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# Physical and surface characteristics of the mechanically alloyed SiBCN powder

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**Abstract**

A powder mixture of cubic silicon, hexagonal boron nitride and graphite, with the molar ratio of Si:BN:C = 2:1:3, was high-energy ball milled for 40 h, under argon atmosphere. The physical and surface characteristics, the microstructures and the behavior on heating of the as-milled SiBCN powder were carefully studied by SEM, nitrogen adsorption–desorption isotherms, XPS, FT-IR, XRD, TEM and thermogravimetry-differential thermal analysis-mass spectrometry-infrared spectroscopy (TG–DTA-MS-IR). Results show that the as-milled powder is amorphous and mainly consists of near-spherical agglomerates, $6.6 \pm 5.3$ μm in size deriving from the hard agglomeration of nano-primary particles. The specific surface area, the specific pore volume and the average pore diameter of the powder are 24.5 $m^2/g$, 0.136207 $cm^3/g$ and 20.3 nm, respectively. The as-milled powder adsorbs water vapor, CO and $CO_2$, and it is easy to oxidize. When heated in helium atmosphere, the powder desorbs water vapor, CO and $CO_2$ at lower temperature, and rapidly degasifies CO and $CO_2$ at temperatures approximately between 1350 °C and 1500 °C.

*Keywords:* Agglomerate; Mechanical alloying; SiBCN powder; TG–DTA-MS-IR

## 1. Introduction

Polymer-derived Si–B–C–N ceramics are well known for possessing special structures and extraordinary high-temperature performances. For example, they have amorphous structures and do not crystallize at temperatures higher than 1700 °C [1–3]; they show negligible weight change when heated to 2000 °C [1,4,5]; and they own nice oxidation resistance or creep resistance at 1600 °C [1,6–8]. Due to these outstanding characteristics, many research works had been carried out in the past years, including the development of new raw materials [9,10], the optimization of pyrolysing parameters [4,11], the study of structure stability [12,13] and the exploitation of potential applications [14,15]. Recently, mechanical alloying and hot pressing techniques were also used to prepare Si–B–C–N powder and ceramic [16,17]. Research reveals that almost amorphous SiBCN powder can be prepared by the mechanical alloying of cubic silicon, hexagonal boron nitride and graphite powders [18]. When hot pressing the as-milled powder at 1800 °C–1900 °C under nitrigen atmosphere for 30 min, dense bulk ceramic can be fabricated, with the phase composition of nano β-SiC, α-SiC and turbostratic BN(C) [17].

Currently, the research of SiBCN powder and nano-ceramic prepared by mechanical alloying and hot pressing is still in its infancy, and much work remains to be done. It is known that, powder characteristics, such as particle shape, size, size distribution, agglomeration, composition, impurity and surface chemistry, may significantly affect the compressibility, the sinterability and the sintered microstructures of powder compact. Therefore, to further understand the prepared ceramic, it is important to carry out research on the physical and surface characteristics of the mechanically alloyed SiBCN powder. This is the focus of the current work. In addition, the behavior on heating of the as-milled powder was also investigated by TG–DTA-MS-IR. The results reveal further knowledges on the as-milled powder, and are expected to be helpful for a better understanding of the Si–B–C–N powder and ceramic preparation.

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## 2. Experimental procedures

### 2.1. Raw materials and SiBCN powder preparation

The used raw materials were commercially available cubic silicon (45.0 μm, 99.5% in purity, Beijing MounTain Technical Development Center, China), hexagonal boron nitride (0.6 μm, 98.0% in purity, Advanced Technology & Materials Co. Ltd., Beijing, China) and graphite powders (8.7 μm, 99.5% in purity, QingDao HuaTai Lubricant Sealing S&T Co. Ltd., China). The chemical composition was designed as Si:BN:C = 2:1:3 in molar ratio. High-quality silicon nitride vials and balls were adopted, and the ball-to-powder mass ratio was set as 20:1. The powder mixture was sealed in vials under argon atmosphere, and was then milled by a planetary ball mill (P4, Fritsch GmbH, Germany) for 40 h. The rotation speed of the main disk was set as 350 rpm and the vials 600 rpm in reverse.

