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SINTERING BEHAVIOR OF ULTRAFINE SILICON CARBIDE POWDERS OBTAINED BY VAPOR PHASE REACTION

Yasuzo Okabe, Kenji Miyachi, Junichi Hojo, and Akio Kato

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The sintering behavior of ultrafine SiC powder with average particle size of about 0.01-0.06 microns produced by a vapor phase reaction of the Me₄Si-H₂ system was studied at the temperature range of 1400-2050°C. It was found that the homogeneous dispersion of C on SiC particles is important to remove the surface oxide layer effectively. B and C had an inhibitive effect on SiC grain growth.
The sintering behavior of $\gamma$-SiC powders with a mean particle size of 0.01-0.06 $\mu$m which were synthesized by $(\text{CH}_3)_4\text{Si-H}_3$ vapor phase reaction (1200-1400°C) was studied at 1400-2050°C. There was a large reduction in the weight of sintered units in a vacuum due to decomposition and vaporization of the SiC. However, decomposition can be controlled at a temperature of even 2050°C by introduction of argon (=300 mmHg) to the atmosphere. However, particle growth of the SiC occurred and densification is not promoted. When 1-2 wt% of both boron powder and carbon powder are added, a sintered unit with a relative density of 90% or more is obtained by sintering at normal pressure and 2050°C. Furthermore, densification up to a density of 97% or more is possible at 2050°C by adding boron only to SiC powders whose chemical composition (C/Si molar ratio) has been adjusted so that the proper amount of excess carbon is contained. This shows that the carbon that separated from the vapor phase reaction is uniformly dispersed over the SiC particle surface and the particle surface oxide layer removal efficiency is therefore improved. Boron controls the particle growth of SiC. Carbon also controls particle growth.

1. Introduction

Improvement of thermal efficiency is an important problem in energy-saving measures. However, the basic point of these countermeasures is to improve the working temperature. Therefore, research and development of new super high temperature materials that can replace conventional thermal-resistant alloys is being emphasized. Of these, silicon carbide (SiC), which has a high thermal strength -1-
and is light weight and readily available, is another material that is preferred, along with silicon nitride (Si₃N₄). In comparison to Si₃N₄, SiC has poor thermal shock resistance [1]. However, it is strong at high temperatures [2] and is superior in oxidation resistance [3]. Moreover, it is said that it is a valuable material that is resistant to higher temperatures [4,5].

At the present time, studies are being carried out on the sinterability of SiC by normal pressure sintering, increased pressure sintering, and reaction sintering. However, increased pressure sintering is mainly being used to sinter SiC with a low thermal strength, high density and high strength [6]. Nevertheless, normal pressure sintering is the most suitable method for manufacturing large amounts of compacts with a high density and strength at a high efficiency.

SiC is hardly sinterable because it has the same strong covalent bonds as Si₃N₄. A high temperature of 2500°C and a high pressure of 20 kbar are necessary to sinter pure SiC powder to the theoretical density [7].

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Consequently, research has been carried out on various sintering agents. However, it has been reported that in 1975 Prochazka [8] showed that the addition of small amounts of boron and carbon has marked effects on the promotion of sintering. Therefore, these agents have been used in normal pressure sintering. Thus far, sintered units with a theoretical density of 95% or more have been obtained by normal pressure sintering at 2000-2200°C of γ-SiC powder with a specific surface area of 8 m²/g (particle diameter of 0.23 μm) synthesized by the vapor phase reaction method using a plasma torch [9] and a mixture of several percent of boron and carbon with γ-SiC powder [10] with a specific surface area of 1.7-87.2 m²/g that has been synthesized by making a silicon compound from carbon black. However, there is a problem with the sintering activity of fine SiC particles obtained by these methods. It is a known fact that vapor phase decomposition of alkylsilane halogenides, etc., silicon compound formation with carbon black, thermal decomposition of polycarbosilane and pulverization of γ-SiC particles are methods for preparing SiC powders [4]. When the crude powder is activated by pulverization of SiC powder and the amount of

agent added is reduced, a strong sintered unit with properties superior to those of SiC only can be obtained. Moreover, there is a marked improvement in the strength of the unit with a reduction in crystal particle diameter\textsuperscript{[11]}. However, it is necessary to obtain a fine crude powder to obtain a fine structure.

