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Influence of ball milling parameters on the structure of the mechanically alloyed SiBCN powder

Pengfei Zhang*, Dechang Jia, Zhihua Yang, Xiaoming Duan, Yu Zhou

Institute for Advanced Ceramics, Harbin Institute of Technology, Harbin 150080, China

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Abstract

SiBCN powders were prepared by an improved mechanical alloying technique, using cubic silicon, graphite and hexagonal boron nitride powders as raw materials. The influences of ball milling parameters on the structures and the particle size distribution of the prepared powders were carefully studied by XRD, HRTEM, EFTEM and particle-size analysis. Results show that well amorphized SiBCN powder can be prepared when the rotation speed of the vials is between 600 and 800 rpm, the ball-to-powder mass ratio is larger than 20:1, and the milling time is longer than 20 h. A higher rotation speed and a larger ball-to-powder mass ratio may enhance the power input into the powder, and hence facilitate the formation of SiC crystallites. While a longer milling time has little influence on the powder microstructure, it promotes the reaction between silicon and carbon atoms. The optimized ball milling parameters are 600 rpm, 20:1, 30 or 40 h, respectively. The prepared SiBCN powders mainly consist of near-spherical agglomerates, 4.6–5.3 μm in the average particle size. The particle size distribution of these powders is slightly affected by the variation of ball milling parameters.

Keywords: Mechanical alloying; SiBCN powder; Microstructure; Particle size distribution

1. Introduction

SiBCN ceramics have attracted great attention in recent years, mainly due to their high structural, mechanical and chemical stabilities at elevated temperatures [1]. These ceramics normally have amorphous structures at 1100–1400 °C [2], and they may change into nanoceramics when they are annealed at higher temperatures in inert atmosphere [3]. These ceramics generally possess high oxidation or creep resistance [4,5], high hardness [6], low internal stress [7], high electronic resistance and some luminescence properties [8]. Currently, the methods used for the preparation of SiBCN ceramics mainly include the organic polymer pyrolyzing route [9], the mechanical alloying plus hot pressing method [10], ion implantation [7], physical vapor deposition (PVD) and thermal plasma chemical vapor deposition (TPCVD) [6,11]. The mechanical alloying plus hot pressing method is studied in recent years for the fabrication of dense bulk SiBCN ceramics with large dimensions. This method uses cheap and nontoxic raw materials, has a simple preparation process, and causes much less pollution, as compared with the polymer pyrolyzing route. At present, the preparation of SiBCN ceramics by the mechanical alloying plus hot pressing method is still in its infancy, and much work needs to be carried out to optimize technical parameters, overcome disadvantages, and improve product quality. Recently, great progress has been made in these areas. For example, well amorphized SiBCN powder free from zirconia contamination and a nanoceramic with small grains have been successfully prepared [12,13]; the crystallization and the microstructural evolution process from the amorphous SiBCN powder to the nano-SiC/BN(C) ceramic have also been carefully studied [10].

It is known that ball milling parameters, such as the rotation speed of vials, the ball-to-powder mass ratio and the milling time, may greatly affect powder characteristics, which in turn may have a strong influence on the compressibility, the sinterability and the sintered microstructure of the powder compact. Since vibratory milling did not work well in the

*Corresponding author. Tel.: +86 451 86402040x8501; fax: +86 451 86414291.
E-mail address: zhangpengfei1984@163.com (P. Zhang).

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amorphization of raw powders, and a little zirconia impurity was often introduced into the powder from vials and balls [14], a planetary ball mill, together with high-quality silicon nitride vials and balls, was used in the recent research to overcome these shortcomings [12,13]. Therefore, the optimization of ball milling parameters and the characteristics of the prepared powders need to be re-examined. These areas have been carefully investigated in our recent work, and the surface characteristics of the prepared SiBCN powder have been discussed in detail in another research article [12]. This paper focuses on the influence of ball milling parameters on the microstructures and the particle size distribution of as-milled powders.

