Slip Casting and Pressureless Sintering of Boron Carbide and Its Application to the Nuclear Field

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Sintered boron carbide is famous for its ultimate lightness, rigidity and hardness. But boron carbide is difficult to sinter, so has been manufactured industrially by hot pressing only. So it is very expensive, and its shape and size are restricted to small tile or the like. In this study, new method of slip casting and pressureless sintering of boron carbide is proposed. This method realize crystal nano-structure without grain boundary layer, which makes its mechanical properties no less than hot-pressed one. This new method set boron carbide ceramics free from restriction of size and shape. And boron carbide is also famous for its ability of neutron absorption or shielding. This boron carbide with free size and shape is applicable to this nuclear field, and neutron shielding design for some nuclear installations has begun to be changed.

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1. Introduction

Boron carbide ceramics, famous for its ultimate rigidity, lightness and hardness among industrial materials, is not widely utilized because it is difficult to sinter densely. So commercial boron carbide product is made by hot-pressing. And its application is limited due to its high cost and restriction of size and shape.

Pressureless sintering of boron carbide with various additives has been researched in these thirty years. As to inorganic or metallic additives, Cr, Co, Ni,1 glass, alumina,2,3 Si, Al, Mg, TiB2, CrB2,4 Al alloys,5 Be2C,6 SiC + Al,7 B + C,8 W3B12,9 TiB2 + C,10 Al, TiB2, AlF3, MgF2, Mg,11 polycarbosilane,12 ZrO2,13 TiC, VC, Cr7C3 and WC14 are effective in densification. Generally speaking, such additives cause an exaggerated grain growth, low mechanical properties, high impurity content or difficulty in sintering condition control. So main research of sintering additive has been directed to carbon, carbon precursor or small amount of other additives thereto. Suzuki et al.15 observed that amorhous carbon addition is effective in nearly theoretical densification of boron carbide, and proposed excess carbon at the grain boundaries would inhibit grain growth and decrease melting point to B4C–C eutectic points. Schwetz et al.15,16 and Prochazka et al.17,18,19 used phenolic resin as a carbon precursor or carbon black and proposed that carbon would act as an inhibitor of surface-to-surface mass transport and observed graphite crystal at the grain boundaries. And our research group tried phenolic resin precoating as a carbon precursor application method for even forming and sintering.20

So far the sintering mechanism of Boron carbide with carbon additive has been qualitatively proposed, but it lacks quantitative analysis from powder to sintered body and nano-structure analysis. So the relation of mechanical properties and pressureless sintering mechanism has not been investigated, and pressureless sintered boron carbide has not been regarded so reliable as hot-pressed one.

In this study, new method of slip casting and pressureless sintering of boron carbide and its quantitative sintering mechanism is proposed. It makes the mechanical properties of pressureless sintered boron carbide no less than hot-pressed one. This method will improve pressureless sintering of boron carbide promising for practical applications. One of these applications is to the nuclear field, in which neutron absorption of boron is utilized.21 And recent application example is introduced in this study.

2. Experimental

Boron carbide powder (D50 = 0.75 μm) precoated with various amount of phenolic resin was mixed by agitator with water (solvent) and polycarboxylic acid ammonium (defloculant; 0.3 wt% of boron carbide powder) to make a slurry. The slurry was poured into porous resin mold, and was deposited by drain casting under the pressure of 1.8 MPa to form a green body of 80 mm diameter and 10 mm thickness. The deposited green body was demoulded and dried. The dried green body was heated under vacuum atmosphere to 1473 K, then under argon atmosphere to sintering temperature. Sintering temperature was 2523 K or 2573 K, and sintering time was four hours.

Bulk density (%) of the theoretical density of sintered body and dried green body was determined by Archimedes’ principle. Microstructure of sintered body was observed by transmission electron microscopy (TEM JEM–4000EX 400KV). Fractural strength of sintered body was determined by JIS–R–1601 using auto graph with four points support.

Quantitative chemical analysis of boron carbide powder was made by stepwise pressure alkali/acid decomposition/mannitol titration method22 and carbon analyzer (Horiba EMIA). Qualitative and quantitative crystal analysis of both boron carbide powder and pulverized sintered body was made by X-ray diffraction (XRD: MXP–18 Mac Science). To determine the lattice parameters, X-ray diffraction (XRD: RINT2200V Rigaku-Denki, CuKα, 40 kV, 50 mA) was used.

