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Fabrication and characterization of amorphous SiBCN powders

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Abstract

A new approach in the synthesis of amorphous SiBCN has been suggested using high-energy shaker ball mill. Hexagonal boron nitride (h-BN), graphite (C) and amorphous silicon (Si) were blended according to the mole ratio of 1:1:1, and then ball milled by different ball-to-powder mass ratio, diameter of ball and milling time. The structural evolution at different stages of milling has been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution electron microscopy (HREM) and electron energy-loss spectroscopy (EELS). The results showed that the SiBCN powders were mainly amorphous with some nanocrystlline phases. The thermal stability of SiBCN powders has been analyzed by thermogravimetry in argon. Mass loss occurred at high temperature, especially above 1000 °C.

Keywords: A. Powders: solid state reaction; B. Electron microscopy; C. Thermal properties; Si–B–C–N ceramics

1. Introduction

During the last few years, non-oxide ceramics, mainly in the system of SiBCN, derived from organo-elemented precursors has aroused ever increasing attention. These kinds of materials are prepared by thermolysis of pre-ceramic polymers at temperature of about 1100 °C [1–6]. The resulting ceramics are amorphous, free of sintering additives and exhibit outstanding high temperature stability [7–9] and superior mechanical properties [10–12]. But the synthesis and pyrolysis of precursors need to be done in inert gases, and the corresponding processes are very complicated and the starting materials are very expensive, so it is necessary to find other routes of synthesis for SiBCN powders and ceramics.

Ball milling-induced solid-state amorphization (SSA, or crystalline-to-amorphous phase transformation) has received considerable scientific attention because the combination of ball milling and subsequent consolidation may offer a way to produce technologically useful bulk amorphous materials [13,14]. Solid-state amorphization by mechanical alloying (MA) involves deformation at much high strain rate, cold welding, fragmentation and dynamic recrystallization [15]. For the microstructure produced by mechanical attrition, the strain and lattice disorder can be retained in highly metastable state [13]. As a result, the composition range for amorphization is usually much greater by mechanically driven processes than that by other techniques, such as rapid solidification.

Synthesis of nano-sized SiC [16–18] or amorphous BCN [19] powders through high-energy ball mill using Si and C or BN and C as starting materials has been reported recently. However, work on the synthesis of Si–B–C–N powders by solid-state reaction has not been reported yet. Thus, a new more efficient way of fabricating amorphous SiBCN powders has been suggested in this paper.

2. Experimental procedure

Commercially available hexagonal boron nitride (h-BN, ca. 0.6 μm, >98% pure), graphite (C, ca. 10 μm, >99.9% pure) and amorphous silicon (a-Si, ca. 15 μm, 99.8% pure) powders were used as starting materials for ball milling. The powders were blended in a 1:1:1 mole ratio and then ball milled in a shaker miller using zirconia balls (10, 8 and 6 mm in diameters) and zirconia vials with an inside diameter of 60 mm and height of 80 mm. In the following experiments, without special notification, mechanical alloying was done by the balls with a diameter of 10 mm. The MA was carried out with a ball-to-powder mass ratio (B/P) of 10:1, 20:1, 40:1, 60:1 and 100:1 for 1–30 h, respectively. After each hour, the milling was stopped for 10 min. All transfers of powders to and from the vials were

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done in a glovebag filled with pure (99.99%) argon. The vial was then sealed and transferred to a shaker mill. The shaking cycle of vial was about 700/min.

The structural characterization of powders was analyzed using X-ray diffraction (XRD) methods with Cu Kα radiation. Particle morphology observation was performed on a JEM-1200EX transmission electron microscope (TEM). The results of the XRD-analysis concerning amorphization were verified by high-resolution electron microscopy (HREM) using a JEOL-2010 HREM instrument operated at 200 kV, selected area diffraction (SAD) and electron energy-loss spectroscopy (EELS). Thermogravimetric analysis (TGA) of the powders was performed in an Al_2O_3 crucible (STA-449C, Netzsch) from room temperature to 1500 °C at heating rates of 10 °C/min in argon.