The authors have studied the synthesis of SiC powders by the vapor phase reaction method and have reported that SiC fine powders with a good dispersability and a powder particle diameter of 0.1 µm or less can be produced by the vapor phase reaction using \((\text{CH}_3)_4\text{Si-H}_2\)\textsuperscript{[12]} and \(\text{SiH}_4-\text{CH}_4-\text{H}_2\)\textsuperscript{[13]}. In this research the authors have carried out normal pressure sintering of \(\gamma\)-SiC fine powder with a mean particle diameter of 0.01-0.06 that has been synthesized by the vapor phase reaction method using \((\text{CH}_3)_4\text{Si-H}_2\) and have studied the effects of particle size and chemical composition on sinterability and the effects of adding boron and carbon as the agents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation conditions</th>
<th>Properties</th>
<th>Median diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>((\text{CH}_3)_4\text{Si-H}_2) (in mol)</td>
<td>C/Si</td>
</tr>
<tr>
<td>S-1</td>
<td>1200</td>
<td>2</td>
<td>1.03</td>
</tr>
<tr>
<td>S-2</td>
<td>1250</td>
<td>2</td>
<td>1.03</td>
</tr>
<tr>
<td>S-3</td>
<td>1300</td>
<td>2</td>
<td>1.03</td>
</tr>
<tr>
<td>S-4</td>
<td>1350</td>
<td>2</td>
<td>1.07</td>
</tr>
<tr>
<td>S-5</td>
<td>1100</td>
<td>2</td>
<td>1.08</td>
</tr>
<tr>
<td>S-6</td>
<td>1200</td>
<td>8</td>
<td>1.14</td>
</tr>
<tr>
<td>S-7</td>
<td>1300</td>
<td>8</td>
<td>1.12</td>
</tr>
<tr>
<td>S-8</td>
<td>1200</td>
<td>6</td>
<td>1.18</td>
</tr>
</tbody>
</table>

\(\#\) Total gas flow rate: S-1-5: 1'000 ml/min, S-6: 300 ml/min, S-7, 8: 400 ml/min.

\(\text{b)}\) Oxygen content of powders was calculated by subtracting the silicon, carbon and H\textsubscript{2}O contents from the sample weight.


2. Experimental Method

2.1 Sintering Materials

SiC powder was synthesized by vapor phase reaction of \((\text{CH}_3)_4\text{Si-H}\) at 1200-1400 °C \([12]\). The chemical composition and particle size were adjusted by varying the reaction temperature, \((\text{CH}_3)_4\text{Si}\) concentration, and total gas flow. The synthesis conditions and properties of the crude powders are shown in Table 1. The powder that was produced was observed under a transmission-type electron microscope (TEM) and the particle diameter was determined. TEM micrographs of powders S-1 and S-3 are shown in Figure 1. The particle diameter distribution is narrow and the particles are round. According to X-ray diffraction, the powders were α-SiC. However, the diffracted rays had crystallinity over a wide region. The amount of carbon was determined by the combustion method and the amount of silicon was determined by the oxidation weight method. The insufficient component of the substance was made the amount of oxygen. Fe, Al, Mg, and Cu (metallic content of impurities was less than 100 ppm or less) were detected as impurities by spectrometry.

The boron powder that was added had a particle diameter of 0.13 μm and was amorphous (Wako Junyaku). The carbon powder was synthesized by thermal decomposition of \(\text{CH}_4\) in nitrogen at 900-1200 °C and had a mean particle diameter of 0.14 μm. These powders were mixed with the SiC powder after ultrasonic wave dispersion in ethanol. Moreover, binder pitch (A-200 made by Ashland) was also used as the carbon additive.
Table 2  Sintering data of undoped β-SiC powders

<table>
<thead>
<tr>
<th>Run</th>
<th>Sample</th>
<th>Air pressure (mbar)</th>
<th>Sintering temperature (°C)</th>
<th>$d_{p}\text{a)}$ ($%$)</th>
<th>$d_{r}\text{a)}$ ($%$)</th>
<th>$\Delta L/L_0\text{b)}$ ($%$)</th>
<th>$\Delta W/W_0\text{c)}$ ($%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S-1</td>
<td>0</td>
<td>1750</td>
<td>33</td>
<td>31</td>
<td>4</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>S-1</td>
<td>0</td>
<td>1900</td>
<td>32</td>
<td>27</td>
<td>7</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>S-1</td>
<td>100</td>
<td>1750</td>
<td>30</td>
<td>31</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>S-1</td>
<td>100</td>
<td>2100</td>
<td>30</td>
<td>31</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>S-1</td>
<td>310</td>
<td>2650</td>
<td>30</td>
<td>32</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>S-1</td>
<td>310</td>
<td>2050</td>
<td>39b)</td>
<td>40</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>7</td>
<td>S-1</td>
<td>310</td>
<td>2050</td>
<td>29</td>
<td>30</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>S-2</td>
<td>310</td>
<td>2050</td>
<td>39b)</td>
<td>40</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>9</td>
<td>S-3</td>
<td>310</td>
<td>2050</td>
<td>39b)</td>
<td>41</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

$d_{p}$: Green density of compact, $d_{r}$: Relative density of sintered body, $\Delta L/L_0$: Linear shrinkage, $\Delta W/W_0$: Weight loss.

a) Based on theoretical density of β-SiC (3.21 g/cm³).

b) Rubber-pressed compact.

