



Microstructures and mechanical properties of SiBCNAI ceramics produced by mechanical alloying and subsequent hot pressing*

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Abstract: Amorphous SiBCNAI powders were prepared via a mechanical alloying (MA) technique using crystalline silicon (Si), hexagonal boron nitride (h-BN), graphite (C), and aluminum (Al) as starting materials. SiBCNAI powders were consolidated by a hot pressing (HP) technique at 1800 °C under a pressure of 30 MPa in argon and nitrogen. The sintering atmosphere had a great influence on the microstructures and mechanical properties of the ceramics. The two ceramics had different phase compositions and fracture surface morphologies. For the ceramics sintered in argon, flexural strength, fracture toughness, elastic modulus and Vickers hardness were 421.90 MPa, 3.40 MPa·m^{1/2}, 174.10 GPa, and 12.74 GPa, respectively. For the ceramics sintered in nitrogen, the mechanical properties increased, except for the Vickers hardness, and the values of the above properties were 526.80 MPa, 5.25 MPa·m^{1/2}, 222.10 GPa, and 11.63 GPa, respectively.

Key words: SiBCNAI ceramics, Hot pressing (HP), Mechanical properties, Microstructure, Mechanical alloying (MA)

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1 Introduction

SiBCN precursor-derived ceramics are promising candidates for high temperature structural applications because of their outstanding high-temperature stability (Riedel *et al.*, 1996), high oxidation resistance (Baldus and Jansen, 1997), and mechanical properties (Riedel *et al.*, 1998; Christ *et al.*, 2000; Jansen *et al.*, 2002). However, oxidation times exceeding 24 h at 1500 °C lead to crystallisation of the formerly amorphous oxide scales with concurrent bubble formation (Butchereit *et al.*, 2001) because of volatilization of boron species. Similar observations were reported from the high-temperature oxidation of sintered SiC containing boron as a sintering additive (Schumacher, 2001). To improve the

scale quality, Müller *et al.* (2004) prepared a new kind of SiBCNAI precursor-derived ceramics and investigated their oxidation behaviour. It was found that the addition of aluminium had a beneficial effect indeed on impeding bubble formation, as well as cracking and spallation of the oxide scales. However, to date, studies on mechanical properties of SiBCNAI ceramics have not yet been reported. This may be because the polymer precursors method limits the fabrication of large size bulk ceramics.

Nowadays, the synthesis and pyrolysis of precursors must be done in inert gases, and the corresponding processes are very complex and the starting materials are very expensive, so it is necessary to find other routes of synthesis for SiBCNAI powders and ceramics. Mechanical alloying (MA) is a solid-state powder processing technique involving repeated welding, fracturing, and rewelding of powder particles in a high-energy ball mill. MA has now been shown to be capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases starting from blended elemental or prealloyed powders. The

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non-equilibrium phases synthesized include super-saturated solid solutions, metastable crystalline, and quasicrystalline phases, nanostructures, and amorphous alloys (Suryanarayana, 2001).

SiC (Xie *et al.*, 1998; Yang *et al.*, 2001; Yamamoto *et al.*, 2004), BCN (Zhang *et al.*, 1999; Torres *et al.*, 2007), AlN (Du *et al.*, 1997; Xia *et al.*, 2005), and SiBCN (Yang *et al.*, 2007) powders have been fabricated by MA. However, work on the synthesis of SiBCNAl powders by solid-state reaction has not yet been reported. In the present paper, SiBCNAl powders were fabricated by MA, and then the consolidation of the powders was accomplished by hot pressing (HP) under different sintering atmospheres. Micro-structures of SiBCNAl powders and ceramics were characterized. Mechanical properties of the ceramics were also tested.

2 Experimental

Commercially available crystalline silicon (c-Si, 2.33 g/cm³, purity>99.5%), hexagonal boron nitride (h-BN, 2.28 g/cm³, purity>98%), graphite (C, 2.16 g/cm³, purity>99.9%), and aluminum (Al, 2.70 g/cm³, 99.9% purity) powders were used as starting materials for high-energy ball milling. The powders were mixed at the ratio of Si:BN:C:Al=1:0.5:1.5:0.3 to give a composition of SiB_{0.5}C_{1.5}N_{0.5}Al_{0.3} and then mechanically alloyed in a high-energy planetary ball mill (Fritsch Pulverisette 4, Germany) using silicon nitride (Si₃N₄) vials and silicon nitride balls (10 mm in diameter). MA was carried out with a ball-to-powder mass ratio (B/P) of 30:1 for 5 and 25 h, respectively. MA was done for 25 h in the following experiments if there is no special information. Transferring the powders into and from the vials was carried out in a glove box filled with pure (99.99%) argon.

