strength of 1 mol% additive containing ceramics after thermal shock has improved by 69.8% comparing with the pristine Si₂BC₃N composites. Meanwhile, the oxidation resistances of Zr-Al incorporated Si₂BC₃N ceramics are obviously improved attributing to improved relative density and the formation of much stable SiO₂-ZrSiO₄ layer.

1. Introduction

The intensive reported high temperature structural ceramics were the carbides, nitrides, and diborides, as well as C/C composites in the past few decades. Actually, quaternary SiBCN ceramics have attracted intensive attentions due to their extraordinary high temperature stability up to 2000 °C without apparent decomposition, which made them one of the state-of-the-art structural ceramics [1–3]. As a promising route, we have successfully prepared bulk SiBCN ceramics from sintering the mechanical alloying (MA) SiBCN powder [4–6]. The mechanical properties [7,8], thermal shock resistance [9,10] and oxidation resistance [10,11], as well as the ablation resistance [12,13] of bulk SiBCN ceramics have attracted intensive attentions. It is revealed that this quaternary compound can be a potential candidate for applications at leading edges and nose-cones for a next generation of sharp re-entry space vehicles and also for the thermal protection material. As for the structural ceramics, the strengthening and toughening is the eternal theme for satisfying the demands of mechanical and thermal stresses resistance. Normally, there are mainly two ways for enhancing the bulk ceramics, one is by the introduction of reinforcements and the other is by the addition of sintering additives.

For SiBCN ceramics, reinforcements such as carbon fibers [9], silicon carbide fibers [14], multi-walled carbon nanotubes [15], graphene [16] and Al₄SiC₄ [17] have been adopted and the crack hindering mechanisms when use these reinforcements were the well-known “crack bridging”, “pull-out” and “crack deflection” etc. As for the sintering additives, LaB₆ was revealed to enhance the development of BN(C) plates and therefore improved the density and mechanical properties [18,19]. In addition, Miao [20] and Zhang [21] et al. investigated the influence of ZrO₂ and AlN on the microstructures and properties of SiBCN ceramics. The addition of AlN or ZrO₂ promoted the densification through accelerating the crystallization and grain growth, which eventually enhanced the properties. Furthermore, the addition of Al [22] or Zr [11] powders could also enhance the mechanical properties of ceramics obviously. In order to comparing the effects of additives, the properties of prepared SiBCN ceramics were listed in Table 1. It was clear that the ZrO₂ and AlN could improve the flexural strength from 331 MPa to 575.4 and 415.7 MPa, respectively. In addition, their fracture toughness reached 3.67 and 4.08 MPa m^{1/2}. In fact, the Zr and Al would also favor the formation of ZrO₂ and Al₂O₃/AlN inevitably and therefore stimulated the structure development and improved the mechanical properties [11,22]. Consequently, it is

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Table 1
Physical and mechanical properties of Si₂BC₃N ceramics (sintered with HP) reported in references.

Index	Bulk density (g/cm ³)	Young's modulus (GPa)	Flexural strength (MPa)	Fracture toughness (MPa m ^{1/2})
Pristine Si ₂ BC ₃ N [21]	2.52	139.4 ± 16.0	331.0 ± 40.5	2.81 ± 0.89
5.0 mol% ZrO ₂ [21]	2.83	159.2 ± 21.7	575.4 ± 73.7	3.67 ± 0.01
5.0 mol% AlN [21]	2.74	148.4 ± 8.3	415.7 ± 147.3	4.08 ± 1.18
8.3 mol% Zr [11]	3.24	242.1 ± 4.6	202.0 ± 9.1	2.34 ± 0.24
10.0 mol% Al [22]	2.90	222.1 ± 27.7	526.8 ± 10.4	5.25 ± 0.20

reasonable to believe that the Zr and Al powders should be potential additives in this non-oxide ceramics. Moreover, it should be also mentioned that the above works mainly investigated the effects of a single additive, and their contents were higher than 5 mol% of the total formulation. Generally, the introduction of a large amount of additive may deteriorate the properties of composites under high temperature, such as oxidation resistance [17]. Based on these considerations, it is of great importance to prepare enhanced bulk SiBCN ceramics with reduced additive content.

Inspired by the former works, the present work was devoted to preparing bulk SiBCN ceramics with enhanced properties while containing less additives. Firstly, amorphous Si₂BC₃N and nano-sized Zr-Al powders were prepared through MA. The Zr-Al modified Si₂BC₃N ceramics were then sintered by SPS method. The phase compositions, microstructures, mechanical properties, thermal shock resistance, and oxidation resistance were investigated in comparison with the pristine Si₂BC₃N ceramics. It has been found that the Zr-Al addition could stimulate the growth of β-SiC and BN(C) plates remarkably through the generation of scattered nano-sized oxides, which stimulates the solid diffusion. In addition, the mechanical properties and thermal shock resistance of Si₂BC₃N ceramics are improved, attributing to the densified and well-developed structure. Besides, the oxidation resistance has also been improved obviously attributing to higher relative density and the formation of high stable SiO₂-ZrSiO₄ oxidation layer.