2.2 Formation and Sintering

The powder materials were made using a conventional pill molding device. Approximately 150 mg of the sample was pulverized slightly after molding under increased pressure (3 t/cm²) to obtain a particle. This was then molded under increased pressure (0.5 t/cm²) in a mold coated with oleic acid. The pellet dimensions were a diameter of 10 mm and thickness of approximately 2 mm. Furthermore, in order to obtain a high density mold, the majority of the samples were obtained by rubber pressing (5 t/cm²) of the metallic press molds. The relative density of the molds was approximately 30% with the mold-type press.
Fig. 2 Effect of additives on sintering of $\beta$-SiC powders

Sample: S-1
Additives:
- $\bullet$, $\Delta$: Boron powders
- $O$, $\Delta$: Carbon powders in a presence of 2 wt% boron powders

Green density of compact: ca. 30%.
Sintering conditions:
- Temperature: 2000~2050°C, Time: 30 min, Heating rate: 20°C/min, Ar pressure: ca. 300 mmHg

Fig. 3 Effect of the addition of boron powder on sintering of $\beta$-SiC powder in a presence of 2 wt% carbon powder

Green density of compact:
- $O$, $\bullet$: ca. 30%, $\bullet$, $\Delta$: ca. 40% (by rubber pressing)
Sample and sintering conditions are the same as in Fig. 2.
and approximately 40% with the rubber pressure mold. The oleic acid that adhered to the surface of the mold was removed by heating in hydrogen at 600°C prior to sintering.

Sintering was carried out in a high frequency induction furnace that used a quartz reaction tube and molybdenum susceptor. The pellets were placed in a graphite container and heated to a maximum of 1000°C in a vacuum ($10^{-3}$ mm Hg) or argon. After the samples were heated to 1400°C in the vacuum, they were degassed. Argon was then introduced to the system. The sample temperature was determined using a thermometer.

2.3 Various Measurements

The dimensions of the molds and sintered units were measured using a cassetometer (reliability of 0.01 mm). The bulk density was determined from the dimensions and weight. Moreover, the relative density of some of the sintered units was determined using water as the immersion liquid (deviation of ±1%). The structural phase of the sintered units was studied by X-ray diffraction (CoKα rays). The fine structure was observed under a scanning electron microscope (SEM).

3. Results

3.1 Sinterability of SiC Powder with No Additives

The sinterability of SiC powder only to which no agents were added was studied in a vacuum and an argon atmosphere. The results are shown in Table 2. By means of sintering of sample S-1 in a vacuum (runs 1 and 2), a compact sintered unit was obtained. However, there was a large reduction in weight, and density also decreased. The inside of the sintered unit was a pale yellow. However, the formation of graphite
on the surface of the unit was noted by X-ray diffraction. The reduction in weight increased with an increase in temperature and the amount of graphite that was produced also increased. The large reduction in weight in a vacuum appears to be due to decomposition and vaporization of the SiC \[14\].

Next, when argon was introduced in order to suppress decomposition and vaporization of the SiC, the reduction in weight was restricted, as shown in Table 2, and the surface and inside of the S-1 sintered unit were pale yellow. However, the density of the sintered unit did not increase by a large extent. Moreover, even though the density was increased by rubber pressing (run 6), the sinterability of the product was not improved. The same results were obtained by sintering of samples S-2 and S-3 in argon. The powder molds made from samples S-1 - S-3 were all black. However,

[14] Drowhart, et al. studied α-SiC by qualitative analysis. The main vaporization molecules and their equilibrium vapor pressure (2149°K) appear to be Si: \(2.1 \times 10^{-5}\) atm., SiC: \(1.9 \times 10^{-6}\) atm., and SiC: \(1.4 \times 10^{-1}\) atm. However, it has also been reported that the equilibrium vapor pressure of Si, SiC, and SiC are 10-15 times those reported by Drowart, et al. \[15\].


the inside and surface of sintered units S-2 and S-3 were black instead of yellow. Although a large amount of oxygen was present in S-1 and the liberated carbon was removed by oxidation during sintering, S-2 and S-3 contained little oxygen and the liberated carbon therefore remained, even after sintering. Therefore, the difference in color appears to be due to a difference in the amount of liberated carbon.

As was previously mentioned, sinterability is poor, even when fine SiC powder is used as the starting material alone. However, as can be seen from the micrographs of the sintered units in Figure 1, particle growth up to 0.7 μm and 1 μm accelerated by sintering in a vacuum at 1750 and 1900°C respectively. Furthermore weak 2θ (CoKα) diffracted rays from β-SiC were observed near 40° with sintered units that had been obtained from S-1 in argon at 2050°C.

