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PRODUCTION, STRUCTURE, PROPERTIES

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# Synthesis and Performance Study of Polycrystalline Cubic Boron Nitride Using WC–B<sub>4</sub>C–Al<sub>2</sub>O<sub>3</sub> as a Binder

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**Abstract**—Using WC–B<sub>4</sub>C–Al<sub>2</sub>O<sub>3</sub> as a binder, polycrystalline cubic boron nitride (PCBN) composite materials were synthesized under high temperature and ultra-high pressure conditions. X-ray diffraction (XRD) and scanning electron microscope (SEM) was used to analyze the phase composition and microstructure of the composite material. At the same time, the porosity, microhardness, flexural strength, and abrasion ratio of the composite material were tested. The research results show that at ultra-high pressure (6 GPa) and temperature between 1250 and 1550°C, the phase components in PCBN are mainly composed of BN, WB<sub>2</sub>, WB, and Al<sub>2</sub>O<sub>3</sub>. During low-temperature sintering, the internal structure of the sample is loose, with holes and gaps, resulting in poor compactness, low bending strength, and low microhardness. With the increase of temperature, the compactness, flexural strength, and microhardness of PCBN are obviously enhanced. When the sintering temperature is 1550°C, the comprehensive mechanical properties of PCBN are the best, with microhardness of 38.6 GPa, flexural strength of 789.6 MPa, and wear ratio of 9371.

**Keywords:** PCBN, WB<sub>2</sub>, high temperature and ultra-high pressure, bonding agent

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## 1. INTRODUCTION

Cubic boron nitride has excellent properties, such as high hardness, good thermal conductivity, and high thermal stability. Besides, because it is chemically inert to ferrous metals and resistant to high temperatures, it is widely used for cutting hardened steel, cast iron, iron powder metal, and heat-resistant alloys [1–5]. However, due to the low sintering activity of cBN single crystal, it is difficult to grow up. To obtain a practical cBN sintered block, it needs to be sintered at a high temperature of 2000°C and an ultra-high pressure of 7 GPa [6, 7]. This increases production costs and limits its application in industry. Therefore, the cBN powder is usually mixed with a binder and then sintered into a polycrystalline cubic boron nitride (PCBN) composite material after high temperature and ultra-high pressure process.

The binder plays an important role in the synthesis of polycrystalline cubic boron nitride materials at high temperature and high pressure. Incorporating an appropriate amount of binders can not only reduce the sintering temperature and pressure but also optimize the performance of the sintered body [8–11]. The type of bonding agent can be divided into ceramic, cermet, and metal bonding agent composite materials. The PCBN composite material bonded by the ceramic bond has high hardness, high temperature stability, and chemical stability; while the PCBN composite material bonded by the metal bond has good toughness. This article mainly uses the WC–B<sub>4</sub>C–Al<sub>2</sub>O<sub>3</sub> system as a bonding agent to synthesize PCBN composite materials under high temperature and high pressure. The micro morphology, phase and mechanical properties of PCBN composites at different sintering temperatures were studied.

**Table 1.** Experimental formula and synthesis process (wt %)

No.	cBN	WC	B <sub>4</sub> C	Al <sub>2</sub> O <sub>3</sub>
A	70	11	18	1

## 2. EXPERIMENTAL

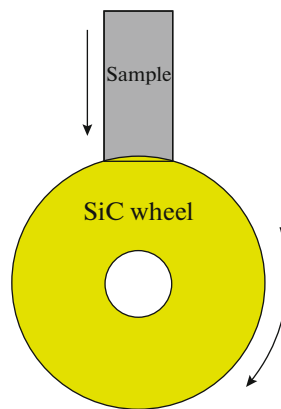
Using cBN (particle size 1–3  $\mu\text{m}$ , purity 99.9%) as raw materials, WC (particle size 1–3  $\mu\text{m}$ , purity 99.9%), B<sub>4</sub>C (particle size 2–3  $\mu\text{m}$ , purity 99.9%) and Al<sub>2</sub>O<sub>3</sub> (particle size 1.5  $\mu\text{m}$ , purity 99.9%) is the binding agent. Ingredients according to a certain quality ratio, as shown in Table 1. Adding WC balls and *n*-heptane as the ball milling media in the stainless steel ball milling tank, grind the mixed materials on a planetary ball mill at 250 rpm for 120 minutes, and then dry them in a drying oven at 100°C for 8 hours. The mixed powder is vacuum treated at high temperature, filled with a cylindrical molybdenum cup with a diameter of 35, and sintered at high temperature and ultra-high pressure on a six-sided top press. The pressure during sintering is 6 GPa, sintering temperatures is 1250–1350–1450–1550°C, and the holding time is 700 s.