3. Results and discussion

In an attempt to prepare amorphous Si–B–C–N powders, a set of experiments with different milling time was conducted. Fig. 1(a) shows the XRD patterns of Si–B–C–N powders milled with ball-to-powder mass ratios of 20:1 for different milling time. It is indicated that the diffraction peaks of BN and C gradually decrease in intensity and increase in width to finally disappear beyond 5 h of milling. The center of broad peaks shifted and broadened with the increase of milling time. But for Si–B–C–N powders milled with ball-to-powder mass ratios of 60:1, the peak of ZrO_2 appeared when the milling time up to 20 h (as shown in Fig. 1(b)).

X-ray diffraction patterns of samples milled for 10 h with different ball-to-powder mass ratio and varied diameters of milling balls are shown in Fig. 2. These XRD patterns indicate that as the ball-to-powder mass ratio increases the milling efficiency in reducing particle size, introducing internal strains and enhancing microstructural evolution and increasing reactions, as suggested by the broadening and shifting of the peaks with the increases in the ball-to-powder mass ratio (as shown in Fig. 2(a)). But the contamination from the milling media (ZrO_2) simultaneously increases.

Fig. 2(b) shows the X-ray diffraction patterns of BN, C and Si powder mixture milled with a ball-to-powder mass ratio of 20:1 using varied diameters of milling balls (6, 8 and 10 mm). The diffraction peak had the lowest intensity for SiBCN powder milled by balls whose diameter is 8 mm. It is obvious that balls with 8 mm in diameter balls have the greatest milling efficiency.

The TEM images of BN, Si and C powder mixtures milled with a ball-to-powder mass ratio of 20:1 for different milling times are shown in Fig. 3. It is generally known that the

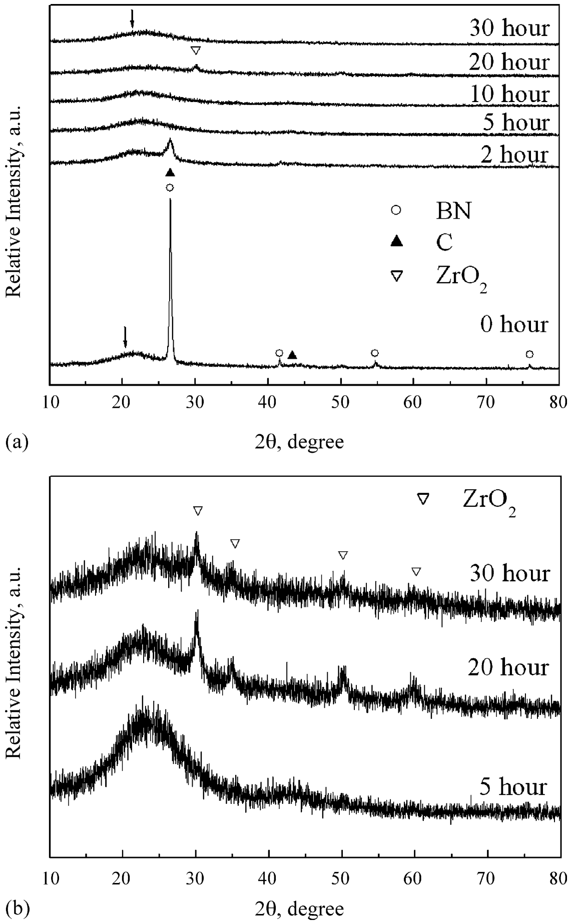

Fig. 1. XRD patterns of the powder milled for different times with a charge of (a) 20:1 and (b) 60:1.