### 2.2. Characteristics and structure analysis

The physical characteristics of the as-milled SiBCN powder were studied by scanning electron microscopy (SEM, 30 KV, Quanta 200 FEG, FEI Co., USA), laser scattering particle-size analyzer (LA-920, Horiba Comp., Japan) and nitrogen adsorption–desorption isotherms (ASAP 2020, Micromeritics Instrument Corp., USA). The surface chemistry was analyzed by X-ray photoelectron spectroscopy (XPS, Al $K_\alpha$, PHI 5700 ESCA System, Electrophysics Co., USA) and Fourier transform infrared spectroscopy (FT-IR, 510P, Nicolet Co., USA). The microstructures of the powder were studied by X-ray diffraction spectrum (XRD, 40KV/100 mA, D/max-γB Cu$K_\alpha$, Rigaku Corp., Japan) and high-resolution transmission electron microscope (HRTEM, Tecnai $G^2$ F30, 300 KV, FEI Co., USA). To investigate the behavior on heating of the as-milled powder, thermogravimetry-differential thermal analysis-mass spectrometry-infrared spectroscopy (TG–DTA-MS-IR, STA 449F3, NETZSCH GmbH, Germany) was employed.

## 3. Results and discussion

### 3.1. The physical characteristics and the microstructures of the mechanically alloyed SiBCN powder

The powder's physical characteristics investigated here include: particle shape, size, size distribution, agglomeration, specific surface area and pore structures. Fig. 1 shows the morphologies of the mechanically alloyed SiBCN powder studied by SEM. In Fig. 1(a), it is found that the powder contains large spheres and fine particles, and the former occupies a considerable proportion. Fig. 1(b) displays the detailed features of the powder, from which the large sphere is found to be actually composed of nano-primary particles, 190.8 ± 33.6 nm in size. In other words, the large spheres are agglomerates of nano-particles. As the agglomerates cannot be broken down easily by pressing, milling or ultrasonic vibration in ethanol, they are most likely hard agglomeration, where the primary particles are chemically bonded by strong bridges. It is known that the fierce and repeated collisions during the high-energy ball milling generally bring large mechanical energy, fracture, short-range diffusion, local high temperature and fusion to powder particles. As a result, the prepared powder may possess a large surface area and disordered surface atoms. To lower the surface energy and also because of the fierce collisions, the nano-particles are inclined to get together. This is in agreement with the current results. The particle size distribution of the as-milled powder is displayed in Fig. 2. The powder has an average particle size of about 6.6 ± 5.3 μm, though particles larger than 15 μm also take a small proportion. The hard agglomerates and the relatively wide size distribution may lead to heterogeneous packing in green body which, in turn, may result in different shrinkage rate at different regions during the sintering stage.