SiBCNAl powders were consolidated by an HP technique at 1800 °C under a pressure of 30 MPa for 30 min in argon and nitrogen. The sintered samples are referred to hereafter as CA and CN, corresponding to their respective sintering atmospheres of argon and nitrogen.

The prepared ceramic samples were cut into bars of 2 mm×4 mm×20 mm (16 mm outer span) for fracture toughness testing with a crosshead speed of

0.05 mm/min. The fracture toughness was determined using the single edge notched beam method (SENB) and the depth of the notches was 2.0 mm and the width about 0.2 mm. The bar dimensions used for flexural strength testing were 3 mm×4 mm×25 mm (20 mm outer span) with a crosshead speed of 0.5 mm/min. Structural characterization of powders and ceramics was conducted using X-ray diffraction (XRD) methods with CuK α radiation. Microstructure investigation of bulk samples was carried out using a scanning electron microscope (SEM) (FEI Quanta 200F, USA) and a transmission electron microscope (TEM) (FEI Tecnai F30, USA) operated at 300 kV. High-resolution transmission electron microscopy (HRTEM) studies were performed by a TEM instrument (FEI Tecnai F30, USA).

3 Results and discussion

A set of experiments with different milling times was conducted to prepare amorphous SiBCNAl powders. The XRD patterns of SiBCNAl powders milled for different milling times (0, 5 and 25 h) are shown in Fig. 1. The diffraction peaks of BN, C, and Al disappear completely, while those of crystalline Si still exist beyond 5 h of milling. This indicates that amorphization of BN, C, and Al is easier than that of Si. When the milling time is up to 25 h, a halo peak, corresponding to an amorphous phase, is observed, and the sample can be considered as completely X-ray amorphous.

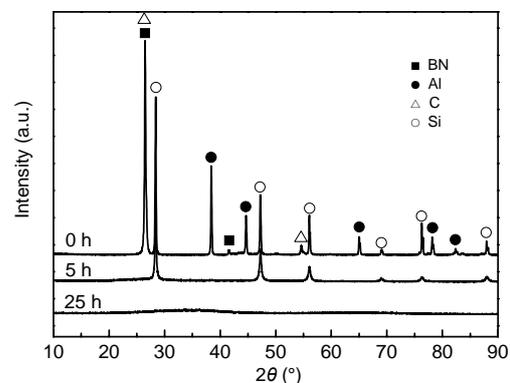


Fig. 1 X-ray diffraction patterns of SiBCNAl powders milled for different times

Fig. 2 shows a typical HRTEM image of SiBCNAI powder particles. A mass of observations on SiBCNAI powder particles by HRTEM show that the particles are completely amorphous and no nanocrystalline structure has been detected anywhere in the specimen, thus supporting the XRD results.

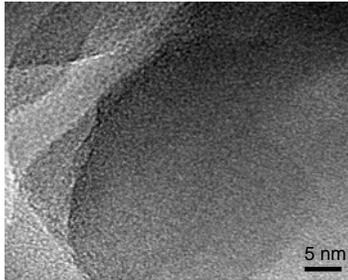


Fig. 2 High-resolution transmission electron microscopy image of SiBCNAI powder particles

Fig. 3 shows the XRD patterns of the bulk samples produced by HP of SiBCNAI powders in different sintering atmospheres. In two cases, clear diffraction peaks are observed, suggesting that most grains have recrystallized during the sintering process, while the broadening at the bottom of the diffraction peaks indicates the presence of some amorphous or nanocrystalline grains. It should be noted that the CA and CN ceramics have different phase compositions. 3C-SiC, AlN (PDF#700779), BCN, and AlON are the same phases for the CA and CN ceramics. In addition, the diffraction peaks of 4H-SiC and AlN (PDF#893446) appear only in the CN ceramics. Because 3C-SiC (β -SiC) is metastable and transforms at higher temperatures into one of the α -polytypes (Page, 1990), the appearance of 4H-SiC (α -SiC) in the CN ceramics is attributed to the transformation of 3C-SiC and the nitrogen atmosphere facilitates the process. AlN (PDF#893446) in the CN ceramics may be the results of reaction between Al powders used as starting material and nitrogen gas. Therefore, the sintering atmosphere has a great influence on phase compositions of the SiBCNAI ceramics.