2. Experimental

2.1. Preparation of nano Zr-Al incorporated amorphous Si₂BC₃N powders

The starting raw materials were well crystalline cubic silicon powder (95.0% in purity, 45.0 μm, Beijing Mountain Technical Development Center, China), hexagonal boron nitride power (98.0% in purity, 0.6 μm, Advanced Technology & Materials Co., Ltd., Beijing, China), graphite flake (99.5% in purity, 8.7 μm, Qingdao Huatai Lubricant Sealing S&T Co., Ltd., China), aluminum (99.9% in purity, 45.0 μm, Shanghai Xiangtian Nano MaterialS Co., Ltd., China) and zirconium (99.9% in purity, 45.0 μm, Shanghai Xiangtian Nano MaterialS Co., Ltd., China). For preparing the amorphous Si₂BC₃N powder, the molar ratio of Si: BN:C was set as 2:1:3 and the ball to powder mass ratio was 20:1 according to our previous works [4,5]. Further the mixed powders were loaded into the silicon nitride vials along with identical component balls under argon atmosphere and milled by a planetary ball mill (P4, Fritsch GmbH, Germany). The rotation speed of the main disk was set as 350 rpm, and the vials were 600 rpm in reverse. The machine was paused for 10 min every 40 min, and the effective milling time was 20 h. As for preparing the nano Zr-Al powder, the molar ratio of Zr: Al: C was set as 1: 2: 2 and kept all the other parameters the same with the above-mentioned ones for the preparing of Si₂BC₃N powder. The addition of graphite

was to guarantee the production of nano powder instead of bulk alloy.

In the present work, mole percent of nano Zr-Al powders was set at 1 mol%, 3 mol% and 5 mol%, which were milled with the amorphous Si₂BC₃N powder. Specifically, for 1 mol% Zr-Al addition, there were 0.01 mol Zr, 0.02 mol Al, and 0.02 mol C, as well as 0.99 mol amorphous Si₂BC₃N powder. For a uniform distribution, planetary mill with silicon nitride vessel and balls were adopted. The ball to powder mass ratio was set as 20:1 and taken ethanol as milling medium. A relative low speed was set at 200 rpm to avoid the ZrO₂ contamination. After that, the slurries were dried at 80 °C for 24 h for evaporating the ethanol. Correspondingly, the powders were named as ZA1, ZA3 and ZA5, respectively.

2.2. Spark plasma sintering and characterization

The prepared Si₂BC₃N-Zr-Al powders were loaded into a cylindrical graphite die of 40 mm in diameter. A sheet of graphite paper was placed between the punch and the powder for removing the sample easily out of the die after cooling. The SPS (FCT-HP25) sintering process was conducted under protection of high purity N₂ and a uniaxial pressure of 40 MPa was applied throughout the sintering. The sintering temperature was set at 1900 °C at a rate of 100 °C/min and a dwell time of 5 min was set. The sintering temperature profiles and variations of shrinkage were kept recording during the sintering process. The sintered samples were also named as ZA1, ZA3 and ZA5, respectively.

The sintered samples were ground and polished with 0.4 μm SiC abrasive paper. The density of samples was measured by the Archimedes method with deionized water as medium. The property measurements were carried out on omnipotence mechanics tester (Instron 5569, Instron Corp., USA) and hardness tester (HVS-5, Laizhou Huayin Testing Instrument Co., Ltd., China). The flexural strength and the Young's moduli were obtained using three-point bending test on 3 mm × 4 mm × 20 mm bars with a span of 16 mm and a crosshead speed of 0.5 mm/min. The Young's moduli were calculated through dividing the stresses by the strains obtained from the three-point bending tests. The fracture toughness was determined using the single edge notched beam method with a crosshead speed of 0.05 mm/min, and the testing bar dimension was 2 mm × 4 mm × 20 mm (16 mm outer span). The depth of the notches was around 2.0 mm and the width about 0.2 mm (Instron5569, Instron Corp., USA). Three bars were tested for an average value. The Vickers hardness was measured on polished sample surface with a load of 10 kg and a holding time of 15 s. The phases and fracture surface of ceramics were analyzed using X-ray diffraction spectrum (XRD, 40 kV/100 mA, D/max-γB CuKa, Rigaku Corp., Japan) and a scanning electron microscopy (SEM, 30 kV, Quanta 200 FEG, FEI Co., USA), respectively. STEM (Talos F200x, 200 kV, FEI Company, USA) was also used to analyze the microstructure details of various Si₂BC₃N ceramics. Additionally, high-resolution TEM (HRTEM)

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