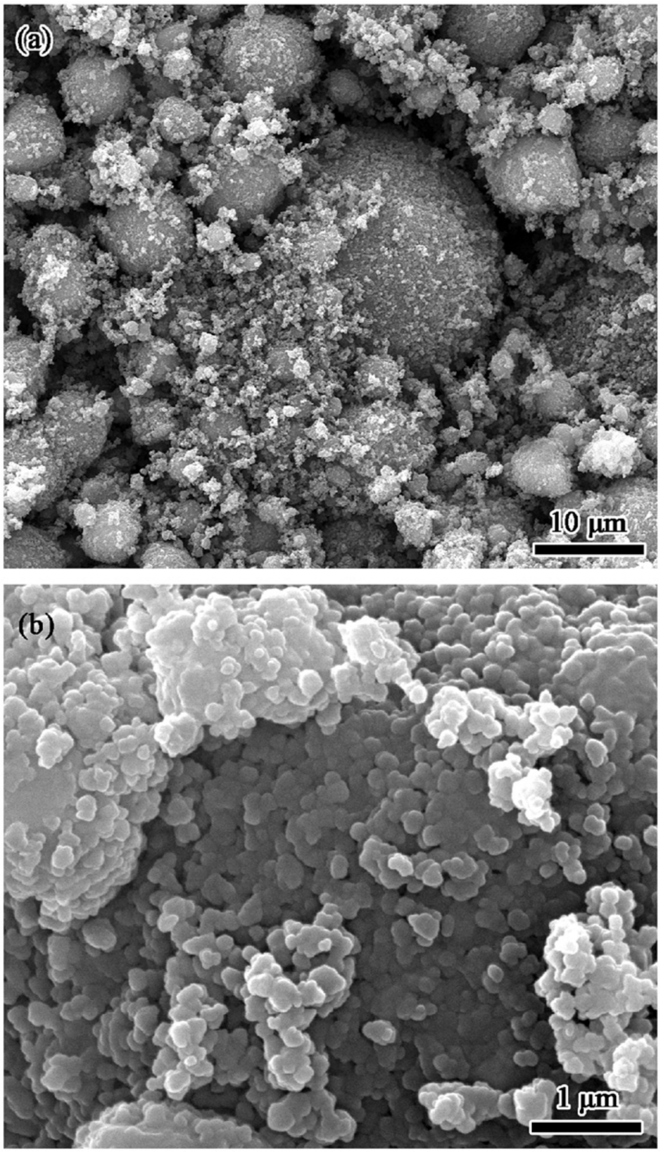

Fig. 1. Morphologies of the mechanically alloyed SiBCN powder, showing the spherical agglomerates (a) and the nano-primary particles (b).

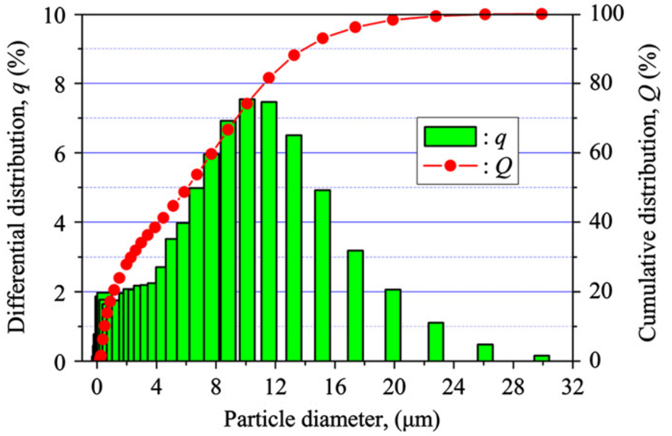

Fig. 2. Particle size distribution of the mechanically alloyed SiBCN powder.

This may lead to the development of large pores in the prepared ceramic, and hence affect the ceramic density and properties.

Fig. 3 displays the XRD spectrum and the HRTEM image of the mechanically alloyed SiBCN powder. The as-milled powder is amorphous, as indicated by three pieces of evidence: the extremely broad XRD peaks in Fig. 3(a), the completely disordered atomic arrangement in HRTEM image and the large diffraction spot in selected area electron diffusion (SAED) pattern in Fig. 3(b). The amorphous structure is attributed to the fierce and repeated collisions during the high-energy ball milling process. In Fig. 3(b), two particles overlap each other and a neck region with the neck width of about 28 nm forms between them. This indicates that the metallurgical bonding and hence the hard agglomeration forms between the particles.

