Additive Effect on Sintering of Boron Carbide

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An additive effect on the pressureless sintering of boron carbide is investigated. Some additive species, Al, TiB₂, and AlF₃ show a remarkable densification effect upon B₄C. The Al-addition provides the best sintered body with the highest bulk density of 95% by means of the firing condition of 2200°C for 30 min under Argon flow. An addition of SiC prevents the densification process. The additive species except for SiC tend to restrain the grain growth and the pore growth, acting probably as an inhibitor for the surface matter transport.

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1. Introduction

Boron carbide (B₄C) ceramic is one of an important group of hard nonmetallic materials, including SiC, Si₃N₄, and diamond. Furthermore, B₄C possesses several attractive properties; its refractory nature (melting point, 2450°C), its low specific weight (theoretical density, 2.52 g/cm³), and its high neutron absorption cross section (⁰B isotope). Because of high-temperature stability, recently boron-rich borides have received attention for use as high-temperature semiconductors. Also, a B₄C rod connected to a graphite tube by a conical fitting, because of its high-thermoelectric power (80 μV/K), has been used as a high-temperature thermocouple (normal operating temperature, 2200°C).

Generally B₄C ceramic is manufactured by hot pressing⁴,⁵ of which process is relatively expensive and can be applied only to simple shapes. However, it is important to develop a sintering process without pressure for expanding applications. From such a standpoint, several researchers have recently studied sintering of B₄C without pressure but with addition of carbon.⁶,⁷

It is the aim of this paper to seek effective additives to provide the theoretical density of B₄C under a normal sintering process.

2. Experimental

2.1 Green body preparation

The B₄C powder (tetrabor 1500) used was supplied by ESK Co. in West Germany; average particle size, 1.0 μm, specific surface area, 12 m²/g, total carbon, 21.3 wt%, total oxygen, 1.46 wt %, and typical metallic impurities: Ca 0.1, Mg 0.01, Al 0.01, Fe 0.1, Si 0.2 wt%.

The starting powder (B₄C+additives) was mixed in a plastic ball mill for 24h under methanol media, evacuated at normal temperatures with a vacuum drier, screened through a 40 mesh sieve, then pressed into disk (11(dia.)×2 mm(t)) at 300kg/cm². The disks were pressed hydrostatically at 2000 kg/cm². The additions used were Al, AlF₃, Mg, MgF₂ (Wako Chemicals), SiC (Central Glass, UF-grade, β-type), and TiB₂ (Daiichi Kigenso Kagaku Kogyo), and each additive was finely ground by mortar and pestle of B₄C ceramic before addition.

2.2 Sintering and evaluation

Sintering was done in flowing argon (purity; 5N) on carbon setters in a carbon resistance furnace at 1900°C to 2200°C. Temperature control of the furnace was conducted with B₄C/C thermocouple⁵ as reported in previous papers.⁶,⁷ Temperature rise was 500°C/h, and was kept at the desired temperature (sintering temperature) for 30 min, while sintering temperature was measured with an optical pyrometer (Chino Co.) through an inspection window. The resultant samples were subjected to density measurement (n-butyl-alcohol displacement by an Archimedeans method) and SEM observation (JEOL JSM-T200, accelerating voltage 15 kV).

3. Results and discussion
3.1 Sintering behavior

Figure 1 shows the effects of sintering temperature on the densification of green compacts with 1 wt% Al added and without additives. The data illustrates that bulk density increases with increase of temperature, which is clearly recognized as the additive effect. However, it is interesting to note that B₄C powder composed of particles of 1.0 μm average diameter could be densified to a considerable level without sintering aids, which is basically different from the sintering behavior of SiC and Si₃N₄.