2. Powder preparation and structural analysis method

In the current work, commercially available cubic silicon, graphite and hexagonal boron nitride powders were used as raw materials. The manufacturers, the average particle size and the purity of these powders have been described in detail in other research articles [12,13]. For an effective amorphization of these raw powders and to reduce oxide impurity as much as possible, the current work adopts a planetary ball mill (P4, Fritsch GmbH, Germany), together with high-quality silicon nitride vials and balls. The chemical composition was set as Si:C:BN = 2:3:1, and the milling process was protected by the argon atmosphere. The rotation speed of the main disk was set as 350 rpm, that of vials as 400, 600, 800 and 1000 rpm, the ball-to-powder mass ratio as 15:1, 20:1, 30:1 and 40:1, and the milling time as 15, 20, 25, 30 and 40 h. When the influence of a certain parameter was studied, the other two parameters were fixed as constants. The microstructures of the prepared powders were studied by the X-ray diffraction spectrum (XRD, 40 kV/100 mA, D/max-γB CuK$_\alpha$, Rigaku Corp., Japan) and a transmission electron microscope (HRTEM and EFTEM, Tecnai G^2 F30, 300 kV, FEI Co., USA). The particle size distribution was analyzed by a laser scattering particle-size analyzer (LA-920, Horiba Comp., Japan).

3. Results and discussion

3.1. Influence of ball milling parameters on microstructures of prepared SiBCN powders

Fig. 1(a) shows the XRD spectra of the SiBCN powders prepared under different rotation speeds of vials. It is found that the rotation speed greatly affects the microstructure of the prepared powder. When raw powders are milled for 20 h under the rotation speed of 400 rpm, h-BN and graphite powders are in amorphous states. However, crystalline silicon still exists, indicating that the amorphization of cubic silicon is relatively difficult. When the rotation speed is set as 600 or 800 rpm, the prepared powders are effectively amorphous. However, when the rotation speed is increased to 1000 rpm, the XRD spectrum of the prepared powder contains weak diffraction peaks of silicon carbide, implying the existence of SiC crystallites. It is known that mechanical alloying is characterized by fierce collisions and great mechanical energy, which may promote the formation of alloys or compounds during the ball milling process. At the rotation speed of 1000 rpm, silicon atoms are most likely to react with carbon atoms, leading to the formation of SiC crystallites. Since there is a hope to prepare SiBCN powder with a well amorphized structure, the rotation speed of vials should be neither too low nor too high. On the other hand, when raw powders are milled under 1000 rpm, it is found that the used balls are greatly damaged and lots of pits appear on their surfaces. Therefore, such a high rotation speed may cause heavy wear to balls and severe contamination to the powder, so it should not be adopted. Fig. 1(b) and (c) shows the XRD spectra of the SiBCN powders prepared under different ball-to-powder mass ratios and different milling times, respectively. It is found that when the ball-to-powder mass ratio is larger than 20:1, or the milling time is longer than 20 h, all of the prepared powders are in well amorphized states. In the following paragraphs, these amorphous powders will be carefully studied by HRTEM.

Figs. 2–4 display the HRTEM images of the amorphous SiBCN powders prepared under different milling conditions. The image shown in Fig. 2(a) indicates that the powder prepared under the rotation speed of 600 rpm has a well amorphized structure, and it is hard to find any nanocrystallites under HRTEM. However, when the powder is milled under 800 rpm, nano-SiC crystallites can be easily found. It appears that a higher rotation speed of vials indeed facilitates the formation of SiC crystallites. To prepare SiBCN powders with well amorphized structures and to reduce wear as much as possible, 600 rpm is adopted as an appropriate rotation speed in the current research. Fig. 3 shows the microstructures of the amorphous SiBCN powders prepared under different ball-to-powder mass ratios. It is found that when the ball-to-power mass ratio is set as relatively small values, for example, 20:1, SiC crystallites are scarce in the as-milled powder. However, when the ball-to-powder mass ratio is increased to 40:1, SiC crystallites with the sizes of 10 nm or so are rather common. It follows that a larger ball-to-powder mass ratio may also promote the formation of SiC crystallites, just like the function of higher rotation speed of vials. It is generally accepted that both higher rotation speed of vials and larger ball-to-powder mass ratio may enhance the energy input into the powder per unit time, and this may be an important reason why SiC crystallites are common in the powders prepared under such conditions.