Table 3  Effect of the addition of binder pitch on sintering of β-SiC powder

<table>
<thead>
<tr>
<th>Carbon source</th>
<th>Solvent</th>
<th>Temperature of mixing</th>
<th>Carbon added</th>
<th>Sintering data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(°C)</td>
<td>(%)</td>
<td>d, (%)</td>
</tr>
<tr>
<td>Carbon powder</td>
<td>-</td>
<td>2.0</td>
<td>56</td>
<td>6</td>
</tr>
<tr>
<td>Binder pitch</td>
<td>Benjene</td>
<td>Room temperature</td>
<td>2.2</td>
<td>56</td>
</tr>
<tr>
<td>Binder pitch</td>
<td>Tetrahydrofuran</td>
<td>Room temperature</td>
<td>2.3</td>
<td>68</td>
</tr>
<tr>
<td>Binder pitch</td>
<td>Tetrahydrofuran 50-50</td>
<td></td>
<td>2.2</td>
<td>90</td>
</tr>
</tbody>
</table>

a) Carbon content determined by combustion method. Binder pitch added was carbonized by heating up to 700°C in helium (carbon yield: ca. 80%).
b) Based on theoretical density of β-SiC (3.21 g/cm³).
Table 4 Sintering data of doped β-SiC powders

Boron added: 1 wt%, Green density: ca. 40%. (by rubber pressing)

Sintering conditions:
Temperature: 2050°C, Time: 30 min, Heating rate: ca. 20°C/min, Ar pressure: ca. 300 mmHg

<table>
<thead>
<tr>
<th>Sample</th>
<th>(d_1) (%)</th>
<th>(\Delta L/L_0) (%)</th>
<th>((JW/W_0)_a) (%)</th>
<th>((JW/W_0)_{gb}) (%)</th>
<th>((C/Si)_{a}) (in mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>48</td>
<td>7</td>
<td>7</td>
<td>5</td>
<td>0.95</td>
</tr>
<tr>
<td>S-2</td>
<td>97(97)</td>
<td>28</td>
<td>4</td>
<td>4</td>
<td>0.96</td>
</tr>
<tr>
<td>S-3</td>
<td>97(96)</td>
<td>25</td>
<td>3</td>
<td>4</td>
<td>0.97</td>
</tr>
<tr>
<td>S-4</td>
<td>95(94)</td>
<td>25</td>
<td>2</td>
<td>4</td>
<td>1.01</td>
</tr>
<tr>
<td>S-5</td>
<td>92(91)</td>
<td>21</td>
<td>2</td>
<td>4</td>
<td>1.03</td>
</tr>
<tr>
<td>S-6</td>
<td>98</td>
<td>25</td>
<td>6</td>
<td>4</td>
<td>1.11</td>
</tr>
<tr>
<td>S-7</td>
<td>91</td>
<td>24</td>
<td>3</td>
<td>7</td>
<td>1.14</td>
</tr>
<tr>
<td>S-8</td>
<td>75</td>
<td>20</td>
<td>3</td>
<td>5</td>
<td>1.10</td>
</tr>
</tbody>
</table>

\(d_1\): Relative density of sintered body, \(\Delta L/L_0\): Linear shrinkage, \((JW/W_0)_a\) : Weight loss observed, \((JW/W_0)_{gb}\) and \((C/Si)_{a}\) : Calculated weight loss and C/Si ratio on a basis of CO evolution due to the reaction of carbon with surface oxygen.

(a) \(d_1\) was based on theoretical density of β-SiC (3.12 g/cm³). The values in parentheses were determined by an immersion method using water as solvent.

Fig. 4 Variations of relative density and weight loss with sintering temperature in sintering of β-SiC powders

Sample:
1. O, △ : S-1 containing 1 wt% boron powder and 2 wt% carbon powder
2. ●, ▲ : S-2 containing 1 wt% boron powder
Green density of powder compact: ca. 40%
Sintering conditions:
Time: 30 min, Heating rate: ca. 20°C/min, Ar pressure: ca. 300 mmHg

Fig. 5 Variations of relative density and weight loss with sintering temperature in sintering of β-SiC powders

Sample:
B added: 1 wt%, Green density of powder compact: ca. 40%
Sintering conditions are the same as in Fig. 4.
3.2 Results of Adding Boron and Carbon

3.2.1 Addition of Boron Powder and Carbon Powder:

Densification does not occur when only SiC is added. Therefore, the effects of adding boron and carbon, which are typical agents that are used with SiC, were studied. S-1 was used as the crude powder. Sintering was carried out at 2000-2050°C in an argon atmosphere. The effects of adding boron powder were first studied. The changes in the relative density and reduction in weight of sintered units with the addition of boron powder are shown in Figure 2. When boron powder is added, the relative density increases slightly with 1-2 wt% of boron. However, the increase is small in comparison to the case where nothing is added. Then tests were carried out on changes with the amount of carbon powder added making the amount of boron powder that was added 2 wt%.

The results are shown in Figure 2. Densification is promoted with the simultaneous addition of boron and carbon and a sintered unit density of approximately 75% is obtained with approximately 2 wt% of carbon. However, more carbon prevents densification to a slight extent.

