Effects of Metallic Boride Dispersion on Fracture Toughness and Oxidation Resistance in SiC Ceramics

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SiCにおける破壊非性と耐酸化性に対する高融点金属ウオウ化物粒子の分散効果
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1. Introduction

In regard to the excellent strength and heat resistivity at high temperature around 1500°C, SiC-B-C ceramic system is interesting for gas turbine and its related component system application. However, its low toughness of around 3 MPa m\(^{-1/2}\), has been the greatest problem to be overcome to achieve structural application such as heat engines. Therefore, many toughening methods have been proposed. Further, the sintering technique of pressureless sintering is more preferable in shape flexibility than that of hot-pressing for heat engine application, so the authors have examined the SiC–B–C ceramic system with dispersion of refractory metal carbide particles (TiC, ZrC, HfC, VC, NbC, TaC and WC, respectively) by pressureless sintering. From the results of toughening in SiC–metal carbide ceramic systems, it is suggested that some other more preferable particulate materials which neither disturbed SiC–B–C matrix densification on sintering nor accelerated corrosive oxidation at high temperature are required to survey.

In the present study, refractory metal borides (TiB\(_2\), ZrB\(_2\), HfB\(_2\), VB\(_2\), NbB\(_2\), TaB\(_2\), MoB and WB) were dispersed in the SiC–B–C ceramic system and the properties of densification, toughening and oxidation were examined for high temperature applications.

2. Experimental

Table 1 shows the characteristics of the starting powders. The sources of boron and carbon, which are additives for sintering, were B\(_2\)C powder and phenol resin powder furnished by Dainippon Ink & Chemicals Co., Ltd.

The amount of boron as additive was fixed to about 0.7 atm\% to the main composition (SiC–metallic boride), and the amount of carbon as additive was fixed to 2.25 times in weight of the amount of oxygen impurity in the main composition. The metallic boride content in the main compositions was selected up to 20 mol%.

A slurry was made from mixed SiC, B\(_2\)C and metallic boride powders, using an acetone solution of a phenol resin and a binder. The slurry was dried, granulated, and pressed into a 33 × 43 × 7 mm shape. The binder was degreased and the resin was carbonized at 800°C under stream of nitrogen gas. Sintering was carried out in vacuum furnace heated by carbon for 2 h at 2050°C. Sintered bodies were cut and polished to the JIS R1601 standard size.

The densities of sintered body were evaluated with the Archimedes method or by measuring the size and the weight. The XRD (X-ray diffraction) technique was used to determine the crystalline phases. Scanning electron microscopy (SEM) was used to observe the microstructures of the sintered bodies. X-ray photoelectron spectroscopy (XPS) was used to investigate the surface oxidation state of the sintered bodies.

Key-words: Silicon carbide, Metal boride, Pressureless sintering, Particle dispersing, Fracture toughness, Oxidation resistance, Refractoriness
used to observe the surfaces, which were polished, indented, or oxidized.

The fracture toughness values were measured only for 7 kinds of boride dispersed specimens. The remaining MoB dispersed samples could not be densified sufficiently to more than 95% TD, which was estimated by the densities of SiC and each metallic boride in Table 1, since the detected crystalline phases in the sintered bodies were SiC and the respective metallic boride only. Toughness “KIC” and hardness “HV” were evaluated from more than 10 Vickers indent measurements. “KIC” value was calculated with following Niihara’s equation \(^{4)}\) under a previously postulated Young’s Modulus of 410 GPa obtained in a dense single phase SiC ceramic.

\[
K_{IC} = 0.0421 \times A^{0.8} \times E^{0.4} \times P^{0.6} \times C^{-1.5} \\
A: \text{Half diagonal of Vickers indent}
\]
\[
P: \text{Load (5 kg, 15 sec)}
\]
\[
C: \text{Radius of median crack}
\]
\[
E: \text{Young’s modulus (410 GPa)}
\]

The high temperature corrosion resistance was examined by the oxidation behavior up to 1000 h at 1500°C in static air atmosphere. Sample rods were laid on and supported with SiC bars in order to avoid unexpected chemical reactions.

3. Results and discussion

3.1 Densification behavior

Figure 1 shows the effects of content of each metallic boride dispersed on density. Density was normalized by each TD. Most of the composites were densified to more than 95% TD from the dispersion free to the 20 mol% boride dispersions. The poor densification in MoB dispersed is considered to be due to the phase transition of MoB at 2000 °C.5) The density of the HfB\(_2\) dispersing system decreased drastically at above 5 mol%; Figure 2 shows XRD peaks of samples with 5 mol% HfB\(_2\) dispersed. Diffraction peaks of HfO\(_2\) were detectable for the sample sintered at 800°C, but these peaks disappeared in a sample sintered at 2050°C. The amount of 5.6 atm% in oxygen impurity was the maximum value for HfB\(_2\) among the metallic boride raw powders, as shown in Table 1. From the thermodynamic consideration of de-oxidation and formation free energies of borides and carbides in standard condition,\(^{6}\) the following reaction could set off over 1350°C and 1610°C, respectively.