Since prolonging milling time cannot change the power input into powder, the SiBCN powders prepared under different milling times may have similar microstructures, and the crystallite content in the prepared powders may have little variation. The inference is confirmed by the

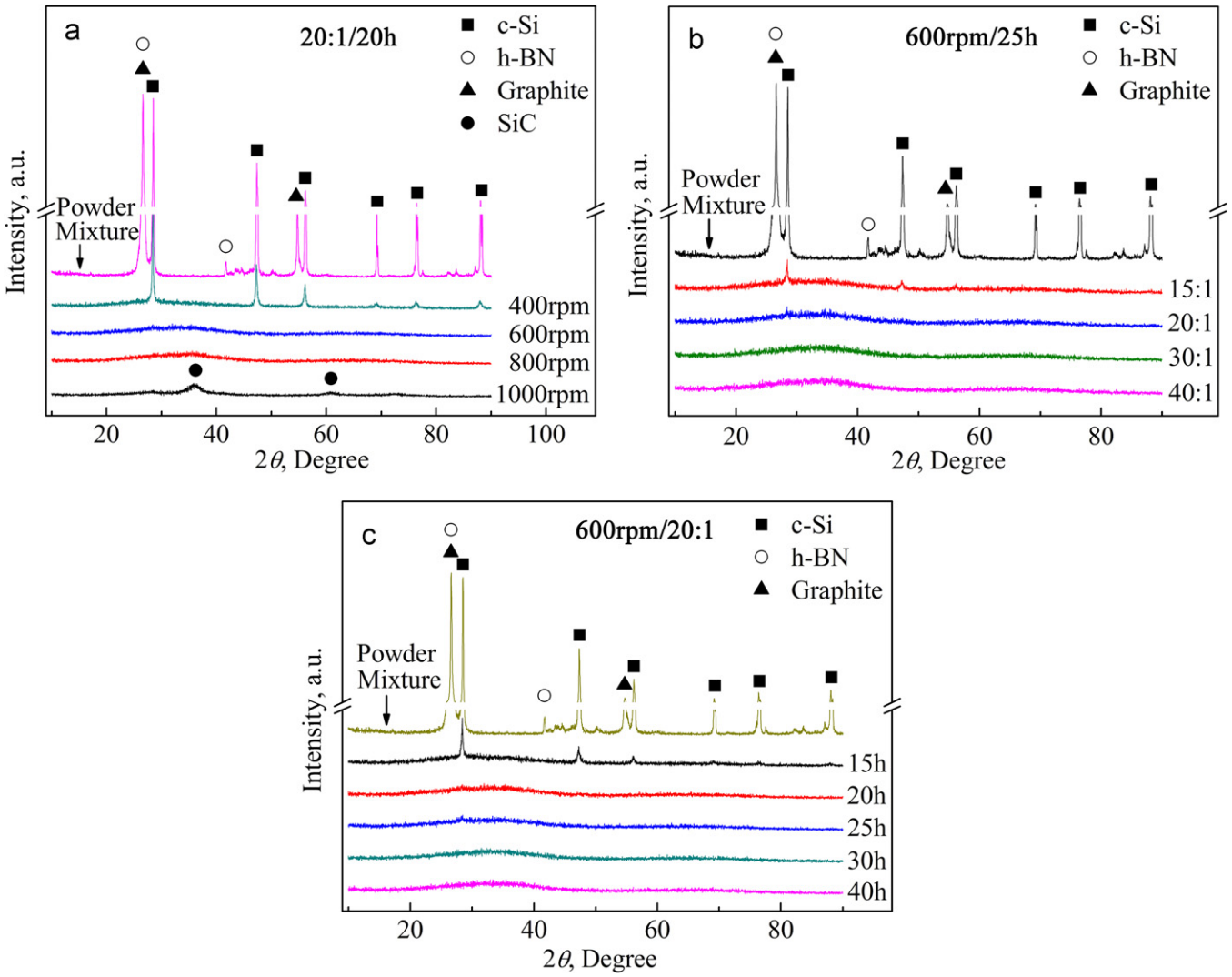

Fig. 1. The XRD spectra of the mechanically alloyed SiBCN powders prepared under different rotation speeds of vials (a), different ball-to-powder mass ratios (b), and different milling times (c). When the influence of a certain parameter is studied, the other two parameters are fixed as constants, as shown by the note in each subfigure.