It is generally thought that covalent-bonding compounds, such as SiC and Si₃N₄, possess a difficult-to-sinter nature, and are almost impossible to densify without any additive. Generally speaking, sintering of SiC begins around 1600°C,10) and that of Si₃N₄, being another typical covalent compound, below 1500°C.10,11)

On the other hand, the sintering starting temperature of B₄C is high, and may be in a range from 1900°C to 1950°C, judging from Fig. 1. The dissociation pressure of B₄C is very low, as compared with SiC and Si₃N₄, and thus B₄C powder can be heated up to a higher temperature near to its melting point. This property leads to easier sintering of B₄C, because surface diffusion is relatively controlled and volume diffusion or grain boundary diffusion occurs vigorously at temperatures higher than 2100°C. Therefore a considerable amount of densification occurs even with the absence of sintering aids.

Figure 2 shows the effects of amount of additive on densification of compacts sintered at 2200°C for 30 min under an argon flow. The data shows that, with Al-addition in a range of 1 to 2 wt%, perhaps, maximum densification was obtained. The sintering results are different from those of other researchers who prefer 4 to 6 wt% C addition.11) In the study on the amount of B and C additions on the sintering of SiC, Tanaka et al.11) found that the β-SiC powders could be sintered to a density of 3.12 g/cm³ with 0.15 to 0.20 wt% B and 1 to 2 wt% C, and β-SiC sintered body showed an exaggerated grain growth when B addition exceeded 0.3%. The sintering mechanism of SiC is generally thought to be a solid-state sintering.

3.2 Effect of additive species and SEM observation

Table 1 lists bulk densities of sintered compacts including various sintering aids of 1 wt% (species; AlF₃, Al, Mg, MgF₂, TiB₂ and SiC), where sintering was done at 2200°C for 30 min. The figures illustrate that, within this experimental condition, the order of effect on densification of B₄C compacts is obtained as Al>TiB₂>AlF₃>MgF₂>Mg, where the last two components (MgF₂, Mg) do not show any significant densification effect on B₄C. The reason why such an additive order was obtained is now under a consideration. The SiC addition causes lowering of green density, and prevents

![Fig. 1. Bulk density of sintered bodies as a function of sintering temperature.](image1)

![Fig. 2. Bulk density of bodies sintered at 2200°C as a function of amount of Al-addition.](image2)

Table 1. Bulk density of pellets sintered at 2200°C for 30 min in pure argon. Each additive is 1 wt%. Green density>63% T.D.

<table>
<thead>
<tr>
<th>ADDITIVE</th>
<th>BULK DENSITY (% T.D.)</th>
</tr>
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<tbody>
<tr>
<td>Al</td>
<td>95</td>
</tr>
<tr>
<td>TiB₂</td>
<td>90</td>
</tr>
<tr>
<td>AlF₃</td>
<td>86</td>
</tr>
<tr>
<td>MgF₂</td>
<td>81</td>
</tr>
<tr>
<td>Mg</td>
<td>80</td>
</tr>
<tr>
<td>NO-ADD.</td>
<td>79</td>
</tr>
<tr>
<td>SiC</td>
<td>71 (GREEN:60% T.D.)</td>
</tr>
</tbody>
</table>
densification of B₄C compacts.

Figure 3 shows some microstructures of fracture surfaces of B₄C sintered bodies, where each body was sintered for 30 min under various conditions as shown in the figure.

The microstructural development of the compacts changes variously with an increase of sintering temperature and by the kind of additive. The additive species except for SiC tend to restrain both grain and pore growth. Without additions and/or with SiC addition, the microstructure develops not only by progressive grain growth but also by pore growth. As a whole, it is obvious that certain sintering aids probably act as
inhibitors for surface-to-surface matter transport. We conclude that it is possible to obtain a high-density sintered body having a fine-pore and fine-grain structure with an average grain size of 10 μm at sintering temperatures lower than 2200°C. In sintering of B₄C, it is reported that secondary recrystallization occurs at above 2220° or 2250°C, where abnormal grain growth is also observed. Therefore, it is important to observe an effective aid which functions sufficiently in temperatures below 2200°C. We can conclude that Al-addition is very effective. However, it is clarified that the free carbon contained in a starting B₄C powder has a significant effect on densification of B₄C, so that it is necessary to investigate the combined effects of Al-carbon and others.

References