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Microstructural and mechanical properties of cBN-Si composites prepared from the high pressure infiltration method

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ABSTRACT

The grain size dependence of the mechanical properties of cBN-Si composites prepared using the high pressure infiltration method has been investigated. Indentation testing indicates that cBN-Si composites have hardness values of 38–43 GPa, which increase with increasing grain size and are harder than traditional polycrystalline cBN composites (PcBNs). Thermostability analyses display that cBN-Si composites with a grain size of >9 μm also possess a higher temperature of oxidation, compared to traditional PcBNs, and the thermostability increases with increasing cBN grain size. Fracture toughness tests show that almost no cracks appear on the polished cBN-Si samples when the loading forces are increased to 294 N and the fracture toughness is better than for commercial samples. Scanning electron microscopy illustrates that deformations and close pores occurred easily between coarse BN grains, leading to denser cBN-Si compacts with better mechanical performances.

1. Introduction

Cubic boron nitride (cBN) is a well-known superhard material in industry, with a hardness second only to diamond. However, cBN possesses superior thermal stability and low chemical reactivity compared to diamond [1], and it is widely used in high speed cutting of ferrous alloy, an application where diamond is completely disabled [2,3]. In addition, cBN cutting tools have also found wide usage in various industrial machining fields for difficult-to-cut materials, such as titanium alloys and nickel based super-alloys [4–6].

It is difficult to sinter cBN and form bonding between sintered cBN grains due to its high melting point (>3000 °C) and metastability under high temperature and low pressure [7]. To obtain complete densification sintered cBN compacts, high pressures (>7 GPa) and temperatures (>2000 °C) are required, leading to an increase in costs in industrial applications [2,8]. Furthermore, the well sintered compacts prepared this way rarely succeed. The use of catalysts/additives can greatly reduce the sintering temperature and pressure [9–11]. Generally, cBN and catalysts/additives are mixed and then sintered at high pressure and high temperature (HPHT). It is common knowledge that the inhomogeneity of catalysts/additives remarkably affects the mechanical and thermal properties of cBN composites [10,12]. However, it is difficult to control the homogeneity of the mixed powder and to form cBN-cBN bonds in sintered compacts, resulting in low hardness, thermal stability and transverse rupture strength [2]. Si is a kind of catalyst (hBN-cBN) and the melting point of Si decreases with increasing the pressure. In the sintering process, the melting Si infiltrates the cBN layer, while open a channel to the cBN layer. Co is usually difficult to infiltrate the cBN layer. Moreover, the cBN powder was sintered on the carbide without any additives, and the results showed that the hardness values of their sintered samples were 29.3–34.5 GPa [10,16]. In our previous study [13], it was shown that the high pressure infiltration method can sufficiently improve the homogeneity of the binder phase and fabricate a large number of cBN-cBN bonds in the sintered compacts, which would not have been obtainable by an ordinary mechanical mixing technique. Moreover, the high pressure infiltration method can automatically optimize the binder content and promote plastic deformation and the close voids between cBN grains. Compared to a conventional mixture method, the high pressure infiltration method is favorable for improving the mechanical properties.

In this present work, the Si powder was replaced by mono-crystalline Si piece and put it between cBN powder and carbide, while commercial cBN compacts are usually sintered on WC-Co substrates so that they can be welded easily on the shank for cutting use. The densification of cBN-Si compacts was achieved using the high pressure infiltration method. We systematically studied the grain size dependence of the hardness,

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oxidation resistance, fracture toughness and microstructure of the cBN-Si composites. On the basis of our experimental results, we also speculate the possible sintering process.

2. Experimental procedures

2.1. Sample preparation

cBN powder (grain size: 0–1, 1–2, 2–4, 4–6, 6–8 and 6–12 μm, >99.9% purity, purchased from Zhongnan Jiete Super-abrasives Co., Ltd., Zhengzhou, China) and mono-crystalline silicon pieces (>99.9% purity, purchased from Lijing silicon material Co., Ltd., Zhejiang, China) were used as the starting materials in our experiments. The starting materials for the high pressure infiltration method were sintered under HPHT conditions. In the high pressure infiltration method, a Si layer was sandwiched between a cBN layer and YG16 (WC - 84% and Co - 16%). In order to remove the impurities and vapor adsorbed on the powder surface, the starting materials were treated in a vacuum of 3.0×10^{-3} Pa and a temperature of 1000 °C for 1 h. The starting materials were sintered under 5.5 GPa and 1500 °C. The experimental assembly is shown in Fig. 1.