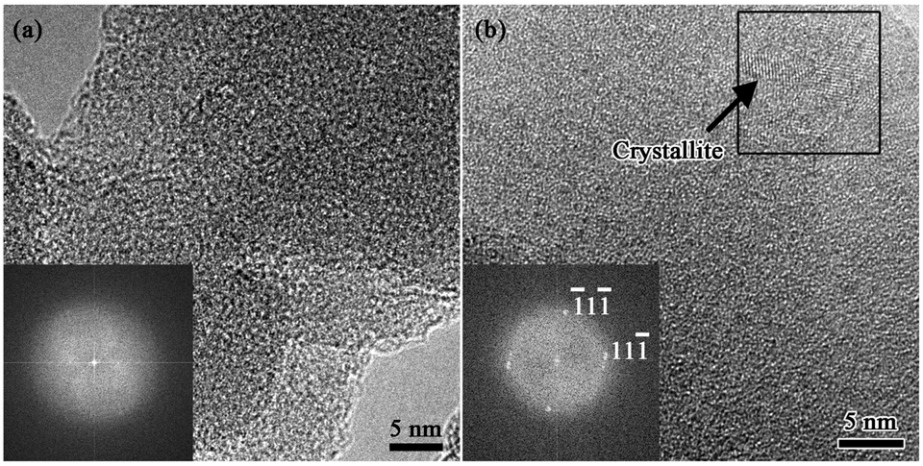

Fig. 2. The microstructures of the SiBCN powders prepared under the rotation speed of 600 rpm (a), and 800 rpm (b), observed under HRTEM. The ball-to-powder mass ratio and the milling time are fixed as 20:1 and 20 h, respectively.

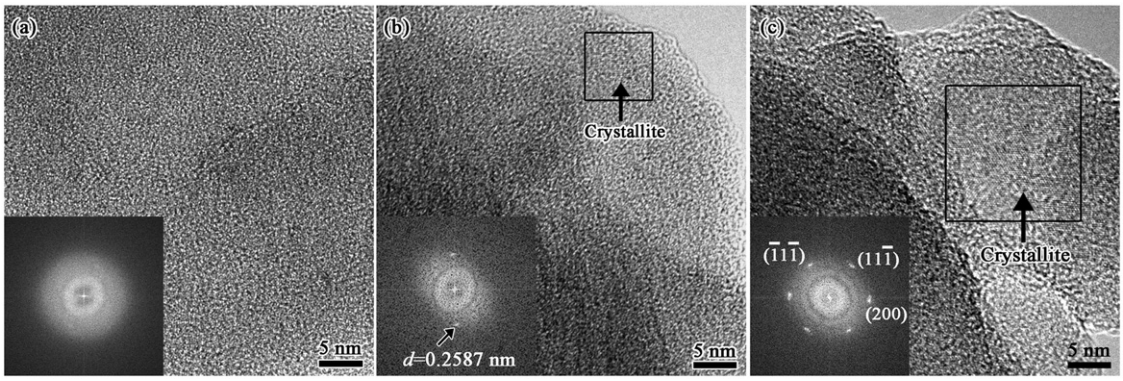

Fig. 3. The microstructures of the SiBCN powders prepared under the ball-to-powder mass ratio of 20:1 (a), 30:1 (b), and 40:1 (c), observed under HRTEM. The rotation speed of vials and the milling time are fixed as 600 rpm and 25 h, respectively.