Fig. 4 displays the nitrogen adsorption–desorption isotherms of the as-mill SiBCN powder. The experiment was carried out at the liquid nitrogen temperature (77 K), and prior to testing, the powder was degasified at 300 °C in vacuum for 3 h. The obtained isotherms and hysteresis loop belong to Type IV and Type H1, respectively, according to the IUPAC classification [19]. This indicates that the powder most likely has mesopore structure with the pore size approximately between 2 nm and 50 nm. It is observed from the adsorption isotherm that monolayer adsorption occurs at lower nitrogen pressure ($P/P_0 < 0.05$). In this stage, the nitrogen adsorption occurs quickly as the increase of nitrogen pressure, but the adsorption quantity is very small. When the nitrogen pressure is enhanced to a higher value ($0.05 < P/P_0$), multiplayer adsorption appears until capillary condensation takes place ($0.35 < P/P_0$). The nitrogen adsorption quantity is first linearly increased, and then rapidly expanded. The specific surface area is determined by the multipoint BET method using the adsorption data in the range of $0.05 < P/P_0 < 0.35$ [20], giving a value of 24.52 $m^2/g$. The large surface area is caused by the great quantity of nano particles, produced by mechanical alloying. The desorption isotherm is used to determine the pore structure of the powder by the BJH method [21]. The increased pore volume, as a dependence of the pore diameter, is shown in the inserted curve. The cumulative pore volume and the average pore size are calculated as 0.136034 $cm^3/g$ and 20.3 nm, respectively. The pore size distribution shows that most pores have diameters approaching to that of mesopores ($2\ nm < d < 50\ nm$). The mesopore structure is caused by the agglomeration of near-spherical nano-particles. Additionally, the appearance of macropores ($50\ nm < d$) may be attributed to the loose packing of nano-particles in some agglomerates.

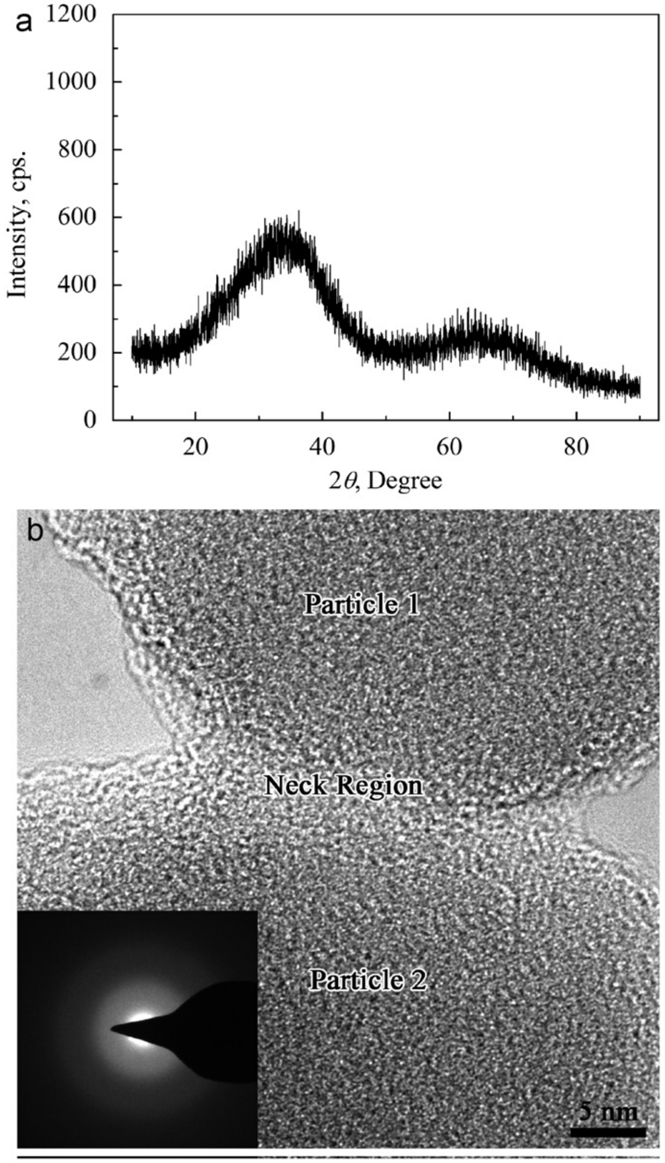

Fig. 3. Microstructures of the mechanically alloyed SiBCN powder. (a) XRD spectrum; (b) HRTEM image and SAED pattern of two overlapped nano-particles.