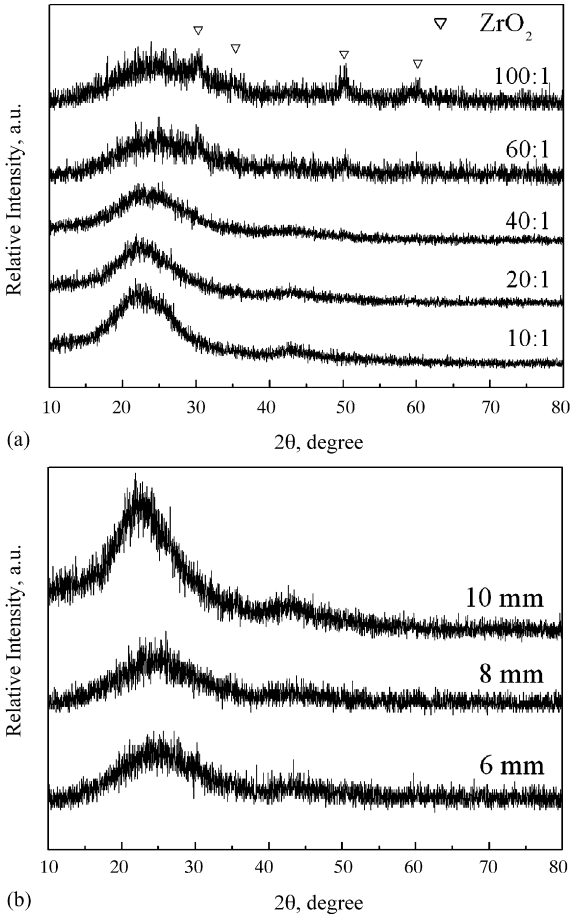

Fig. 2. XRD patterns of the powder mixture milled for 10 h with (a) different ball-to-powder mass ratio and (b) using balls in different diameters.

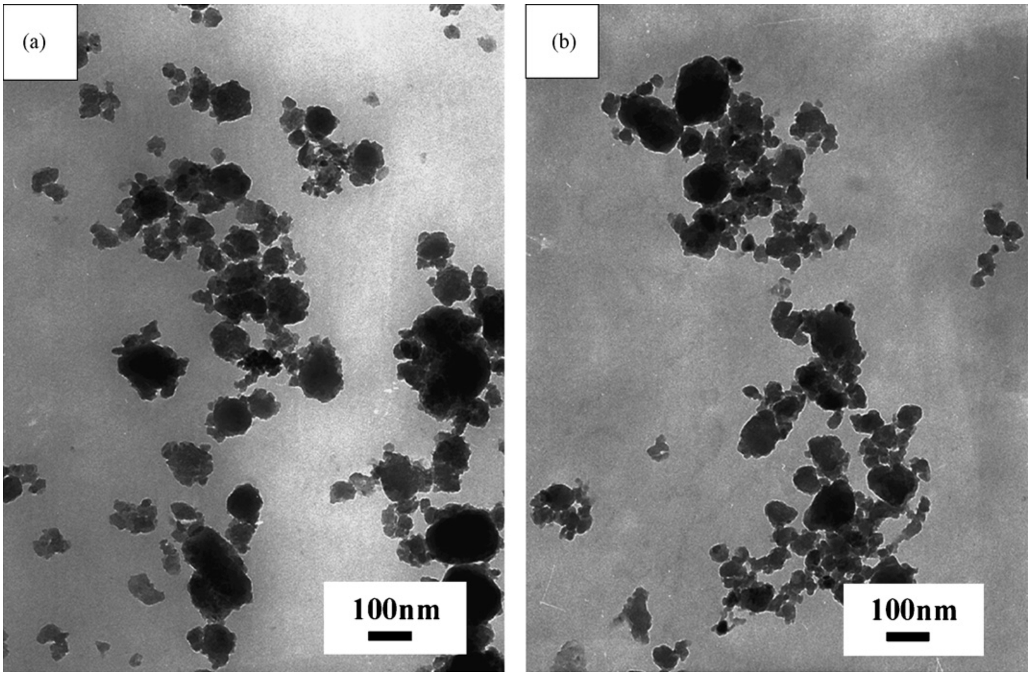

Fig. 3. TEM images of the powder mixtures milled with a ball-to-powder mass ratio of 20:1 for (a) 10 h and (b) 30 h.

mechanical alloy process reaches a steady state where the particles have homogeneous size and shape when the milled time up to a certain time. So as shown in the TEM images, the powder particle sizes changed little with further increase of milling time. It should be noted that the small particles and the edge of the large particle of the bright-field images are featureless, suggesting that these small particles and the edge of large particle might be amorphous.