High pressure sintering experiments were carried out in a DS 6 × 14 MN cubic press. The pressure was calibrated at ambient temperature by means of the well-known pressure-induced phase transitions of Bi, Tl and Ba. The temperature was estimated from the relation between the input power and temperature, which was obtained in advance using Pt6%Rh-Pt30%Rh thermocouples. In our experiments, samples were first compressed to a target pressure and then heated to the desired temperature with a heating rate of about 100 °C/min. After being maintained for a desired treatment time, the samples were quenched to ambient temperature with a cooling rate of about 70 °C/min and then decompressed to ambient pressure.

2.2. Sample characterization

The recovered samples were polished to a smooth mirror surface using a polishing machine with 10 and 1.5 μm diamond pastes. X-ray diffraction analysis (XRD; DX-2500, Dandong, China) and scanning electron microscopy (SEM; JSM-6490, JEOL, Akishima, Japan) equipped with an energy-dispersive spectrometer (EDS; EDAX, Mahwah, NJ) were performed on the polished surface to detect the microstructure and composition of the samples. Differential scanning calorimetry analysis (DSC; TG-Q600, TG-Q2000, USA) was carried out with a heating rate of 10 °C to determine the oxidation resistance of the samples. In order to determine the mechanical properties of the sintered samples, Vickers hardness (Model FV-700, Future-Tech., Japan) was tested with an applied loading force of 29.4 N and a fixed indenting time of 15 s. The fracture toughness was also calculated qualitatively by indentation.

3. Results and discussion

3.1. Sample analysis by XRD

Fig. 2 displays the XRD patterns of samples sintered under HPHT. XRD patterns show that cBN did not react with Si under *P-T* conditions of 5.5 GPa and 1500 °C. However, $CoSi_2$ and CoSi formed during the sintering process and the content increased with decreasing cBN particle size. We speculated that the decrease of the $CoSi_2$ and CoSi may result from the fact that the surface area of the fine-grains was larger than for the coarse grains, and the amount of sediment was more than that for the coarse particles. The deformation of the larger grain size is relatively heavier compared to the smaller one, and Si and Co were less able to infiltrate the cBN layer under the same pressure and temperature conditions. It is known that an excess of catalyst will surely affect the hardness, strength and mechanical properties of sintered samples. The Vickers hardness of the cBN-Si composites increased with increasing cBN grain size. Therefore, according to our results, we suggest that the comprehensive performance was better sintered with a cBN grain size of about 10 μm through the high pressure infiltration method in the cBN-Si system.

3.2. Microstructural and mechanical property tests

3.2.1. Microstructural characterization

Fig. 3 shows the SEM micrographs of different crystalline-size samples sintered using the high pressure infiltration method. The energy-dispersive X-ray (EDS) test results are also given (see Table 1). The EDS results show that the grey portions on the surface of the polished samples are rich in B and N, corresponding to cBN, while the white portions are the rich zones of Si and Co. As can be seen in Fig. 3, Si and Co are distributed uniformly between the grain boundaries of cBN, which indicates that the high pressure infiltration method can indeed improve the homogeneity of samples. However, the grain boundaries of cBN are more clear and the Si and Co contents decrease with increasing grain size. As shown in Fig. 3(e) and (f), limited Si and Co exist around the cBN particles and part of the cBN grains are directly bonded to each other, suggesting that the cBN-cBN bonds were formed and the pores are more easily closed during the coarse grain sintering process. Through comparison of the different grain sizes of cBN, the coarse grained surface energy is lower than for the fine-grains and