SEM images of SiBCNAI ceramics are shown in Fig. 4. Figs. 4a and 4b show SEM images of polished surface of CA and CN, respectively. In two cases, the surfaces are level and non-porous suggesting the CA and CN ceramics are compact, and the microstructures are fine and homogeneous. There are no obvious grain boundaries between particles, which may be due to incomplete crystallization. SEM images of fracture

surface of CA and CN are shown in Figs. 4c and 4d, respectively. The microstructures of the fracture surfaces are different for CA and CN. Compared with the CA ceramics, lamellar crystallines are observed in the fractograph of the CN ceramics, the reason for which may be related to the sintering atmospheres of nitrogen which promoted crystallization of lamellar BCN.

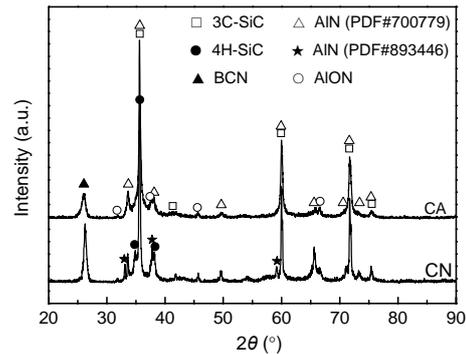


Fig. 3 X-ray diffraction patterns of the bulk samples produced by hot pressing of SiBCNAI powders in different sintering atmospheres

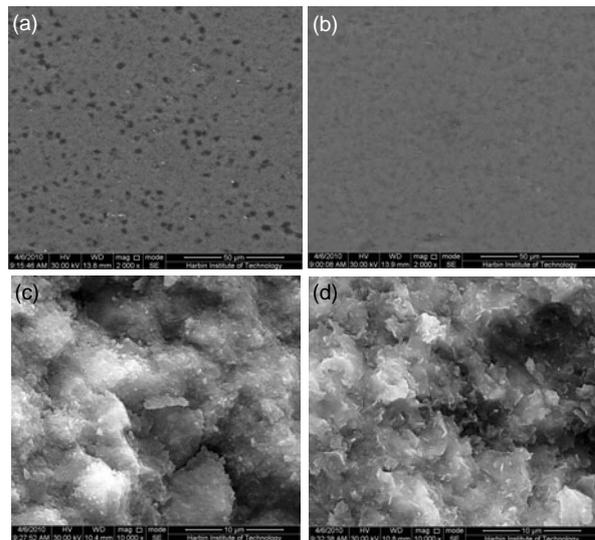


Fig. 4 SEM images of SiBCNAI ceramics (a) Polished surface of CA; (b) Polished surface of CN; (c) Fracture surface of CA; (d) Fracture surface of CN

Fig. 5 shows the TEM images of CA and CN ceramics. SiC and lamellar BCN phases are observed in Fig. 5a, which gives a typical microstructure image of CN. An HRTEM image of the interface between SiC and another phase is presented in Fig. 5b. A thin layer of amorphous phases was found at the interface. Amorphous phases at the interface may remain from the as-milled amorphous powders, so they should not