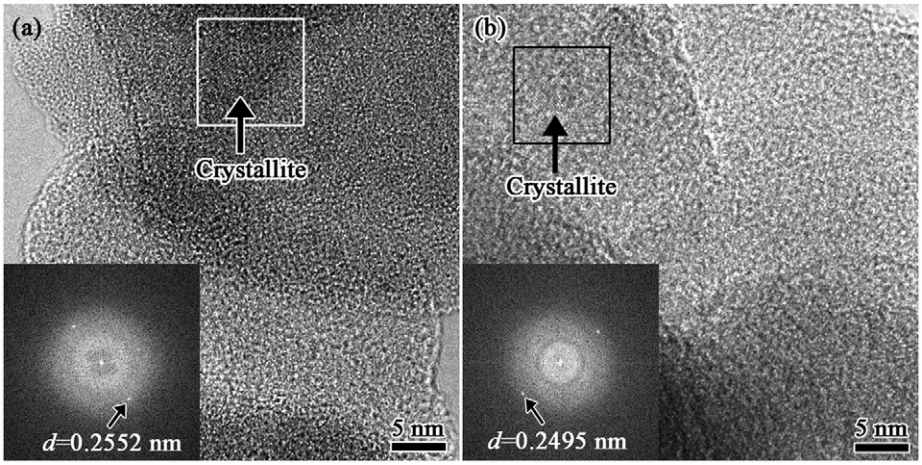

Fig. 4. The microstructures of the SiBCN powders prepared under the milling time of 30 h (a), and 40 h (b), observed under HRTEM. The rotation speed of vials and the ball-to-powder mass ratio are fixed as 600 rpm and 20:1, respectively.

HRTEM images shown in Fig. 4. When raw powders are milled for 30 or 40 h, nano-SiC crystallites appear in the as-milled powders. However, the crystallite quantity is small and it is relatively difficult to find them under HRTEM. Compared to the microstructure of the powder prepared for 20 or 25 h, as shown in Figs. 2 and 3(a), it is found that the variation of milling time indeed has little influence on the quantity and the sizes of SiC crystallites. However, the images shown in Fig. 5 indicate that the change of milling time may affect the reaction between silicon and carbon atoms. In the EFTEM images of the prepared powders, the green area represents the distribution of silicon atoms and the color depth stands for their bonding states. In the image shown in Fig. 5(a), the existence of a light green area indicates that the silicon in the as-milled powder may exist as a simple substance. In other words, when raw powders are milled for 25 h, they may just change into amorphous bodies, while the reactions between different elements may be scarce. When the milling time is extended to 40 h, the color of the silicon-existing area changes into dark green, indicating that most silicon atoms may be bonded with carbon atoms and they exist in Si–C bonds. This shows that when raw powders are milled for 40 h, they may not only change into amorphous bodies, but reactions may occur between silicon and carbon atoms. Since the reactions between different elements are helpful for the chemical and structural stability of SiBCN powders, a longer milling time may be favorable for the preparation of SiBCN powder with a higher thermal stability. Therefore, the appropriate milling time is adopted as 30 or 40 h.