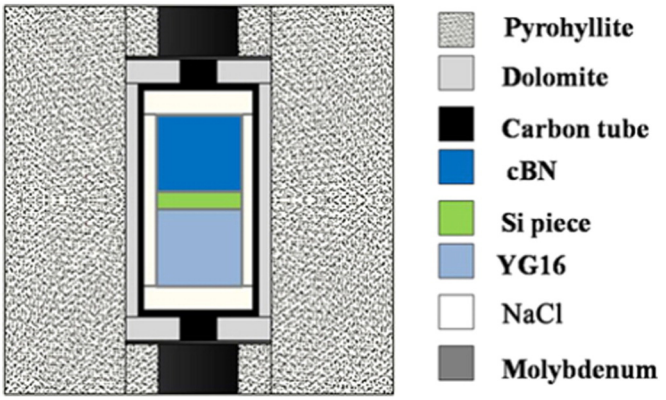

Fig. 1. Illustration of the experimental assembly.

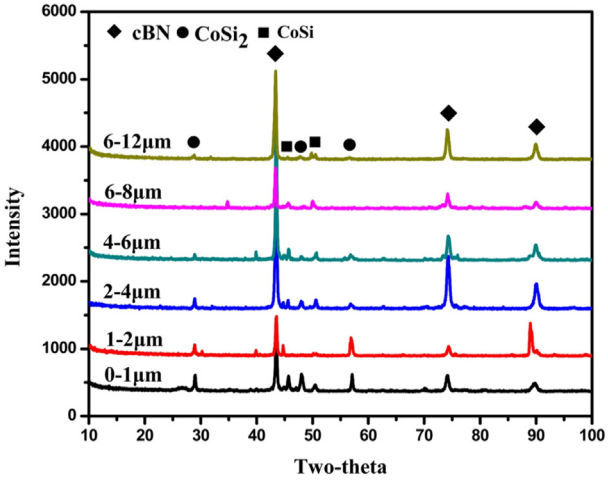

Fig. 2. XRD patterns of the samples sintered at HPHT.