Next, the amount of boron added was varied while keeping the amount of carbon added at 2 wt%. The results are shown in Figure 3. Although the density of the sintered unit is low with carbon only, when 0.5 wt% of boron is added in the presence of the carbon, the density of the sintered unit is markedly improved. The density of a sintered unit containing approximately 0.5-1 wt% of boron is approximately 80%. The density of a sintered unit is approximately 90% when the mold density is increased by rubber pressing. The density of the sintered unit decreases when the amount of
boron added exceeds 2 wt%. As was previously mentioned, simultaneous addition of carbon and boron is efficient in sintering of sample S-1.

3.2.2 Addition of Carbon by Organic Compounds:

As was previously mentioned, carbon and boron are effective sintering agents. Consequently, when carbon is dispersed, strong accelerating effects can be anticipated. Therefore, an attempt was made to dissolve binder pitch as the carbon agent in benzene and tetrahydrofuran (THF) and then add the carbon uniformly to the SiC powder (S-1) [17]. The mixture was carbonized by heating to 700°C in helium (carbonization yield of approximately 80%).

The sinterability of this sample was studied by adding 1 wt% of boron powder and heating at 1900°C in argon. The results are shown in Table 3.

When carbon powder was added, density of the sintered unit was low at 1900°C. When binder pitch was added, there was no difference between the density of a sintered unit when benzene solvent with a low solubility was used and when no carbon powder was used. However, when THF solvent with a high solubility was used, the powder showed improved density at room temperature. However, density increased to 90% when the additive was added at 50-60°C (THF boiling point: 66°C). This fact shows that sinterability is improved when the carbon is uniformly dispersed.

Prochazka [8] also showed that when polymethylphenylene is used for the carbon agent, a sintered unit with a relatively high

[17] The benzene soluble component of binder pitch is 64.5% and the THF soluble component of binder pitch is 77.1% at normal temperature.
density can be obtained with an added amount that is less than carbon black. Therefore, it is clear that when carbon is added as the accelerator, the dispersion conditions have a strong effect on sinterability.

3.3 Adjustment of Amount of Carbon During Synthesis of SiC Powder

The amount of carbon contained in the powder that is produced can be controlled by the reaction conditions during the synthesis of SiC powder by an (CH₃)₄Si-H₂ vapor phase reaction [12]. In this case, the liberated carbon separates from the (CH₃)₄Si and is a byproduct of thermal decomposition of the hydrocarbons. Therefore, there is a strong chance that it will uniformly deposit on the SiC particle surfaces. Consequently, when the amount of carbon is controlled during vapor phase synthesis, the process whereby carbon is added can be eliminated and high sinterability can be obtained by uniform distribution of the carbon. Therefore, various SiC powders with different carbon contents were synthesized by varying the total flow of the reaction gas, the reaction temperature and the (CH₃)₄Si concentration. The synthesis conditions and properties of the SiC powders are shown in Table 1. The sintering results are shown in Table 4.

Sintering was carried out with 1 wt% of boron in an argon atmosphere at 2050°C. The amount of carbon did not change with a synthesis temperature of 1200-1300°C. However, it increased at a higher temperature. The amount of oxygen decreased with an increase in temperature. The density of the sintered unit increased markedly when the synthesis temperature was increased from 1200°C to 1250°C. Moreover, a relative density of 97% was obtained by synthesis at
1250-1300°C. The density decreased at a higher synthesis temperature.

S-6-8 samples were obtained by varying the mean particle diameter and carbon content with the \((\text{CH}_3)_4\text{Si}\) concentration and total gas flow. Although the C/Si molar ratio and O/Si molar ratio are approximately the same for S-6 and S-7, the sinterability of S-6, which has a small mean particle diameter, is high. This appears to be the result of the particle diameter of the SiC powder. On the other hand, there is a large difference in the sinterability of S-7 and S-8, which have the same mean particle diameters. Moreover, the sinterability of S-1, which has the smallest particle diameter, is low. These facts, the results of adding carbon in Figure 2, and the results of particle diameter show that the chemical
composition (excess carbon and oxygen contents) of the original powders and the particle diameter have a strong effect on sinterability.

In contrast to the fact that a density of 91% is obtained when carbon and boron are added to S-1 and heated at 2050 °C, the density of units sintered at 2050 °C after boron only is added to S-2, S-3 and S-6 is extremely high at 97% or more. According to the results of uniform addition of carbon by organic compounds shown in Table 3, it is clear that the carbon is uniformly dispersed due to restricted carbon contents during vapor phase reaction synthesis. Therefore, when boron was added by adding BCl₃ to the reaction system (reaction temperature of 1400 °C, (CH₃)₄Si=1.4%, BCl₃=0.1%), the SiC powder that was obtained provided a sintered unit with a high density of 95% by sintering at 1900 °C. Therefore, uniform addition of boron is also important. The uniform addition of boron is not being studied in detail.