The sintered PCBN sample is ground and polished with a metallographic grinder. Using X-ray diffraction (X'Pert PRO, PANalytical, Netherlands) to determine the final phase after sintering and analyze the occurrence of corresponding chemical reactions during the sintering process. The porosity of PCBN samples were determined by Archimedes drainage method. Using the Vickers microhardness tester to determine the microhardness of PCBN (load 5 kg, holding time is 15 s), select 5–7 points evenly at different positions of the sample for testing (MH-6). Characterize the cross-sectional structure and compactness of PCBN samples by scanning electron microscope (FSEM) (S-4800, Hitachi High-Technologies Corporation/ Oxford Instruments, Japan/England). The flexural strength is measured with a universal testing machine (model AG-1 50KN), the span is 10 mm, and the loading speed is 0.5 mm/min. The grinding performance of the sintered samples was tested using an abrasion ratio tester through the grinding between the SiC grinding wheel and the sintered samples according to “JB/T 3235–1999 Method for determination of the abrasion ratio of the artificial diamond sintered body.” The abrasion ratio was defined as the ratio between the weight loss of the grinding wheel wear and the abrasion loss of the samples. In our experiments, the weight loss of the grinding wheel and the samples was measured with a common scale and the one over ten thousand scale, respectively. During our tests, each sample was tested for 3 min, with the linear velocity of the grinding wheel of 25 m/s and the frequency of the pendulum of the workbench of 40/min, Fig. 1. shows the schematic of the process.

## 3. RESULTS AND DISCUSSION

### 3.1. X-ray Diffraction Analysis

Figure 2 shows the XRD patterns of PCBN samples at different sintering temperatures. It can be seen from the figure that at the temperature of 1250–1550°C, the types of products in PCBN samples are different. The main difference are the increase and decrease of WB and WB<sub>2</sub> content. The B<sub>4</sub>C added in the



**Fig. 1.** Abrasive ratio measurement diagram.

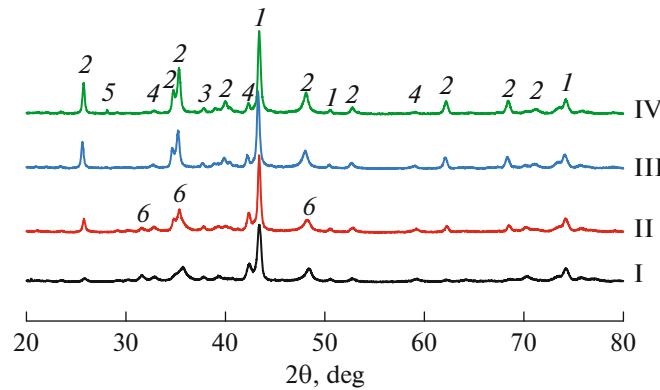


Fig. 2. XRD patterns of PCBN samples at different sintering temperatures (1, BN; 2,  $\text{WB}_2$ ; 3,  $\text{Al}_2\text{O}_3$ ; 4, WB, 5, C; 6, WC).