The above results and discussion reveal that well amorphized SiBCN powders can be prepared when the rotation speed of vials is between 600 and 800 rpm, the ball-to-powder mass ratio is larger than 20:1, and the milling time is longer than 20 h. Actually, the key factor affecting the powder microstructure is most likely the input power, that is, the energy input into the powder per second. A higher rotation speed of vials or a larger ball-to-powder mass ratio may increase the collision frequency or the collision strength between powder particles, and may hence enhance the input power. As a result, the formation of SiC crystallites is relatively easy under such conditions. However, the input power is difficult to change by altering milling time, and thus SiC crystallites

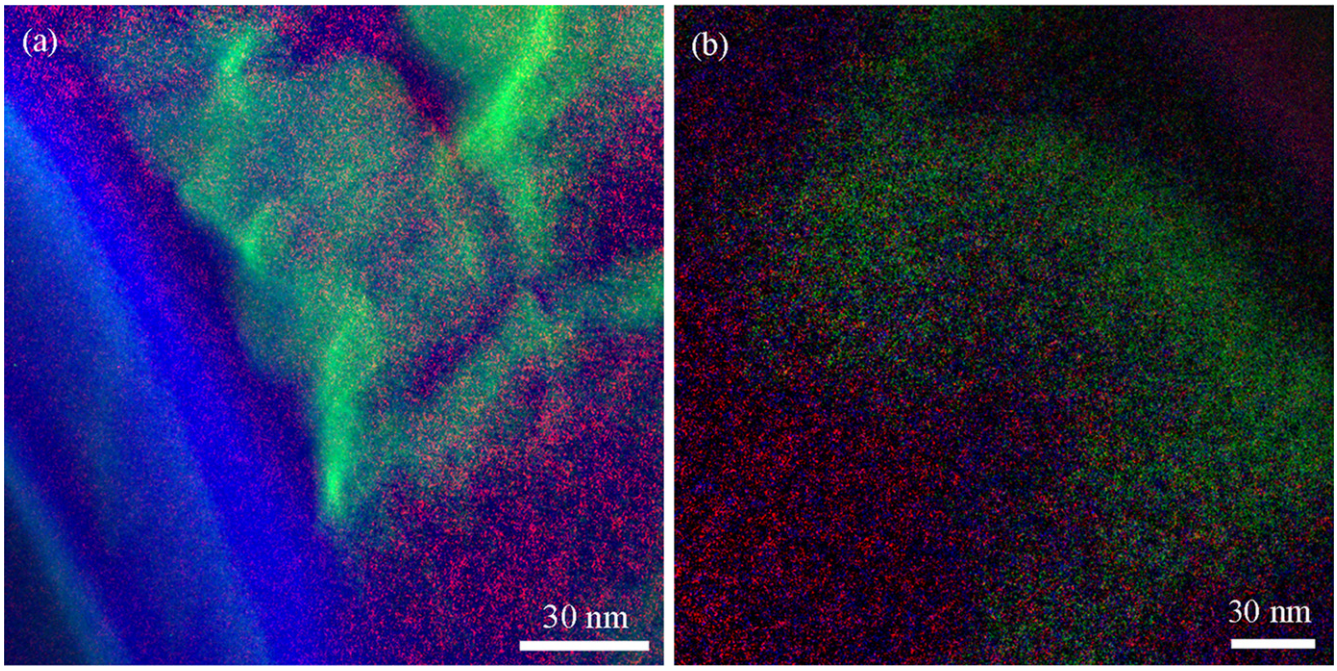

Fig. 5. EFTEM images of the SiBCN powders prepared under the milling time of 25 h (a), and 40 h (b). The rotation speed of vials and the ball-to-powder mass ratio are fixed as 600 rpm and 20:1, respectively. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