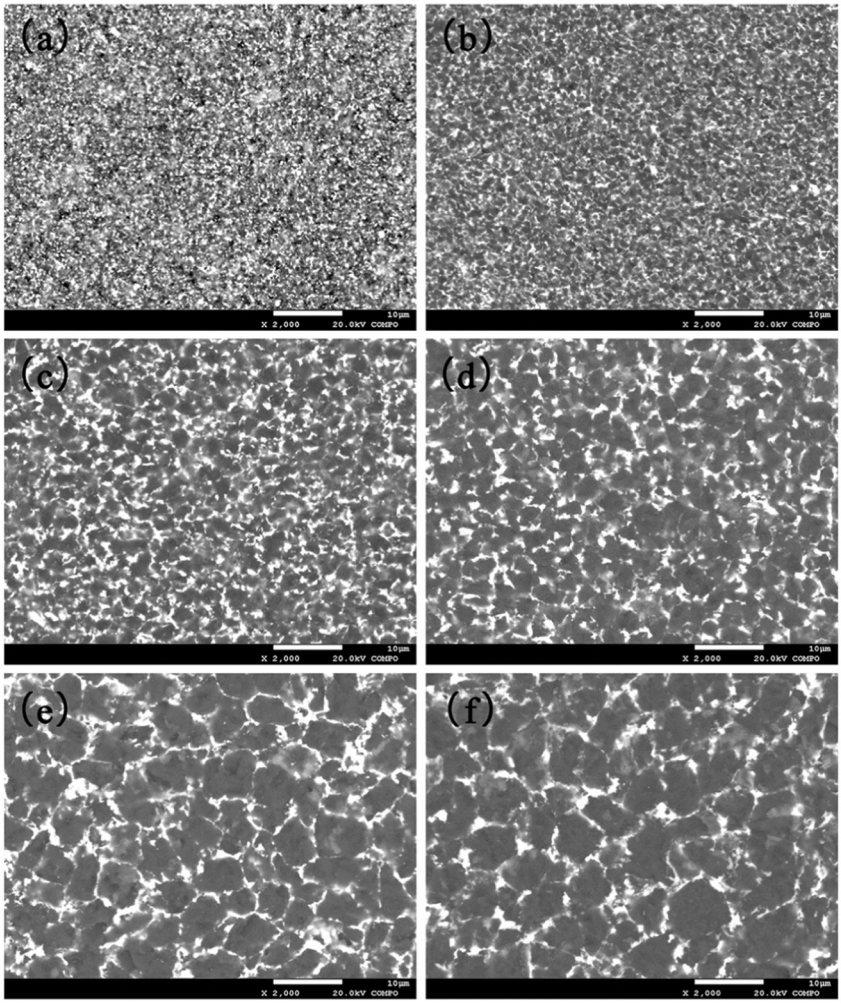

Fig. 3. SEM micrographs of the samples sintered at 5.5 GPa and 1500 °C with (a) 0–1, (b) 1–2, (c) 2–4, (d) 4–6, (e) 6–8 and (f) 6–12 μm.

with the increment of cell pressure, the deformations of the cBN particles occurred more easily and the contact areas of coarse grain may be enlarged, accompanied by the closing of the voids. Conversely, it is difficult to induce pore closure during the fine-grain sintering. As the temperature increased to the melting point of Si and Co, the Si and Co began to melt and permeate toward the cBN layers, and finally fulfill these residual voids. As a result, the Si and Co content of the coarse grained samples is less than the fine-grained samples fully surrounded by Si and Co. There is Si residue after infiltration at the interface between cBN and carbide, which affected the interface strength, and delamination may even appear. In contrast, the phenomenon does not exist during the fine-grained sintering process. Therefore, the thin Si piece was used to improve the interface strength between cBN and carbide when sintered the coarse grained samples. As the sintering process proceeded, Si reacted with Co to generate CoSi and $CoSi_2$, which were deposited on the surface, as well as the connecting boundaries of the cBN particles. Therefore, the coarse grained samples have greater densification and better mechanical properties than the fine-grained samples.

Table 1
EDS and density results.

	Wt% 0–1 μm	Wt% 1–2 μm	Wt% 2–4 μm	Wt% 4–6 μm	Wt% 6–8 μm	Wt% 6–12 μm
BK	40.71	44.09	44.63	43.47	45.56	46.83
NK	48.49	46.51	49.77	51.23	49.49	49.57
SiK	6.48	5.64	3.36	3.18	2.97	2.16
CoK	4.32	3.76	2.24	2.12	1.98	1.44
$\rho(g/cm^{-3})$	3.000	3.714	3.800	3.818	3.909	3.952

3.2.2. Vickers hardness test

The Vickers hardness of the cBN-Si composites increased with increasing cBN grain size. The minimum Vickers hardness of these composites could reach 38.1 GPa, clearly superior to the traditional cBN composite [14,15], as shown in Fig. 4a. The sintered cBN-Si compacts with a grain size of 9 μm have the maximum Vickers hardness value of 42.7 GPa. Archimedes' principle was used to measure the density of the cBN-Si composites, as shown in Table 1. We found that the compactness of these samples increased with increasing particle size, and achieved a maximum compactness, similarly when the cBN grain size exceeding 9 μm. This means that the density affects the hardness of the sintered samples, and the greater the density, the higher the hardness at the same sintering *P-T* conditions. The Vickers hardness values of the samples sintered on the carbide without any additives were 29.5–34.5 GPa [10,16]. Therefore, Si played an important role in the sintering process. To further determine the mechanical properties of the whole samples, the Vickers hardness of section of sintered samples was measured. Starting from the Si layer, the hardness was measured at regular