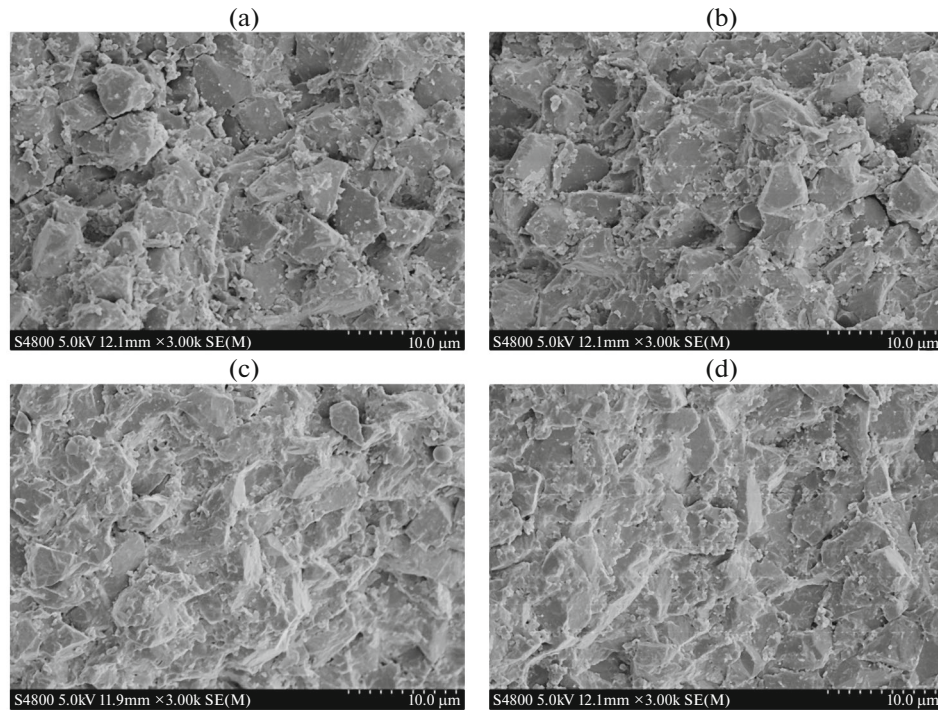
raw material has been completely decomposed during the sintering process, and chemically reacted with the internal substances of the sintered body and converted into other substances. When sintering at 1250 and 1350°C, more WC was detected in the XRD pattern, and the WC gradually disappeared as the temperature increased. It is speculated that WC slightly reacts with  $\text{B}_4\text{C}$  inside the system during low-temperature sintering, and a small amount of WB and  $\text{WB}_2$  are generated. The gradual increase in temperature aggravates the chemical reaction inside the sintered body. WC completely reacts to form  $\text{WB}_2$  and WB. W–B series compounds have the characteristics of high melting point, high conductivity, high hardness and high oxidation resistance, and have been widely used [12–16]. It can be seen from the XRD pattern that the diffraction peak of WB gradually weakens with the increase of temperature, and the diffraction peak of  $\text{WB}_2$  gradually strengthens, indicating that the increase of temperature promotes the diffusion of B atoms in the system and accelerates the reaction of B atoms with WB. Only a small amount of C was detected in the system, and it is speculated that C atoms and O atoms combined to generate  $\text{CO}_2$ , which was discharged from the sintered body.