Fig. 4 shows the high-resolution electron microscope image and the corresponding SAD patterns of SiBCN powders milled with a ball-to-powder mass ratio of 100:1 for 10 h. It is evident that the microstructure of the edge of powder is predominantly amorphous with a small volume fraction of nanocrystalline structure (as shown with the arrow in Fig. 4(a)). The broad and diffused halo ring (inset of Fig. 4(a)) indicates the main phase of edge of powder being amorphous. The edge of powder presents the sheet-like microstructure.

The microstructure reveals a typical amorphous + nanocrystalline composite aggregate in the center of SiBCN powders, but the number of nanocrystalline composite aggregate is a few. Fig. 4(b) shows the microstructure consists of some very fine crystallites (about 4–5 nm) embedded in amorphous matrix. The

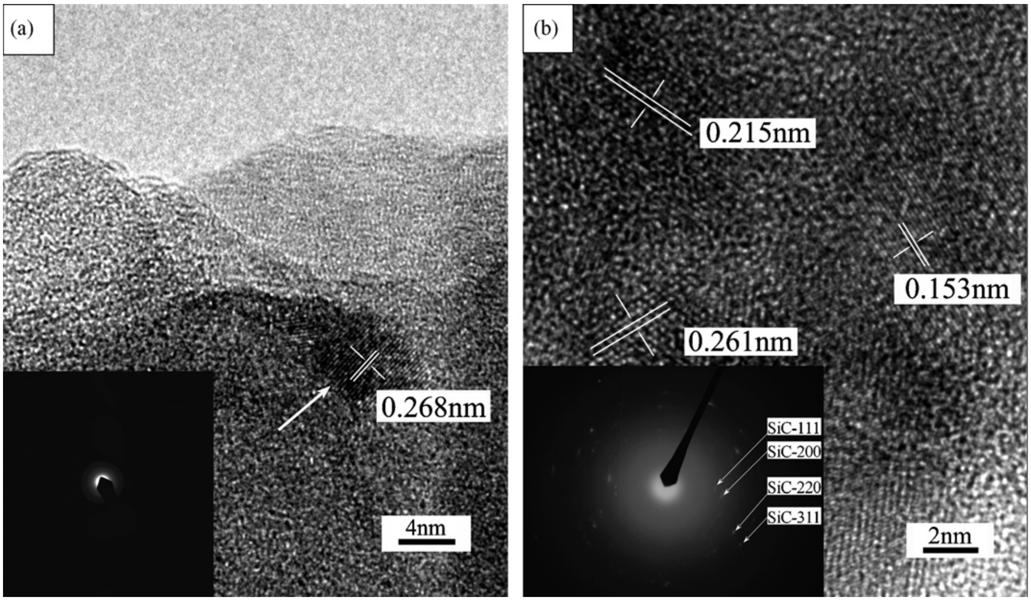

Fig. 4. HREM images and the corresponding SAD patterns of SiBCN powders milled with a ball-to-powder mass ratio of 100:1 for 10 h. (a) The edge of powder and the SAD pattern of amorphous structure; (b) the center of powder and the SAD pattern of crystalline structure.

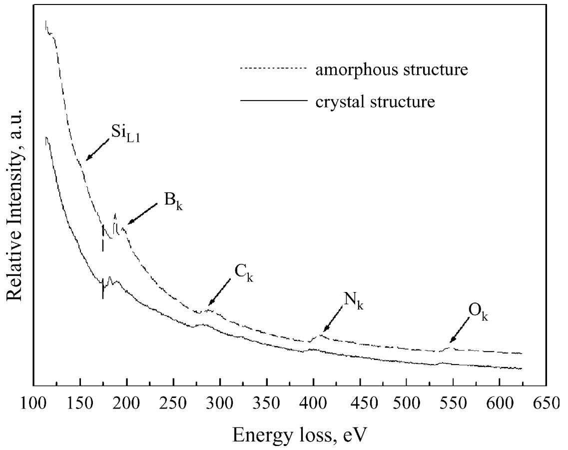

Fig. 5. EELS curves obtained from amorphous and crystal structures in SiBCN powder.

SAD pattern obtained from nanocrystalline composite is shown in Fig. 4(b), where several diffraction halos and spots can be seen despite faint diffraction. The SAD pattern reveals nanocrystalline composites mainly contain β-SiC (inset of indicates Fig. 4(b)), and few diffraction spots cannot distinguish through crystallographic data of SiC, Si_3N_4, B_4C, BN and BCN, indicating that the diffraction spots may arise from a or some non-equilibrium phase.