### 3.2. Surface characteristics of the mechanically alloyed SiBCN powder

To study the surface chemistry of the as-milled SiBCN powder, XPS and FT-IR methods are used and the obtained spectra are shown in Fig. 5. In Fig. 5(a), the

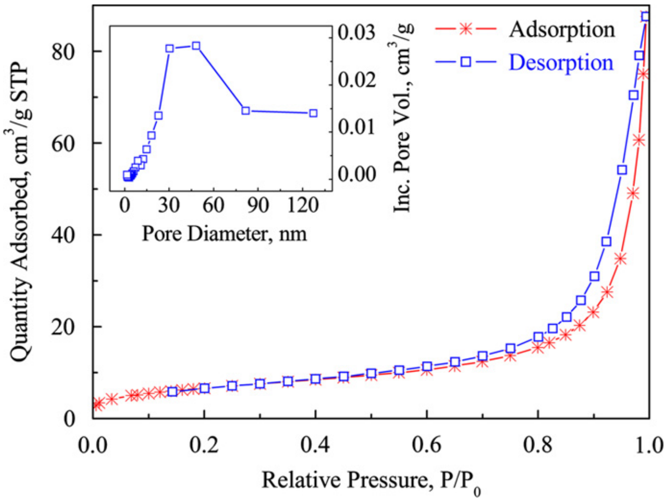

Fig. 4. Nitrogen adsorption–desorption isotherms of the mechanically alloyed SiBCN powder, detected at the liquid nitrogen temperature (77 K). The inset is the pore size distribution calculated by the BJH method using the desorption isotherm.

XPS peaks at 104.4 eV and 155.6 eV are assigned to Si 2p and Si 2s core-level lines in Si–O bond, respectively. This is because their positions are shifted towards the higher binding energy by about 5.0 eV when compared with that in silicon. The chemical shift suggests stronger binding force, and indicates that silicon atoms may lose electrons and have positive charge. The appearance of Si–O bonds suggests that oxide film may form on the powder surface. Moreover, since the atoms in the surface layer are disordered, as revealed by the HRTEM image in Fig. 3(b), it is believed that the oxide film is amorphous. The oxidation is confirmed by the strong intensity of O 1s core-level line at about 535.0 eV, suggesting a considerable content of oxygen. However, the binding energy is slightly higher than that in Si–O bond, implying the existence of other chemical bonds containing oxygen, except for the Si–O bonds. The B 1s core-level line at 193.2 eV has higher binding energy than that in boron by about 5.8 eV, but approaches to that in B–O or B–N bonds. Since the N 1s core-level line at 400.2 eV is also caused by B–N bonds, BN most likely exist within the detecting depth (1–3 nm). The binding energy of C 1s core-level line (286.8 eV) is higher than that in graphite by about 2.2 eV or higher than that in Si–C bond by about 3.3 eV, and is lower than that in C–O bond by about 4.0 eV. Hence, C atoms may be bonded with N atoms or water molecules. Additionally, the XPS peak at about 982.8 eV is assigned to Nd 3d5/2 core-level line, and the impurity may be introduced in the process of powder preparation, storage or analyses. These results imply that the mechanically alloyed SiBCN powder is easy to oxidize, leading to the formation of oxide film on the powder surface.