### 3.2. Microstructure Analysis

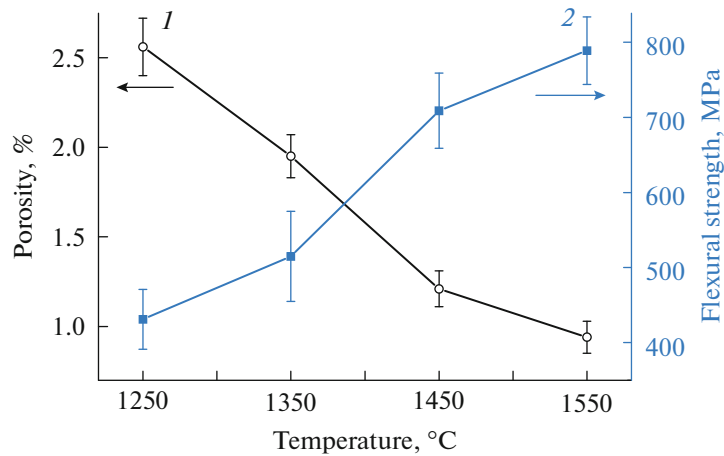
Figure 3 shows the SEM images of PCBN samples synthesized by the cBN–WC– $\text{B}_4\text{C}$ – $\text{Al}_2\text{O}_3$  system at different sintering temperatures. The PCBN sample after sintering was ground and polished, and the flexural strength test was carried out with a universal material mechanics testing machine. Take the sample after the flexural strength test for section scanning analysis. It can be seen from the SEM image that the distribution of cBN particles and binders in the sample is ideal, and there is no large number of cBN particles or binders gathered together. When sintering at low temperatures of 1250 and 1350°C, obvious holes and gaps were found in the section, indicating that the sintering temperature was low at this time, the sample was not fully sintered, and the bonding agent was loose and not completely melted. It also shows that the cBN particles and the cBN particles cannot be completely bonded together, and the bonding agent needs to be used to achieve bonding. As the temperature increases, the particles in the system begin to gradually melt, and the chemical reaction between each other strengthen. It can be seen from the SEM image that the compactness of the sample gets better and better as the temperature rises, and the cBN particles achieve internal densification through the connection and filling of the newly generated adhesive.

### 3.3. Porosity and Flexural Strength Analysis

Figure 4 shows the porosity and flexural strength of PCBN samples synthesized by the cBN–WC– $\text{B}_4\text{C}$ – $\text{Al}_2\text{O}_3$  system at different sintering temperatures. It can be seen from Fig. 4 that as the temperature increases, the porosity of the sample gradually decreases. When the sintering temperature is 1250°C, the porosity is 2.56%, and when the sintering temperature is 1550°C, the porosity is 0.94%. During the sintering process, the amount of liquid phase has a greater impact on the densification of the sample. During low-temperature sintering, the driving force for sintering is small, the sinterability of the sample is poor, and the amount of liquid phase produced is small, which is not conducive to the densification of the sample. As the temperature increases, the mobility of the substance increases, and the amount of liquid phase in the molten state inside the sample begins to increase, which promotes the flow of powder particles



**Fig. 3.** The fracture surface images of the PCBN prepared at different synthesis temperature (a) 1250°C, (b) 1350°C, (c) 1450°C, (d) 1550°C).

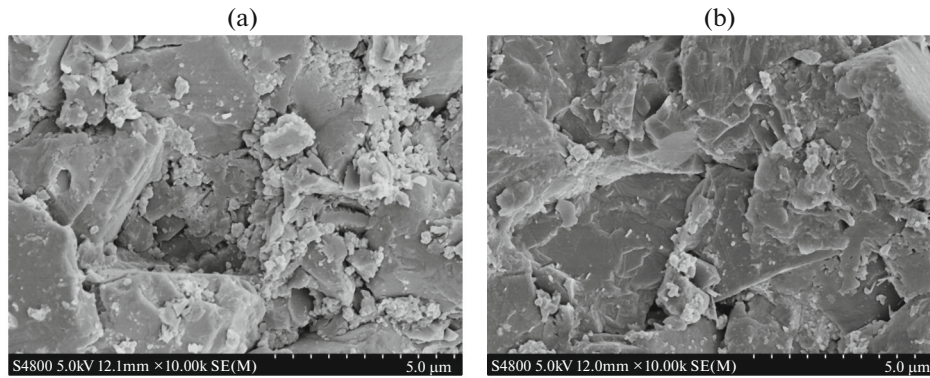


**Fig. 4.** The porosity (1) and flexural strength (2) curves of PCBN at different sintering temperatures.

inside and improves the compactness of the sample. It can be seen from the figure that the flexural strength of PCBN samples gradually increases with the increase of sintering temperature. Increased from 431.2 to 789.6 MPa. According to Griffith fracture theory, the flexural strength of a material has the following relationship with the size of the defect [17]:

$$\sigma_f = A \left( \frac{E\gamma}{c} \right)^{\frac{1}{2}}$$

In the formula:  $\gamma$  represents the fracture energy;  $\sigma_f$  represents the fracture stress;  $c$  represents the defect size;  $E$  represents the modulus of elasticity;  $A$  is a constant meaningless, depending on the geometry of the sample and the defect. It can be seen from the relationship that the fracture strength of the material is