3. Results and discussion

Figure 1 shows the effect of phenolic resin addition on the densification of the sintered body at 2573 K. Amount of resin addition is calculated by subtracting resin amount dissolved in the filtrate in slip casting process. The density of dried green body was constantly about 60% regardless of resin addition amount. Sintered body density was improved by resin addition, and maximum density of 98.5% was obtained by resin addition of about 7 wt%.

Figure 2 shows the microstructure of the sample with 7.9 wt% resin addition and sintered at 2523 K. Edged boron carbide grains with 2–4 μm size are tightly packed. And at the triple
points, there remained graphite crystals with 0.05–0.2 μm size. And Figure 3 shows the grain boundary of the same sample. Between boron carbide crystals, no boundary layer or amorphous layer is observed. It shows that main sintering mechanism is solid phase mass transport, especially boundary mass transport promoted by the carbon function as a surface-to-surface mass transport inhibitor.

To discuss carbon function while sintering, B/C molecular ratio of boron carbide crystal in the raw material powder was estimated as follows. Table 1 shows chemical formula of boron carbide powder. The total amount of carbon 20.49 wt% can be classified by carbon analyzer into two peaks. The first sharp peak around 800 K is supposed to be free amorphous carbon of 3.19 wt%, and the second broad peak in a higher temperature to be carbon content in boron carbide crystal of 17.3 wt%. And all of oxygen is supposed to exist as B2O3 and adsorbed water, and all of nitrogen is supposed to exist as BN.

Calculation from above results shows that the boron carbide powder contains boron carbide crystal with B/C molecular ratio of 4.76 and 3.19 wt% free carbon.

Figure 4 shows XRD patterns of raw material boron carbide powder and sintered sample with 7.9 wt% resin addition and 2573 K sintering. It is clear that graphite crystal is generated by sintering. And the amount of graphite was estimated to 2.47 wt% by XRD analysis.

By comparing weight loss by sintering sample of no resin addition with samples of various amounts of resin addition, the amount of carbon residue from resin addition and the amount of evaporated carbon from free carbon in raw material powder are calculated. And the remained carbon related to sintering reaction is supposed to be converted to graphite crystal or absorbed to boron carbide crystal. Calculation above shows that sintered sample with 7.9 wt% resin addition and 2573 K sintering contains boron carbide crystal with B/C

![Figure 1](image1.png)

**Fig. 1.** Effect of phenolic resin addition on the densification of the sintered body at 2573 K.

![Figure 2](image2.png)

**Fig. 2.** TEM image of the sample with 7.9 wt% resin addition and 2523 K sintering.

![Figure 3](image3.png)

**Fig. 3.** HR-TEM image of the grain boundary of the sample with 7.9 wt% resin addition and 2523 K sintering.

| Table 1. Chemical Formula of Boron Carbide Powder |
|---|---|---|---|---|---|---|---|---|---|---|
| B | C | O | N | Si | Al | Fe | Ti | Ca | Mg | K | Na |
| 75.52 | 20.49 | 2.96 | 0.62 | 0.28 | <0.01 | 0.03 | <0.01 | 0.06 | <0.01 | <0.01 | <0.01 |
molecular ratio of 4.02.

The crystal structure of boron carbide is known to be rhombohedral unit consisted of B\textsubscript{12} icosahedron linked by linear C\textsubscript{3} chains. But other than this stoichiometric B\textsubscript{12}C\textsubscript{3} (B\textsubscript{12}C\textsubscript{3}), many types with substitution of boron or carbon for another are known or discussed, and most widely accepted is B\textsubscript{13}C\textsubscript{2} with C–B–C linking chains. These B\textsubscript{4}C or B\textsubscript{13}C\textsubscript{2} have almost same XRD pattern as shown in Fig. 4, but slightly differs in lattice parameters. Our previous research\cite{20} shows that, by checking the hexagonal lattice parameters of raw material boron carbide powder and sintered sample, the relation of the lattice parameters and B/C ratios of powder and sintered sample harmonizes well with that of ASTM cards of B\textsubscript{12}C\textsubscript{2} (26–233) and B\textsubscript{13}C\textsubscript{2} (35–798).