The oxidation is further confirmed by the FT-IR spectrum of the powder, as shown in Fig. 5(b). The spectrum mainly contains four infrared absorption peaks, revealing further information about the surface chemistry. The strong absorption peak at 840 cm$^{-1}$ is caused by the vibration of Si–C bands, and the peak broadening may be due to the disordered structure. The weak peak at 1100 cm$^{-1}$ is attributed to the Si–O stretching vibration, confirming the existence of silicon oxide film on the powder surface. The appearance of water molecules is corroborated by the absorption peaks at 1625 cm$^{-1}$ and 3412 cm$^{-1}$. These results indicate that the surface layer mainly contains Si–C bonds, Si–O bonds and water molecules, while other chemical bonds, such as C–C, C–N, B–C and Si–N, may rarely exist.

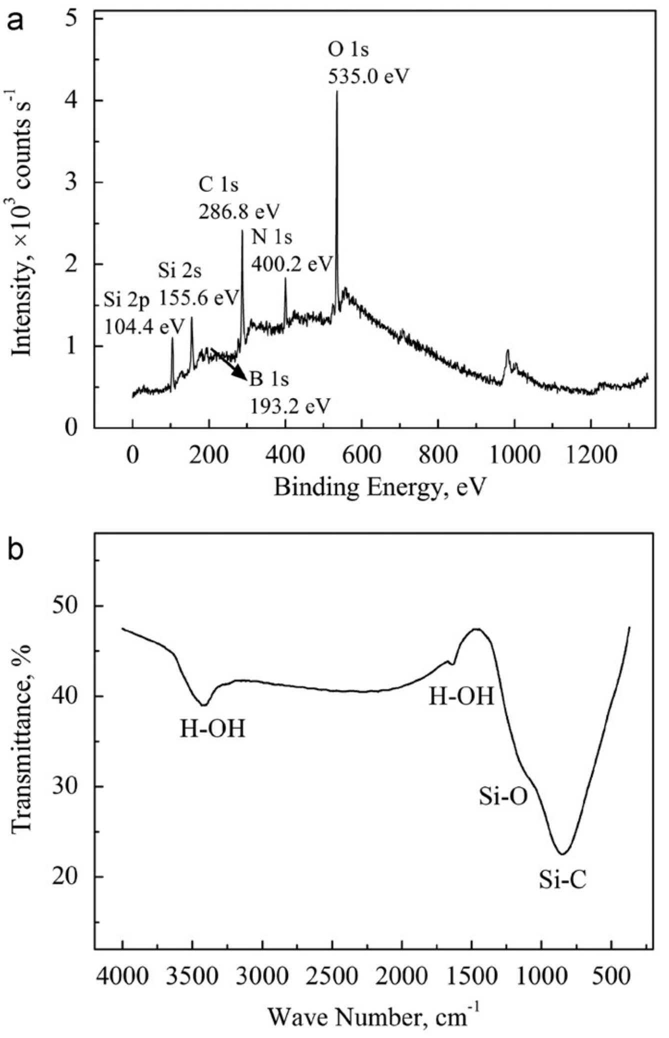

Fig. 5. XPS (a) and FT-IR (b) spectra of the mechanically alloyed SiBCN powder, showing the oxidation and water molecule adsorption on the powder surface.

It is known from the above results that, the mechanically alloyed SiBCN powder has small particle size, large surface area and amorphous structure. Hence, the disordered surface atoms are highly active and easily combined with oxygen, water molecule, carbon dioxide or other substances to lower the surface energy. In addition, the gas adsorption effect is enhanced by the mesopore structure of the powder. In the process of powder preparation or analyses, oxygen or other contaminations may be introduced by various routes, such as the oxide film on raw silicon or boron nitride powder surface, the impurities in glove box or argon atmosphere and the exposure to air before analyzing. It is advisable to keep these in mind when studying or processing the as-milled SiBCN powder, as the variation in the surface chemical composition may affect the behavior on heating or sintering.