**Fig. 5.** The enlarged view of the fracture morphology of the PCBN sample synthesized by the cBN–WC–B<sub>4</sub>C–Al<sub>2</sub>O<sub>3</sub> system: (a) 1250°C, (b) 1550°C.

greatly affected by the size of the defect. Therefore, the change law of the strength of the PCBN sample is consistent with the change law of compactness. As shown in Fig. 5, it is the fracture morphology of PCBN samples synthesized by the cBN–WC–B<sub>4</sub>C–Al<sub>2</sub>O<sub>3</sub> system at 1250 and 1550°C sintering temperature. It can be seen from the figure that at lower temperatures, the internal structure of the PCBN sample is loose, there are a lot of pores, and the flexural strength between the particles is low, resulting in the strength of the sample being only 431.2 MPa. As the temperature rises, the pores inside the system are filled by the binder, the internal structure tends to be dense, the defect size is reduced, and the flexural strength is greatly improved, reaching a maximum of 789.6 MPa. Through observation, we can see that obvious grain boundaries and smooth crystal planes can be observed in the figure, indicating that all samples have intergranular fractures. As shown in Fig. 5b, the samples sintered at 1550°C have more obvious jagged grains during the fracture process. The presence of jagged crystal grains indicates that the interface between cBN and the binder is strong, and the crystal grains are difficult to fall off during the fracture process. The occurrence of transcrystalline fracture in the sample makes the flexural strength of PCBN significantly improved.

### 3.4. Hardness Analysis

Figure 6 shows the hardness curves of PCBN samples synthesized by the cBN–WC–B<sub>4</sub>C–Al<sub>2</sub>O<sub>3</sub> system at different sintering temperatures. Five Vickers indentations were pressed on the surface of each PCBN sample, and the final hardness value was obtained according to their average value. It can be seen from Fig. 6 that the microhardness of the sample increases with the increase of sintering temperature. Increased from 28.2 to 38.6 GPa, a large increase. We speculate that this result is attributable to the uneven and non-compact microstructure of the samples sintered at lower temperatures (for example, 1250 and 1350°C), which leads to lower hardness at low temperatures. Therefore, the hardness of the sample is greatly affected by the compactness of the sample. The higher the temperature, the tighter the internal structure of the sample and the higher its microhardness. At the same time, according to relevant literature reports, the hardness of transition metal boride WB<sub>2</sub> can reach 40 GPa, which is a superhard material second only to diamond and cBN. It can be seen from XRD analysis that the amount of WB<sub>2</sub> gradually increases as the temperature increases, and its crystallinity is getting better and better, so the crystallinity and content of WB<sub>2</sub> are the key factors affecting the hardness of the sample. Therefore, the hardness of PCBN samples gradually increased, and the hardness of PCBN samples reached 38.6 GPa at 1550°C.

### 3.5. Abrasion Ratio Analysis

Figure 7 shows the abrasion ratio curves of PCBN samples synthesized by the cBN–WC–B<sub>4</sub>C–Al<sub>2</sub>O<sub>3</sub> system at different sintering temperatures. The wear ratio is an important indicator for testing the wear resistance of PCBN composite materials for cutting tools, and it can directly reflect whether the PCBN material is fully sintered. In order to ensure the accuracy of the measurement, before and after the test, each sample is cleaned with an ultrasonic cleaner to remove impurities on the surface of the sample, and then dried in a drying oven to a constant weight, and then weighed. Each PCBN sample was tested 3 times, and the average value were taken as the final wear ratio. It can be seen from Fig. 7 that the wear