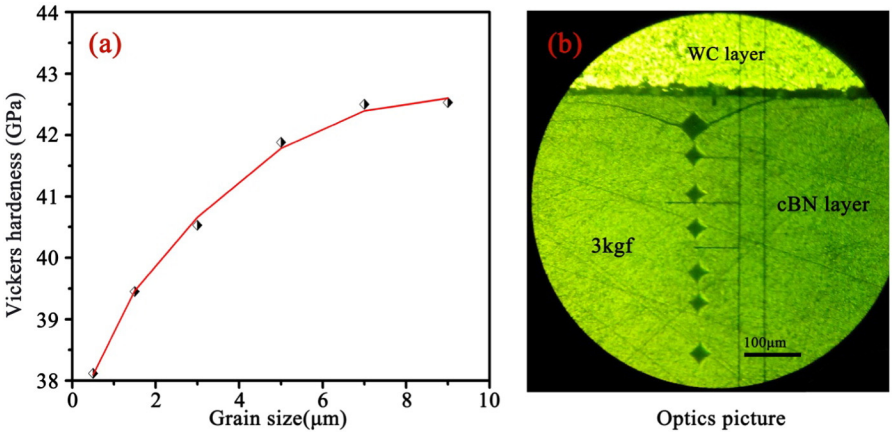

Fig. 4. (a) Vickers hardness of the samples and (b) optical images.

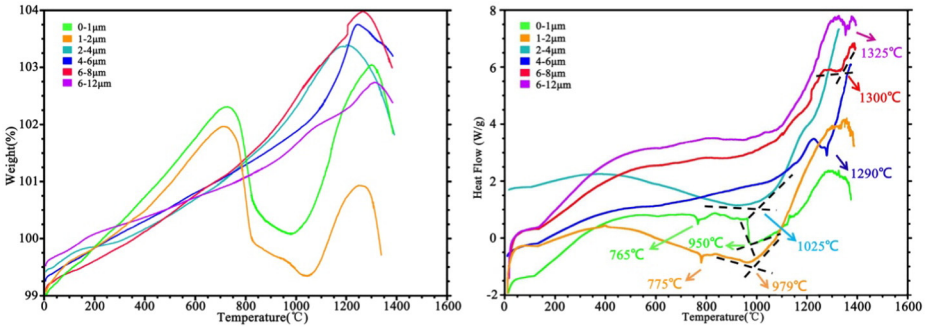

Fig. 5. TG and DSC results of the samples sintered at 5.5 GPa and 1500 °C.

distances and the indentation was also given, as shown in Fig. 4b. It can be seen that all the hardness values are almost equal except for the position close to the Si layer, which the content of Si aggregated heavily. This fully illustrates that the overall performance of the cBN-Si composites prepared with the high pressure infiltration method is homogeneous, which is consistent with the results of SEM.

3.2.3. Oxidation resistance test

The oxidation resistance testing results of samples sintered with different cBN grain sizes at 5.5 GPa and 1500 °C are shown in Fig. 5 and Table 2. The onset temperatures of oxidation are determined from the exothermic trough in the heat flow curve measured by DSC. DSC curves of cBN-Si samples show that the onset temperature of oxidation increased with increasing cBN grain size, and for the 0–1 and 1–2 μm samples, two exothermic peaks appear due to oxidation of the abundant Co and Si for the cBN-Si composites. The corresponding thermogravimetric curves for the 0–1 and 1–2 μm samples show two peaks as well. Oxidation of Co, Si and B leads to the emergence of exothermal peaks. The fine-grain samples obviously exhibited exothermal peaks due to an excess content of Co and Si in the sintered samples. For the second exothermal peaks, we deduced that the deformations are greater for the coarse grained samples, and the boundaries formed cBN-cBN bonds and combined closely between the grains. Therefore, it is more difficult for the coarse grained samples to decompose due to the reduced surface to volume ratio.

3.2.4. Fracture toughness testing

The fracture toughness determination by indentation is the rapid evaluation of the toughness of small samples. The recovered samples and commercial holistic PcBN (purchased from Funaike, China (c) and Rijin, Korea (d)) were polished and subsequently tested with different applied loading forces and an fixed indenting time of 15 s until the crack appeared. The fracture toughness was calculated by the indentation equation. The fracture toughness was measured at different applied loading forces (49, 98 and 294 N). At each applied loading force, five tests were performed to provide good statistics. At low applied loading forces (49 and 98 N), no cracks appeared for all samples other than the commercial samples ((c)), as shown in Fig. 6(c). The results indicate that the cBN-Si composites obtained from the high pressure infiltration method have higher fracture toughness compared to traditional PcBN materials. Only a small crack appears for the coarse grained samples and the commercial samples ((d)) under a high load of 294 N, as shown in Fig. 6(b) and (d). However, as shown in Fig. 6(a), for the fine-grained samples still no crack appears. The fracture toughness tests indicate that the fracture toughness increased with the decrease of particle size and the fine-grained samples were superior to the commercial PcBN materials. We

Table 2
Onset temperatures of oxidation.