3.4 Effects of Sintering Temperature

Changes in 5 types of sinters from samples 1-5 in Table 1 with regard to relative density of the sintered unit and the reduction in weight of the sintered unit were studied by varying the sintering temperature. Temperature was increased at a rate of 20-25 °C/min and the desired temperature was held for 30 minutes. The results of adding 1 wt% of boron and 2 wt% of carbon to S-1 and of adding 1 wt% of boron to S-2 are shown in Figure 4 and the results of adding 1 wt% of boron to S-3 - S-5 are shown in Figure 5.

Density curves were the same for S-1 to which boron and carbon had been added and S-2 to which boron had been added.
The densification rate of the sintered units increased markedly at 1900°C or more. On the other hand, in the case of S-3-5 to which boron powder had been added, densification suddenly proceeded near 1800°C, which is approximately 100°C lower than that seen with S-1 and S-2. The temperature properties therefore appear to be of two types. However, this appears to be due to a difference in the addition of carbon and to the carbon and oxygen contents of the samples.

The majority of the reduction in weight of sintered units occurs during degassing up to 1400°C in a vacuum. The reduction in weight during heating in argon at 1400°C or more is small. This appears to be due to the fact that CO is produced as a result of a reaction between impure oxygen and liberated carbon or bonded carbon. These reactions are more obvious at 1400°C or less.
3.5 Sintering Unit Structure

SEM micrographs of sintered units that were obtained by adding 1 wt% of boron to S-1 powder, adding no agent to S-1-3 powders, and adding 2 wt% of carbon to S-1 powder are shown in Figure 6. Densification does not occur when nothing is added to S-1. Particle growth is considerable as in the case with a vacuum (Figure 1). The particles are as large as $5 \mu m$. When boron is added to S-1, particle growth is restricted to $1 \mu m$ or less. When carbon powder is added, particle growth is also restricted and particle diameter is $0.5-4 \mu m$. However, adhesion at the particle surface occurs. Particle growth of sintered units made from S-2 and S-3 to which no agents were added was restricted to the same extent as that of S-1 powder to which carbon had been added. Moreover, thread-like adhesion was noted.

Changes in the fine structure of sintered units made of S-1 to which 1 wt% of boron and 2 wt% of carbon and were added sintered units of S-2 and S-3 to which 1 wt% of boron was added with changes in sintering temperature are shown in
Figure 7. With sintered units made of S-1, the particle diameter is approximately 0.2 μm when the sintering temperature is 1900°C (some of the particles are as large as 2 μm). However, the particles grow to 2-3 μm at 2050°C, where densification is accelerated. With sintered units of S-2 samples, the particles are usually less than 0.1 μm with a sintering temperature of 1600°C (Figure 7, S-2, A2). However, some particles grow to 0.5 μm (Figure 7, S-2 A1). The particle diameter at 1800 and 1900°C is 0.3 μm or less. Moreover, particle growth up to 3 μm occurs at 2050°C as in the case of S-1 samples. The particle diameter of S-3 samples is small in comparison to that of S-2 sintered units at 1600°C (less than 0.1 μm). Moreover, the particle diameter of S-3 at 1800°C is smaller than that of S-2 samples at 0.1 μm. In addition, the particles grow to 2 μm at 1900°C, at which densification is accelerated.

The changes in temperature and particle growth vary considerably with S-2 and S-3. When the sintered units of each sample are compared at 2050°C, it is clear that the sintered units of S-2 and S-3 with a high density have a dense particle bonding and that the pores between particles and inside particles are only 0.3 μm.
Fig. 7 Variations of microstructures of S-1, S-2 and S-3 sintered with sintering temperature

Time: 30 min, \( d_r \): Relative density

Additive:
- S-1: 1 wt\% boron powder and 2 wt\% carbon powder
- S-2, S-3: 1 wt\% boron powder

Sintering temperature (°C):
- A: 1600, B: 1800, C: 1900, D: 2050
4. Considerations

4.1 Sintering Properties of SiC without Additives

Particle growth only occurs when sintering agents are not added (Figure 6A) and densification is not accelerated with fine SiC powders with a particle size of 0.01 μm. This fact shows that sintering of SiC only occurs by surface diffusion or vaporization-condensation, as was suggested by Billington, et al. [18].

4.2 Results of Adding Boron and Carbon

The Accelerating effects of boron and carbon were described. Two or three suggestions have been made with regard to the mechanism by which these agents accelerate sintering of SiC. Prochazka [8] has mentioned that densification is promoted because the ratio $\gamma_{GB}/\gamma_{SV}$ of the particle boundary energy $\gamma_{GS}$ and the surface energy $\gamma_{SV}$ is greater than the thermodynamic value of $\sqrt{3}$ with regard to sintering of pure-β-SiC. However, boron reduces the $\gamma_{GB}$ by bending the particle boundary and carbon reacts with the oxide layer of the particle. When these are excluded sintering can be promoted by increasing the $\gamma_{SV}$ because the $\gamma_{GB}/\gamma_{SV}$ ratio is reduced. Senshi, et al. [19] also determined that $\gamma_{GB}/\gamma_{SV}>1.88$ from model calculations of the reaction between lattice points and measurements of very pure β-SiC twin crystals. They report that a thermodynamic limit does exist with regard to sintering of SiC.