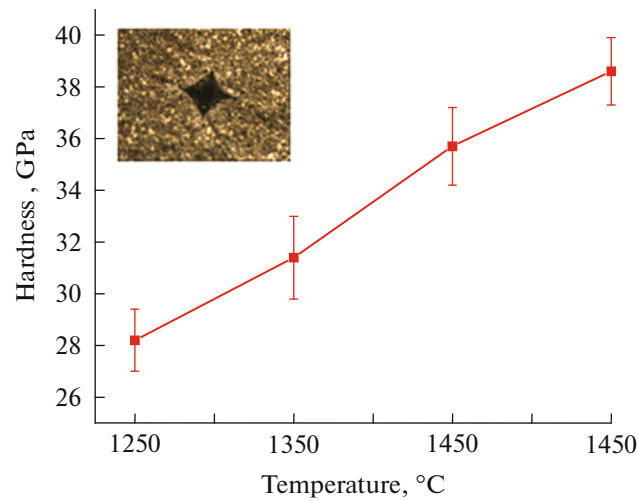


Fig. 6. The hardness of PCBN samples at different sintering temperatures.

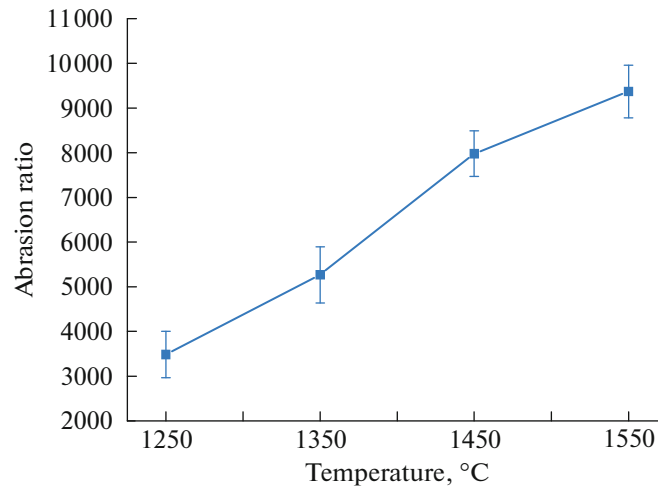


Fig. 7. The abrasion ratio of PCBN samples at different sintering temperatures.

ratio increases with the continuous increase of the sintering temperature, from 3485 to 9371. We speculate that this phenomenon is related to the pores and gaps in the sintered sample. When the sintering temperature is lower than 1350°C, the abrasion ratio is very low, because the bonding agent does not completely react and the bonding agent to the cBN particles is weak. During the abrasion ratio test, the cBN crystal grains are very easy to fall, which leads to a sharp drop in the wear resistance of PCBN. The abrasion ratio test result is consistent with the SEM observation result. When the sintering temperature increased to 1450 and 1550°C, the holding force of the binder on the cBN particles increased, and the cBN particles were not easy to fall off during the grinding process, so the wear ratio of the sample increased.

#### 4. CONCLUSIONS

This article mainly uses the WC–B<sub>4</sub>C–Al<sub>2</sub>O<sub>3</sub> system as a bonding agent to synthesize PCBN composite materials under high temperature and high pressure. The micro morphology, phase and mechanical properties of PCBN composites at different sintering temperatures were studied. The relevant conclusions are as follows:

- (1) PCBN composite materials are mainly composed of BN, WB<sub>2</sub>, WB, and Al<sub>2</sub>O<sub>3</sub>.

(2) When the sintering temperature is 1250–1350°C, the sinterability of the sample is poor and the internal structure is relatively loose. As the temperature increases, the internal pores and gaps gradually decrease, and the sample structure becomes more compact.

(3) When the sintering temperature is 1550°C, the comprehensive mechanical properties of PCBN composites are the best, with a microhardness of 38.6 GPa, a bending strength of 789.6 MPa and a wear ratio of 9371.