### 3.3. The behavior on heating of the mechanically alloyed SiBCN powder studied by TG–DTA-MS-IR

To investigate the behavior on heating of the as-milled SiBCN powder, TG–DTA-MS-IR is used for a comprehensive analysis. When heating the as-milled powder to 1500 °C with a heating rate of 10 °C/min under helium atmosphere, the TG–DTA curve, MS and IR spectra were recorded, as shown in Figs. 6 and 7. The weight loss at lower temperatures ($T < 100$ °C) may be due to the desorption of adsorbed water molecules, carbon monoxide and carbon dioxide. This is confirmed by the detected MS and IR spectra. The MS spectra, with the mass ($m$) to charge ($e$) ratio of $m/e = 12$, 28 and 44, correspond to that of $C^+$, $CO^+$ and $CO_2^+$, respectively. At lower temperatures, relatively strong ion beam intensity is detected for these ions, implying the desorption of CO and $CO_2$. The IR spectra in Fig. 7 shows the desorption of water molecules at lower temperatures, but continuous release of CO and $CO_2$ in the entire experimental temperature range.

In the medium temperature range (about 400 °C–1300 °C), the powder shows persistent weight increase, accompanied by a continuous endothermic process. This implies that certain endothermic reactions may occur between powder and other substances. As the powder is almost impossible to react with helium, the phenomenon requires further experimental data to verify and explain. The three-dimensional IR spectrum and the MS spectrum in this stage indicate that CO and $CO_2$ are persistently degasified, but the gas emission rate has no significant change. When the temperature locates approximately between 1350 °C and 1500 °C, the powder shows a fast weight loss. This may be attributed to the rapid release of CO and $CO_2$, as revealed by the fast intensity increase in the MS and three-dimensional IR spectra. The main reason for the rapid degasification of CO and $CO_2$ at high temperature is considered to be the carbothermal reduction of the silicon oxide film on the powder surface. Possible reactions related to the gas formation are as follows:

$$SiO_2 + C \rightarrow SiC(s \text{ or } g) + CO \text{ and/or } CO_2$$

$$SiO_2 + CO \rightarrow SiC(s \text{ or } g) + CO_2$$

$$CO_2 + C \rightarrow CO$$

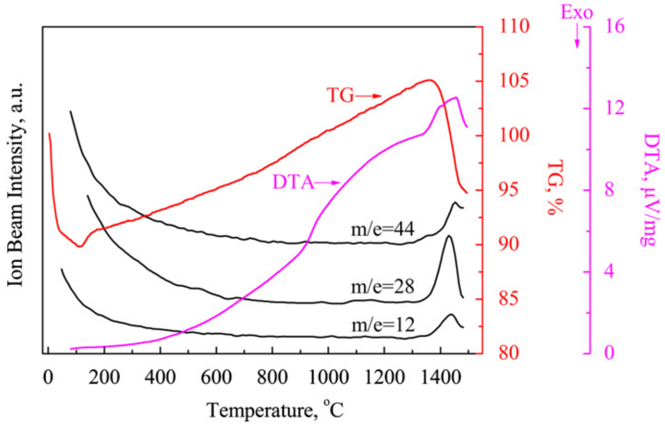

Fig. 6. TG–DTA curves and MS spectra (with the mass to charge ratio $m/e = 12$, 28 and 44) of the mechanically alloyed SiBCN powder, when heated to 1500 °C under helium atmosphere with a heating rate of 10 °C/min.