EELS spectra were recorded during HREM characterization to confirm the compositional elements of the SiBCN powders. Spectra were obtained using a probe beam with a diameter of 2.4 nm. Typical EELS spectrums for the amorphous and crystal structures are shown in Fig. 5. It reveals the expected distinct Si–L_1, B–K, C–K, N–K and O–K edge structures in the both of amorphous and crystal structures. This suggests that the Si, B, C and N are mixed at the level of atom and to form SiBCN ceramic powders. The appearance of oxygen may be caused by the preparation of sample that was exposed to the air for about 15 h.

The present experimental data clearly indicate that the amorphization of SiBCN powders enhanced by long milling time and large ball-to-powder mass ratios. To avoid contamination of ZrO_2, the optimum milling parameters are: charge ratio being 20:1, milling time being 20 h and the diameter of ball being 8 mm.

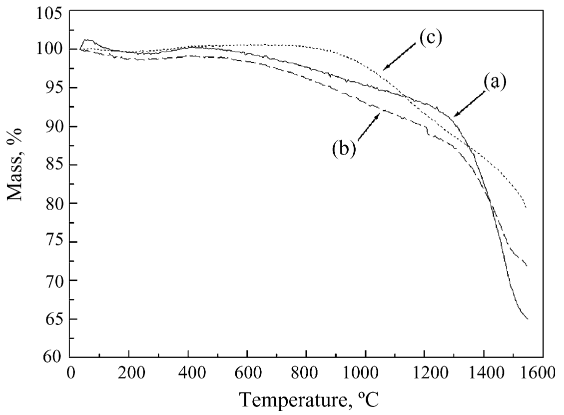

Fig. 6. Thermal stabilities of SiBCN powders at high temperature in argon.

The thermal stability of SiBCN powders was analyzed by thermogravimetric analysis. As shown in Fig. 6, the mass loss happened at high temperature for three SiBCN powders, especially above 1000 °C. But the mass losses of powders abated with increase of ball-to-powder mass ratio and milling time. BN and C have high melting point and cannot decompose below 2000 °C. But the melting point of element Si is 1423 °C, and the melting point will decrease with the decrease of dimension of Si powder. So the mass loss of SiBCN powders should be attributed to the volatilization of Si. The volatilization of Si may be explained by two reasons. One reason is that partial element Si existed in the SiBCN powders, because graphite and h-BN have similar diagrams, so the graphite may be easier to form BCN solid solution with BN than to form SiC with Si. The other reason is that the chemical bond of Si–C is weak and leads to break of bond during high temperature.

4. Conclusion

From the present study, it appears that amorphous SiBCN powders were fabricated by high-energy ball mill using C, h-BN and amorphous Si and elements of Si, B, C and N compounded at atom level. Large ball-to-powder mass ratios and long milling time enhance the formation of amorphous SiBCN powders, but the over many ball-to-powder mass ratios and overtime milling time lead to the contamination of milling ball. The SiBCN powders were mainly amorphous, and some nanocrystlline SiC and other crystals lied in the amorphous matrix. The thermal stabilities of SiBCN powders were not good, and the loss of mass happened at high temperature in argon, especially above 1000 °C.

Reference

[1] Zhi Chang Wang, Peter Gerstel, Gerhard Kaiser, Joachim Bill, Fritz Aldinger, Synthesis of ultrahigh-temperature Si–B–C–N ceramic from polymeric waste gas, J. Am. Ceram. Soc. 88 (10) (2005) 2709–2712.

[2] Ralf Riedel, Wolfgang, Dressler, Chemical formation of ceramics, Ceram. Int. 22 (1996) 233–239.

[3] H. Schmidt, G. Borchadt, S. Weber, H. Scherrer, H. Baumann, A. Muller, J. Bill, Comparison of ^{30}Si diffusion in amorphous Si–C–N and Si–B–C–N precursor-derived ceramics, J. Non-Cryst. Solids 298 (2002) 232–240.