On the other hand, Nagatani, et al. [20] discovered that $\gamma_{GB}/\gamma_{SV}=1.39$ from determination on 2 planes between sintered particles of $\gamma$-SiC and showed that there is no thermodynamic limit with sintering of $\gamma$-SiC. In addition, Greskovich, et al. [5] also showed that the same conclusion can be reached for $\gamma$-SiC to which carbon has been added. Moreover, Nagatani, et al. [20] and Greskovich, et al. [5] have noted that in contrast to the fact that the sinterability of pure SiC is low, the sinterability is controlled by a surface diffusion mechanism at a relatively low temperature and particles become larger as the temperature increases. Therefore, densification can be controlled by an increase in surface area at high temperatures. In addition, the following results were obtained with regard to the addition of carbon and boron sintering agents.

Greskovich, et al. determined the relative surface area of $\gamma$-SiC sintered units and determined that although densification is not promoted with carbon only at $1250^\circ C$ or more, particle growth is restricted at $1500^\circ C$ or less and densification begins at approximately the same temperature when carbon and boron are simultaneously added. Therefore, it is clear that particle growth is limited by an increase in the SiC surface area and densification is promoted by this increase. Furthermore, particle growth can be controlled by addition of boron only to the same extent as when boron and carbon are simultaneously added. However, densification speed is slow and it is necessary to remove the surface oxide layer of the SiC by carbon in order to promote densification.

On the other hand, Tagatani, et al also showed that although the particle growth can be controlled by adding carbon only to the same extent as when boron and carbon are simultaneously added, carbon alone is not effective with regard to densification and it is necessary to add boron and carbon simultaneously to promote densification. Particle boundary expansion is promoted by the formation of a particle boundary phase by the boron-carbon system. Moreover, densification is also promoted.

There is marked growth of sintered particles of sample S-1 to which no additive has been added. However, when carbon powder or silicon powder are added, SiC particle growth is restricted (Figure 6B and C). Moreover, the same restriction of particle growth as when carbon powder is added to S-1 is seen when no carbon is added to S-2 and S-3 sintered units, which contain little oxygen and a large amount of carbon in comparison to S-1 (Figure 6D and E).

In this study it was noted that particle growth is restricted by the addition of boron, as was noted by Greskovich, et al. [5], and by the addition of carbon, as was noted by Nagatani [21]. The growth restricting effects are greater with boron (1 wt%) than with carbon (2 wt%). Moreover, small particles of 0.3 \( \mu \)m were observed in sintered units at 2050°C to which boron and carbon had been simultaneously added and the simultaneous addition of the two agents appears to restrict that particle growth even further at low temperatures.

Although the restricting effects on particle growth of simultaneous addition of boron and carbon are slight, they are greater than those of boron only. Densification of the sintered unit is promoted by the simultaneous addition of boron and carbon. However, the restriction of particle growth plays a large role in this result.

In addition to restricting particle growth, carbon also removes the oxide layer of the SiC particle and promotes sintering. As shown in Figure 2, the addition of carbon has strong effects. From the composition of sample S-1 it is clear that the amount of carbon necessary to remove oxygen, which was determined assuming the production of CO, is 1.5 wt%. The optimum amount is actually 2 wt%. A slight excess of carbon is necessary. On the other hand, a sintered unit with a high density can be obtained by adding only boron, depending on the chemical composition of the synthetic powder.

Table 4 shows the actual reduction in weight, the calculated reduction in weight \( \Delta W/W_0 \) determined assuming that oxygen is removed as CO, and the estimated value \( (C/\text{Si})_c \) of the molar ratio of C/Si after sintering. The sinterability of products with an \( (C/\text{Si})_c \) molar ratio of 1.00 is high. Therefore, in order to improve the sinterability of the SiC powder, it is necessary to balance the amount of carbon and the amount of oxygen. The actual reduction in weight is in agreement with the calculation assuming that CO is produced. However, the actual value is greater than the calculated value with S-1 samples. There is a possibility that part of the oxygen will vaporize as SiO. Moreover, the actual values are less than the calculated values.
of samples S-3 to S-8. There is therefore a chance that part of the oxygen will form a solid solution inside the particles.

As was previously mentioned, the particle restricting effects of boron and carbon and the oxide layer removal effects of carbon are important in the sintering of SiC. Moreover, the importance of the reduction in particle boundary energy by boron of Prochazka [8] and the boron-carbon system of Nagatani [21] is still unclear.