These results illustrated in Figure 5 shows that raw material boron carbide powder is the mixture of B\textsubscript{12}C\textsubscript{3} and B\textsubscript{13}C\textsubscript{2}, and free amorphous carbon. By sintering, the solid solution of boron carbide absorbs the amorphous carbon and that from converted resin, and grain growth and densification progress by boundary mass transport. Finally it is converted to almost stoichiometric B\textsubscript{12}C\textsubscript{3}. And unabsorbed amorphous carbon is converted to graphite crystal, which remains at triple point.

This sintering mechanism is characterized that no boundary layer or amorphous layer is remained between boron carbide crystals although so much sintering aid, amorphous carbon, is added. This characteristic is connected with higher mechanical properties. The fexural strength of the sample with 7.9 wt% resin addition and sintered at 2573 K is 500 N/mm\textsuperscript{2}. On the other hand, flexural strength of the hot-pressed boron carbide in the market is only 400–450 N/mm\textsuperscript{2} although it contains almost no pore.

For this quantitative carbon control, even existence of amorphous carbon around boron carbide powder in sintering process is indispensable. And this evenness can be achieved by application of resin precoated powder to slip casting process. This resin functions as forming aid, and is converted to amorphous carbon, then functions as sintering aid, and is absorbed to boron carbide crystal with no grain boundary layer at last.

4. Application to the nuclear field

Boron carbide is famous for its ability of neutron absorption or shielding. This ability comes from the neutron absorbing function of boron ten which is contained 18.8% in natural boron.

![Fig. 5. Pressureless sintering mechanism of boron carbide.](image)

\[ ^7\text{B} + ^1\text{n} (\text{neutron}) \rightarrow ^3\text{He} + ^3\text{Li} + 2.4 \text{MeV} \]

And boron carbide has largest boron contents among industrial structural materials. So hot-pressed boron carbide tile has been partly applied to the spots where high neutron absorbing ability is requested. But of course combination of small tile cannot be fit to various application. So main neutron shielding method of nuclear installation is enclosing of the neutron source by various materials such as cement, metal and plastics containing boron carbide powder. But adding ratio of boron carbide powder to such materials is restricted to 3–15\% for not spoiling the original material properties. So its neutron shielding ability is so inferior that the neutron source is covered heavily, for example cement of several meters thickness.

Appearance of pressureless sintered boron carbide parts with small restriction of size and shape has been changing this situation. Such thick enclosing is no longer needed, and compact boron carbide shielding has been changing the design of some nuclear installations.

Figure 6 shows the neutron shielding test result measured by Japan Atomic Energy Research Institute.\cite{31} Neutron source of this test is thermal neutron 0.2 nm from JRR–3M (direct neutron beam in Figure 6). Neutron shielding ability was compared between packed powder and sintered boron carbide. Boron carbide powder is often used for shielding neutron packed in the container of requested shape. But Figure 6 shows such packed powder is much more inferior to sintered one for shielding neutron. And pressureless-sintered and hot-pressed boron carbide have almost no difference in neutron shielding ability.

Figure 7 shows the example of neutron shielding parts of slip-casted and pressureless-sintered boron carbide. This is ap-

![Fig. 6. Comparison of neutron shielding ability.](image)
applied to the neutron detector shield of neutron topography installed in JRR–3M of Japan Atomic Energy Research Institute Tokai. By this sintered boron carbide application, neutron background decreases in more than 2 figures to compare with packed boron carbide powder unit, so precise analysis can be achieved. Neutron is very useful for such analytic apparatus, medical instruments and nondestructive inspection instrument, but it was not utilized widely because shielding of very harmful neutron is difficult so far. Sintered boron carbide has begun to be applied to such neutron utilizing instruments. And next step will be the application to large scaled neutron source such as radioactive waste disposal institution or nuclear power plant.

5. Conclusions

Pressureless sintering mechanism of boron carbide is that boron rich boron carbide crystal mainly comprising substitutional solid solution absorbs amorphous carbon from converted sintering aid and that from powder itself, and is sintered to almost stoichiometric B₄C by boundary mass transport with grain growth and densification. And this sintering mechanism is characterized that amorphous carbon does not remain at the grain boundary, but exist at triple points converted to graphite crystal, resulting in excellent mechanical properties.

This quantitative process control can be realized by application of resin precoated powder to slip casting process. And this slip casting and pressureless sintering process makes boron carbide ceramics applicable to various industrial fields, one of which is nuclear field. Boron carbide is excellent in neutron absorbing ability, so sintered boron carbide with large or complicated shape has begun to be utilized for neutron shielding parts.

References