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#### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

#### REFERENCES

- Liu, Y.J., He, D.W., Wang, P., et al., Microstructural and mechanical properties of cBN-Si composites prepared from the high pressure infiltration method, *Int. J. Refract. Met. Hard Mater.*, 2016, vol. 61, pp. 1–5.
- Mettaya, K., Akihiko, I., Zhang, J.F., and Takashi, G., Densification and mechanical properties of cBN–TiN–TiB<sub>2</sub> composites prepared by spark plasma sintering of SiO<sub>2</sub>-coated cBN powder, *J. Eur. Ceram. Soc.*, 2014, vol. 34, pp. 3619–3626.
- Mo, P.C., Chen, C., Chen, J.R., Jia, G., Xie, D.L., Xiao, L.Y., Pan, X.Y., and Lin, F., Effect of sintering temperature on synthesis of PCBN in cBN–Ti–Al–W system, *Diamond Relat. Mater.*, 2020, vol. 103, art. 107714.
- Mckie, A., Winzer, J., Sigalas, I., Herrmann, M., Weiler, L., Rodel, J., and Can, N., Mechanical properties of cBN–Al composite materials, *Ceram. Int.*, 2011, vol. 37, no. 1, pp. 1–8.
- Yuan, Y.G., Cheng, X.Z., Chang, R., Li, T.H., Zang, J.B., Wang, Y.H., Yu, Y.Q., Lu, J., and Xu, X.P., Reactive sintering cBN–Ti–Al composites by spark plasma sintering, *Diamond Relat. Mater.*, 2016, vol. 69, pp. 138–143.
- Li, Y., Kou, Z., Wang, H., et al., High pressure sintering behavior and mechanical properties of cBN–Ti<sub>3</sub>Al and cBN–Ti<sub>3</sub>Al–Al composite materials, *High Pressure Res.*, 2012, vol. 32, no. 4, pp. 524–531.
- Kitiwan, M., Ito, A., Zhang, J., et al., Densification and mechanical properties of cBN–TiN–TiB<sub>2</sub> composites prepared by spark plasma sintering of SiO<sub>2</sub>-coated cBN powder, *J. Eur. Ceram. Soc.*, 2014, vol. 34, no. 15, pp. 3619–3626.
- Mckie, A., Winzer, J., Sigalas, I., et al., Mechanical properties of cBN–Al composite materials, *Ceram. Int.*, 2011, vol. 37, no. 1, pp. 1–8.
- Yuan, Y., Cheng, X., Chang, R., et al., Reactive sintering cBN–Ti–Al composites by spark plasma sintering, *Diamond Relat. Mater.*, 2016, vol. 69, pp. 138–143.
- Li, L.Q., Zhao, Y.B., Sun, K., et al., Composition, microstructure and mechanical properties of cBN-based composites sintered with AlN–Al–Ni binder, *Ceram. Int.*, 2018, vol. 44, pp. 16915–16922.
- Li, M.-L., Liang, L.-X., Wang, H.-L., et al., Processing and properties of PcBN composites fabricated by HPHT using PSN and Al as sintering additive, *Rare Met.*, 2020, vol. 39, no. 2, pp. 570–576.
- Sun, H., *Synthesis and Characterization of Tungsten Disulfide and Tungsten Borides*, Jilin University, 2017.
- Ingole, S., Liang, H., Usta, M., et al., Multi-scale wear of a boride coating on tungsten, *Wear*, 2005, vol. 259, no. 7, pp. 849–860.
- Wang, C.C., *The Mechanical Properties of Tungsten Borides and Nitrides Prepared at High Pressure and High Temperature*, Jilin University, 2017.
- Wang, C.C., Tao, Q., Ma, S.L., et al., WB<sub>2</sub>: not a superhard material for strong polarization character of inter-layer W–B bonding, *Phys. Chem. Chem. Phys.*, 2017, vol. 19, no. 13, pp. 8919–8924.
- Hao, X.F., Xu, Y.H., Wu, Z.J., et al., Low-compressibility and hard materials ReB<sub>2</sub> and WB<sub>2</sub>: Prediction from first-principles study, *Phys. Rev. B*, 2006, vol. 74, no. 22, pp. 4070–4079.
- Gao, J.M., *Mechanical Properties of Materials*, Wuhan: Wuhan University of Technology Press, 2004.