Size(μm)	The onset temperatures of oxidation(°C)
0–1 μm	765/950 °C
1–2 μm	775/979 °C
2–4 μm	1025 °C
4–6 μm	1290 °C
6–8 μm	1300 °C
6–12 μm	1325 °C

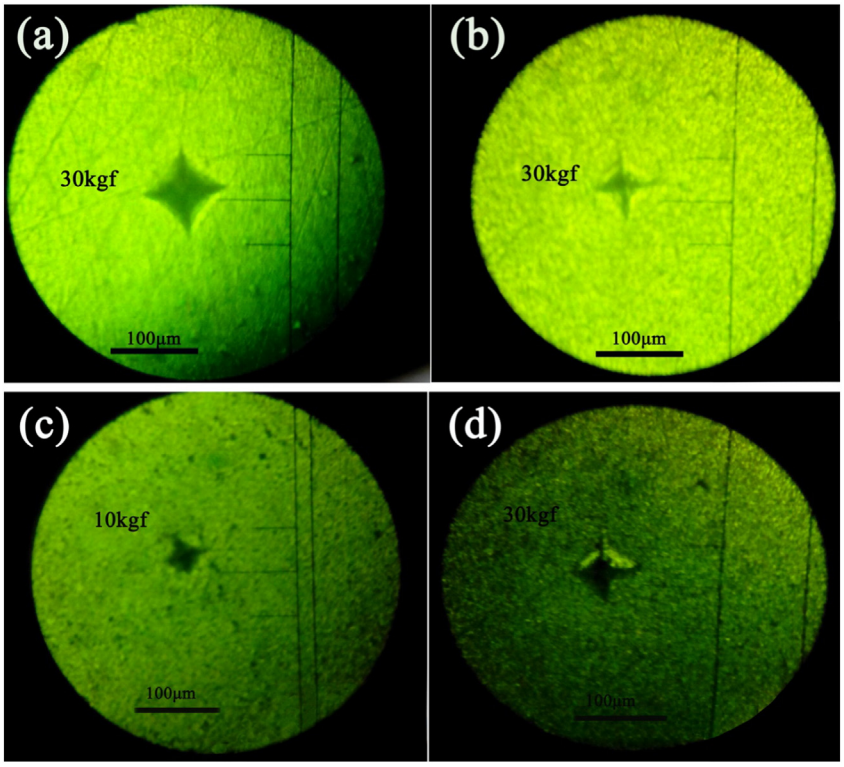

Fig. 6. Indentation of sintered samples with grain sizes of (a) 0–1 and (b) 6–12 μm of cBN, and the indentation of the commercial samples, (c) and (d).

speculated that the fracture toughness depends on grain size and is related to the content of Co and Si in the sintered samples. Generally, the larger particle size, the lower the fracture toughness. In addition, the excess emergence of Co and Si for the fine-grained samples better improved the fracture toughness than the coarse grained samples.

4. Conclusions

In present study, we have systematically investigated the grain size dependence of the mechanical properties of cBN-Si composites prepared using the high pressure infiltration method. The hardness of the cBN-Si composites is high as expected due to the exceptionally homogeneous microstructures with Si and Co finely distributed at the cBN grain boundaries, which is difficult to obtain with ordinary mechanical mixing techniques. The hardness and thermostability increased with increasing cBN grain size and fracture toughness is superior to the commercial PcBN samples. A greater homogeneity of the microstructure resulted in a higher amount of solid state reactions at the interface during sintering of the polycrystalline compact resulting in enhanced performance of the compacts. The deformation occurred more easily for the coarse grain cBN than the fine-grained cBN at high pressure and temperature. When the grain size of cBN exceeded 9 μm, the deformation tended to be the largest. Therefore, the grain size of cBN at about 10 μm sintered with the high pressure infiltration method in the cBN-Si system presented excellent mechanical properties.

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