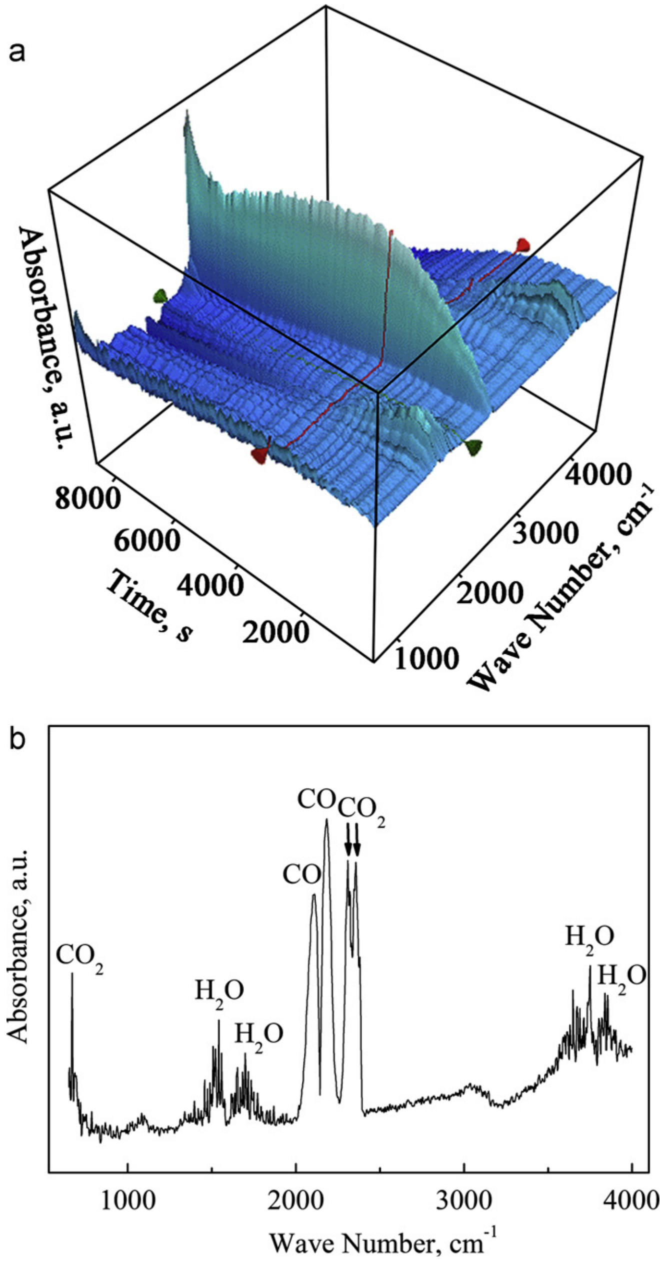

Fig. 7. Three-dimensional (a) and projected two-dimensional (b) IR spectra of the mechanically alloyed SiBCN powder, when heated to 1500 °C under helium atmosphere with a heating rate of 10 °C/min.

The rapid degasification of CO and $CO_2$ in this temperature range had been observed for other silicon-containing ceramic powders, and the above reactions had also been confirmed by experimental data [22,23]. Additionally, no MS signal concerning denitrification is detected until the temperature reaches 1500 °C, indicating that the as-milled SiBCN powder may have scarce Si–N bonds and hence the following reaction: $Si_3N_4+C\rightarrow SiC+N_2$ rarely occur.

## 4. Conclusions

Current research has investigated the physical characteristics (including particle shape, size, size distribution, agglomeration, specific surface area and pore structure), surface characteristics (e.g., surface chemistry), microstructures and the behavior on heating of the mechanically alloyed SiBCN powder. Results show that the as-milled SiBCN powder is amorphous and mainly consists of near-spherical agglomerates, $6.6\pm5.3$ μm in size deriving from the hard agglomeration of nano primary particles. The powder has mesopore structure, with specific surface area, specific pore volume and average pore size of 24.5 $m^2/g$, 0.136207 $cm^3/g$ and 20.3 nm, respectively. The as-milled powder adsorbs water vapor, CO and $CO_2$, and it is easy to oxidize, leading to the formation of amorphous silicon oxide film on the powder surface. Heated in helium atmosphere, the powder desorbs water vapor, CO and $CO_2$ at lower temperature, and rapidly degasifies CO and $CO_2$ at temperatures approximately between 1350 °C and 1500 °C.

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