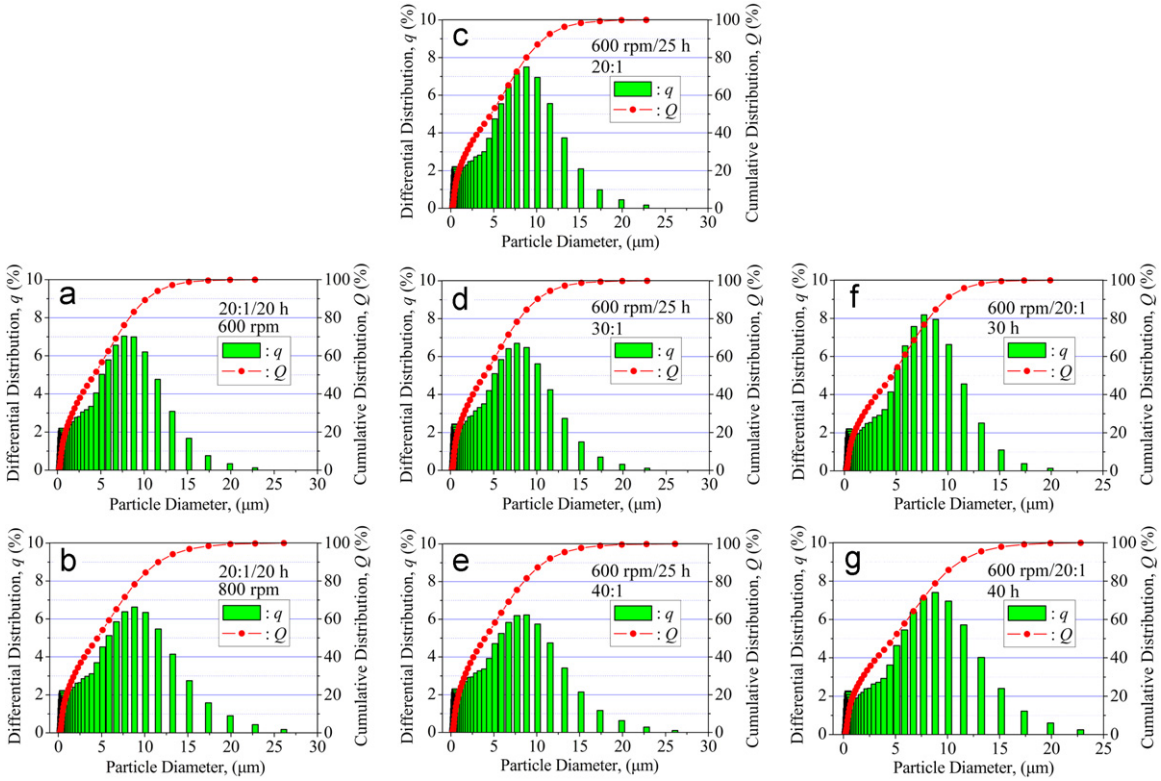

Fig. 6. The particle size distribution of the SiBCN powders prepared under different milling conditions (a) and (b), under the rotation speed of 600 and 800 rpm, respectively; (c), (d) and (e), under the ball-to-powder mass ratio of 20:1, 30:1 and 40:1, respectively; (f) and (g), under the milling time of 30 and 40 h, respectively. When the influence of a certain parameter is studied, the other two parameters are fixed as constants, as shown by the note in each subfigure.

are scarce when the milling time is extended even to 40 h. While a longer milling time slightly affects the powder microstructure, it promotes the reactions between silicon and carbon atoms. Therefore, a relatively lower rotation speed of vials, a smaller ball-to-powder mass ratio and a longer milling time may be favorable for the preparation of

SiBCN powder by the current method. Additionally, a lower rotation speed may reduce the wear of balls and vials, and a smaller ball-to-powder mass ratio may produce a higher powder yield. As a result, the optimized ball milling parameters are 600 rpm, 20:1, and 30 or 40 h, respectively.