[4] Joachim Bill, W. Thomas, Kamphowe, Anita Muller, Thomas Wichmann, Achim Zern, Precursor-derived Si–(B–)C–N ceramics: thermolysis, amorphous state and crystallization, Appl. Organomet. Chem. 15 (2001) 777–793.

[5] W.R. Schmidt, D.M. Narsavage-Heald, D.M. Jones, P.S. Marchetti, D. Raker, G.E. Maciel, Poly(borosilazane) precursors to ceramic nanocomposites, Chem. Mater. 11 (6) (1999) 1455–1464.

[6] Jörg Haberecht, Reinhard Nesper, Hansjörg Grűtzmacher, A construction kit for Si–B–C–N ceramic materials based on borazine precursors, Chem. Mater. 17 (9) (2005) 2340–2347.

[7] Ralf Riedel, Andreas Kienzle, Wolfgang Dressler, Lutz Ruwisch, Joachim Bill, Fritz, Aldinger, A silicoboron carbonitride ceramic stable to 2000 °C, Nature 382 (29) (1996) 796–798.

[8] Narayanan Janakirarnan, Markus, Weinmann, Jörg Schuhmacher, Klaus Műller, Joachim Bill, Fritz Aldinger, Paramanand Singh, Thermal stability, phase evolution, and crystallization in Si–B–C–N ceramics derived from a polyborosilazane precursor, J. Am. Ceram. Soc. 85 (7) (2002) 1807–1814.

[9] Anita Muller, Achim Zern, Peter Gerstel, Joachim Bill, Fritz, Aldinger, Boron-modified poly(propenysilazane)-derived Si–B–C–N ceramics: preparation and high temperature properties, J. Eur. Ceram. Soc. 22 (2002) 1631–1643.

[10] Ralf Riedel, M. Lutz, Ruswisch, Linan An, Rishi Raj, Amorphous siliconboron carbonitride ceramic with very high viscosity at temperatures above 1500 °C, J. Am. Ceram. Soc. 81 (12) (1998) 3341–3344.

[11] Martin Christ, Günter Thurn, Markus Weinmann, Joachim Bill, Fritz, Aldinger, High-temperature mechanical properties of Si–B–C–N-precursor-derived amorphous ceramics and the applicability of deformation models developed for metallic glasses, J. Am. Ceram. Soc. 83 (12) (2000) 3025–3032.

[12] Martin Jansen, Britta Jäschke, Thomas, Jäschke, Amorphous multinary ceramics in the Si–B–N–C systems, Struct. Bond. 101 (2002) 138–191.

[13] D.L. Zhang, Processing of advanced materials using high-energy mechanical milling, Prog. Mater. Sci. 49 (2004) 537–560.

[14] Y.H. Zhao, Y.T. Zhu, T. Liu, Mechanism of solid-state amorphization of Se induced by mechanical milling, J. Appl. Phys. 95 (12) (2004) 7674–7680.

[15] I. Manna, P. Nandi, B. Bandyopadhyay, K. Ghoshray, A. Ghoshray, Microstructural and nuclear magnetic resonance studies of solid-state amorphization in Al–Ti–Si composites prepared by mechanical alloying, Acta Mater. 52 (2004) 4133–4142.

[16] X.Y. Yang, Z.W. Huang, Y.K. Wu, H.Q. Ye, HREM observations of the synthesized process of nano-sized SiC by ball milling of Si and C mixed powders, Mater. Sci. Eng. A 300 (2001) 278–283.

[17] Xiangqun Xie, Zhenguo Yang, Ruiming Ren, L. Leon, Shaw, Solid state ^{29}Si magic angle spinning NMR: investigation of bond formation and crystallinity of silicon and graphite powder mixtures during high energy milling, Mater. Sci. Eng. A 255 (1998) 39–48.

[18] Takeshi Yamamoto, Hidetoshi Kitaura, Yasuhiro Kodera, Takashi Ishii, Manshi Ohyanagi, Zuhair, A. Munir, Consolidation of nanostructured b-SiC by spark plasma sintering, J. Am. Ceram. Soc. 87 (8) (2004) 1436–1441.

[19] B. Yao, L. Liu, W.H. Su, Formation, characterization, and properties of a new boron–carbon–nitrogen crystal, J. Appl. Phys. 86 (5) (1999) 2464–2467.