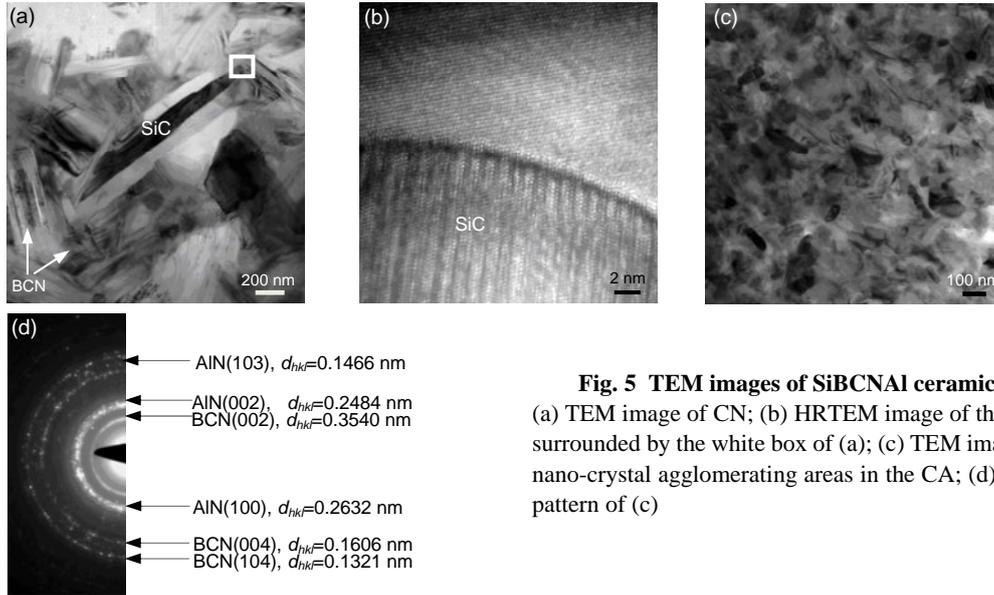


Fig. 5 TEM images of SiBCNAI ceramics
 (a) TEM image of CN; (b) HRTEM image of the area surrounded by the white box of (a); (c) TEM image of nano-crystal agglomerating areas in the CA; (d) SAD pattern of (c)

have an unfavourable effect on mechanical properties. There are some agglomerating areas of very small grains in the SiBCNAI ceramics, thus supporting the XRD results. Fig. 5c shows the TEM image of the nano-crystal agglomerating areas in the CA ceramics. Grain sizes of nano-crystal are smaller in the CA ceramics than in the CN ceramics. The corresponding selected area diffraction (SAD) pattern (Fig. 5d) indicated that phases in the agglomerating areas were mainly BCN and AlN.

Mechanical properties of the SiBCNAI ceramics are summarized in Table 1. It can be seen that CN has better mechanical properties than CA, except for the similar Vickers hardness. Flexural strength and elastic modulus of CN are 1.2 times larger than those of CA. Fracture toughness of CN is 1.5 times larger than that of CA. Because the densities of CA and CN are 2.77 and 2.90 g/cm³, respectively, the higher flexural strength for CN can be attributed to the larger relative density. And the ceramics which have a higher content of α -SiC have higher fracture toughness (Zhan *et al.*, 2001). Thus, the CN ceramics which involve 4H-SiC (α -SiC) show higher fracture toughness than the CA ceramics. Compared with the SiC ceramics (Table 1), the CN ceramics have higher flexural strength and fracture toughness, but the elastic modulus of the CN ceramics is only 54% of that of the SiC ceramics. The lower elastic modulus allows the CN ceramics to be more extensively applied at high temperatures.

Table 1 Mechanical properties of SiBCNAI and SiC ceramics

Sample	Flexural strength (MPa)	Elastic modulus (GPa)	Fracture toughness (MPa·m ^{1/2})	Vickers hardness (GPa)
CA	421.9±27.3	174.1±10.2	3.40±0.15	12.74±0.32
CN	526.8±10.4	222.1±27.7	5.25±0.20	11.63±0.49
SiC (Pan <i>et al.</i> , 1998)	450	410	4	—

4 Conclusions

SiBCNAI powders were prepared by an MA method, and the consolidation of the powders was subsequently accomplished by an HP technique at 1800 °C under a pressure of 30 MPa for 30 min in argon and nitrogen. The sintering atmosphere had a great influence on the microstructures and mechanical properties of ceramics. 3C-SiC, AlN (PDF#700779), BCN, and AlON are the same phases for the two ceramics, while 4H-SiC and AlN (PDF#893446) appear only in the ceramics sintered in nitrogen. Lamellar crystallines are observed in the fractograph of the ceramics sintered in nitrogen, but not in the ceramics sintered in argon. There are some nano-crystal agglomerating areas in the SiBCNAI ceramics. The ceramics sintered in nitrogen have better mechanical properties than those sintered in argon, except for the similar Vickers hardness.

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