4.3 Temperature Properties of Densification

The densification properties of S-1 and 2 in Figure 4 and the densification properties of S-3 to 5 in Figure 5 are considerably different. In comparison to samples S-3 through 5, Sample S-2 contains a large amount of oxygen and it is therefore necessary to add carbon to sample S-1 for densification. The difference in the chemical structure (C/Si molar ratio) and the amount of carbon appear to have a large effect on densification properties.

In tests on sintering by adding both boron and carbon Prochzka [8] made clear that there is a difference in the rate to which boron particles move to the SiC particle surface and the rate at which carbon particles move to the SiC particle surface. The boron particles move quickly while the carbon particles move slowly. Suzuki, et al. [22] note that when boron is heated in the SiC crucible, boron moves quite fast at 1500°C. Consequently,

in order to sufficiently develop the effects of the agent, carbon should be uniformly dispersed. This fact was also confirmed in our study. The low temperature at which densification begins with samples S-3 through S-5 which contain a relatively large amount of carbon in comparison to oxygen appears to be due to the development of agent effects at low temperature because of the uniform distribution of carbon at the particle surface during vapor phase synthesis. The necessity of a high temperature for heating sinter S-2 containing a large amount of oxygen also appears to be due to the fact that the amount of carbon is insufficient and some of the surface oxide layer still remains.

Furthermore, the particle diameter of S-2 at 1600-1800°C is larger than that of S-3, as shown in Figure 7. Since the amount of carbon is insufficient, particle growth restrictions are insufficient. Particle growth at this low temperature is also a factor in the reduction of the sinterability of S-2. The high temperature at which densification begins with samples obtained by adding carbon powder to S-1 is due to a delay in the speed at which the carbon spreads to the SiC particle surface. Consequently, the uniform dispersion of carbon is an important point in vapor phase synthesis.

5. Conclusion

Sintering of α-SiC with a mean particle diameter that was formed by a vapor phase reaction of (CH₃)₄Si−H₂ at 1200-1400°C was carried out at 1400-2050°C and the following results were obtained.
(1) The weight of the sintered unit was greatly reduced due to vaporization of SiC in a vacuum. The amount of weight reduction was curtailed by the introduction of argon to the atmosphere (≤ 300 mmHg). However, particle growth occurs and densification therefore does not occur with SiC only, in both a vacuum and argon.

(2) Boron and carbon sintering agents are very effective. Simultaneous addition of carbon powder is essential with samples containing large amounts of oxygen. Sintered units with a relative density of 90% or more were obtained by normal pressure sintering at approximately 2000°C when 1-2 wt% each of boron powder and carbon powder were added.

(3) Restriction of the chemical composition is important with regard to the sinterability of the SiC fine powder. By controlling the chemical composition (mainly the amount of carbon) of the SiC powder during vapor phase synthesis, it is possible to suddenly increase densification from 1900°C with the addition of boron only. Densification of the sintered unit reaches 97% or more at 2050°C. The uniform addition of the agent, particularly carbon with a low diffusion speed, is very important in obtaining a high density sintered unit.

(4) Removal of the oxide layer by carbon and restriction of particle growth by boron and carbon are important in the sintering of SiC. Moreover, it is important that the amount of liberated carbon in the SiC powder and the relative size of the oxygen content of the particle surface be noted for densification. When the oxygen is removed as CO, a powder with a high sinterability and a molar ratio \((C/\text{Si})_C\) of approximately 1.0
can be obtained. Densification is restricted by the oxide layer when the \((C/Si)_c\) is less than 1.0 and by the excess carbon when the \((C/Si)_c\) is greater than 1.0.

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Sintering Behaviour of Ultrafine Silicon Carbide Powders Obtained by a Vapor Phase Reaction

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The sintering behaviour of ultrafine \(\beta\)-SiC powder with the average particle size of 0.01~0.06\,\mu m produced by a vapor phase reaction of the \((\mathrm{CH}_2)_2\mathrm{SiH}_3\) system (1200~1400°C) was investigated at the temperature range of 1400~2050°C. In vacuum, a large weight loss of the compact owing to the vaporization of SiC was observed, whereas the introduction of Ar (=300 mmHg) suppressed the weight loss to a negligible extent even at 2050°C. The compact of undoped SiC powders was hardly densified at 2050°C, although the grain grew up to \(\sim 5\,\mu\)m. The additions of both boron and carbon powders by 1~2 wt\% promoted the densification and gave the sintered body with the relative density of above 90% by the pressureless-sintering at 2050°C. When an adequate amount of carbon was deposited for the oxygen content of SiC powders in the course of vapor phase reaction, the powder showed a high sinterability, giving the sintered body with a relative density above 97% by the addition of boron powder alone. This indicates that the homogeneous dispersion of carbon on SiC particles is important to remove the surface oxide layer effectively. Boron and carbon had the inhibitive effect for the grain growth of SiC.