3.2. Influence of ball milling parameters on particle size distribution of prepared SiBCN powders

Fig. 6 shows the particle size distribution of the SiBCN powders prepared under different rotation speeds of vials, different ball-to-powder mass ratios or different milling times. It is found that the average particle size of these powders is about 4.6–5.3 μm; the median particle size is about $d_{50\%} \approx 4.0$–5.0 μm; and approximately 90% of these powder particles are smaller than 11.0 μm. The variation of ball milling parameters has little influence on these data. Fig. 7(a) shows the general morphology of the prepared SiBCN powder, observed under SEM. The powder mainly consists of near-spherical agglomerates, whose diameters are about several micrometers. The sizes are in agreement with the data collected by the laser scattering particle-size analyzer, indicating that the above particle size distribution may be seen in general cases when preparing the SiBCN powder by the current method. The image shown in Fig. 7(b) indicates that the agglomerates are actually derived from nano-primary particles, whose average diameter is about 190.8 ± 33.6 nm. Since these large agglomerates cannot be broken down by ball milling, pressing or ultrasonic vibration in ethanol, the data collected by the laser scattering particle-size analyzer shows the particle size distribution of secondary particles, while the diameters of primary particles can be counted only under SEM. It is known that fierce and repeated collisions during mechanical alloying may cause rupture, local high temperature, fusion and large energy into the powder. As a result, the prepared powder may have a large surface area and a large surface energy, and hence nanoparticles are inclined to get together to lower the total energy. These have been discussed in detail in another research article [12].

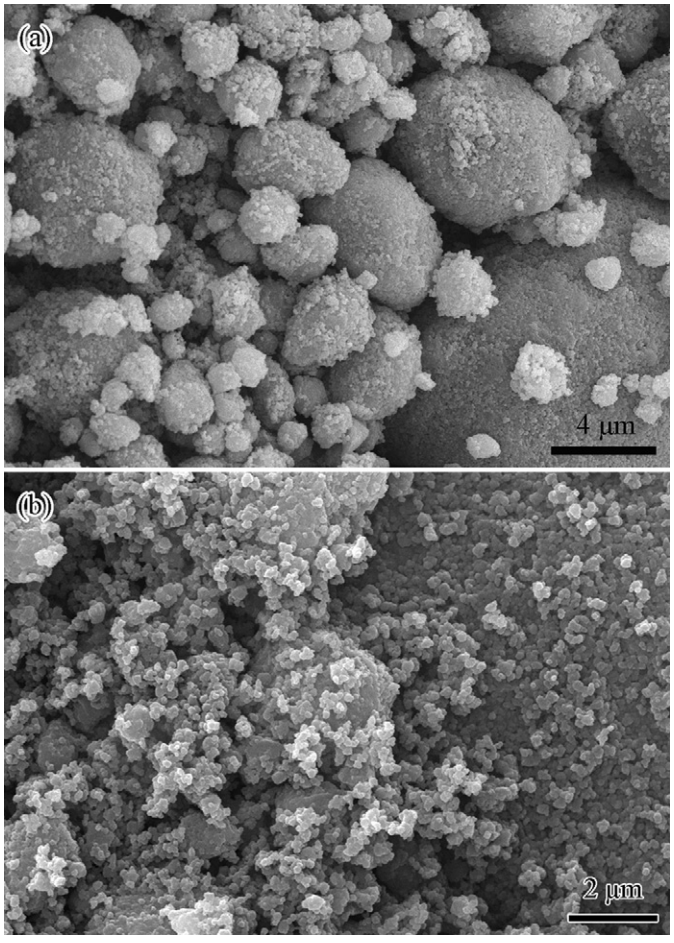

Fig. 7. The morphology of the SiBCN powder prepared under the milling condition of 600 rpm/20:1/40 h.

4. Conclusions

Results in this work show that well amorphized SiBCN powder can be prepared by an improved mechanical alloying technique, using inorganic powders as raw materials and adopting appropriate ball milling parameters. While a higher rotation speed of vials and a larger ball-to-powder mass ratio may facilitate the formation of SiC crystallites, a longer milling time has little influence on the microstructure of the prepared powder. The variation of ball milling parameters may change the power input into the powder, and hence affect the powder microstructure or the reactions between different elements. However, the particle size distribution of the prepared SiBCN powder is slightly affected by the variation of ball milling parameters. For the amorphization of raw powders, the reactions between different elements, the reduction of wear, and the production of a higher powder yield, the optimized ball milling parameters are 600 rpm, 20:1, and 30 or 40 h, respectively.

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