\[
\text{HfO}_2 + 3/2\text{C} + 1/2\text{B}_4\text{C} = \text{HfB}_2 + 2\text{CO}(g) : T > 1350°C \quad (2)
\]

\[
\text{HfO}_2 + 3\text{C} = \text{HfC} + 2\text{CO}(g) : T > 1610°C \quad (3)
\]

As shown in Fig. 2, when a HfO\(_2\) powder containing no boron and no carbon was heated in vacuum using the same furnace and capsule, diffraction peaks corresponding to HfB\(_2\) and HfC appeared at 1450° and 1850°C, respectively. The HfO\(_2\) powder absorbed boron and carbon from the surroundings in high temperature. However, stability of HfC should thermodynamically be less than that of HfB\(_2\) in the sintering temperature region. Under these condition, it is considered that the formation of HfB\(_2\) is the dominant reaction in SiC–B–C–(HfB\(_2\)–HfO\(_2\)) system unless the amount of boron as additive is small. In Eq. (2), the dispersion of 6 mol% HfB\(_2\) raw powder containing 5.6 atm% in oxygen impurity is sufficient to react with all amount of boron as additive. Therefore, the amount of 10 mol% HfB\(_2\) dispersed into SiC–B–C system must reduce the remaining amount of boron as effective additive to an amount less than 0.15 atm% which is the critical amount for densification of SiC matrix.\(^{7}\)

![Fig. 1. Densification behavior of metallic boride–SiC–B–C system on sintering at 2050°C for 2 h in vacuum.](image1)

![Fig. 2. XRD peaks variation in heating on 95 mol% SiC–5 mol% HfB\(_2\) system and HfO\(_2\).](image2)
Consequently, if the amount of oxygen impurity should be reduced in the raw HfB$_2$ powder, the SiC–B–C dispersed 20 mol% HfB$_2$ would be fully sintered.

3.2 Micro-structures and mechanical properties

Figure 3 shows representative polished surfaces. The bright particles are dispersed boride grains, and the dark spots are closed pores of intrinsic pores and off-falling boride particles during polishing process. The boride particles were isolated from each other in 5 mol% dispersion, while they began to contact each other in 20 mol% dispersion.

Figure 4 shows the composition dependencies of Vickers hardness “H$_v$” and fracture toughness “K$_{IC}$”. The variations of “H$_v$” by boride dispersion are taken as almost the same in every borides and approximately constant. On the other hand, the “K$_{IC}$” values increase linearly with increasing the content of each boride from 3.2 MPa·m$^{1/2}$ to about 5.2 MPa·m$^{1/2}$.

The sample with 20 mol% VB$_2$ dispersed showed the highest toughness. The increase of “K$_{IC}$” in SiC dispersed 20 mol% VB$_2$ is quite corresponding to that of “H$_v$”. The reason why both “H$_v$” and “K$_{IC}$” increased with increasing the amount of VB$_2$ is not clear yet.

The effect of addition of each boride on toughening seems to be approximately same due to their large standard deviations as shown in Fig. 4, in spite of the fact that the intrinsic Young’s modulus of the individual borides should vary with depending on the kind of refractory metal in the borides.

The properties of the individual borides were listed in Table 2, in order to examine the constant “E” postulation in Eq. (1).

The Young’s modulus of the particle dispersed composite was approximated as Eq. (4) according to the cubic particle dispersion model by Paul $^{9)}$

$$
\frac{E}{E_p} = \left( \frac{E_p + (E_M - E_p)(1 - V_p)^{2/3}}{E_p + (E_M - E_p)(1 - V_p)^{2/3} [1 - (1 - V_p)^{1/3}]} \right) ^{0.4}
$$

(4)

$V_p$ : Volume fraction of particles

P, M : Suffix indicating particle and matrix, respectively

Since the largest deviations in Eq. (1) found at the 20 mol% dispersion, “(E/E$_M$)$^{0.4}$” was estimated to be within the following range.

0.962 (20 mol% TaB$_2$) < (E/E$_M$)$^{0.4}$ < 1.034 (20 mol% ZrB$_2$)

(5)

Since the deviation of Young’s modulus mentioned above is negligibly smaller than the standard deviation of 10 measured values, it is considered that the
constant “E” postulation is preferable in the present measurement results.

On the other hand, the volume fractions for individual borides ranged from 12.4 cm³/mol for WB to 18.5 cm³/mol for ZrB₂, as shown in Table 1. Even when the content of boride in Fig. 4 is changed from “mol%” to “vol%”, the effect of amount of WB dispersed on toughening should become intensified.

Moreover, the toughening effect of dispersed boride particles is considered to be affected by the size of dispersing boride particles and SiC matrix grains. Accordingly, it is extremely difficult to narrow down the most effective boride compounds for toughening a SiC-B-C ceramic under the present experimental data.

3.3 High temperature oxidation behavior

Figure 5 shows the relationship between weight change and oxidation time through 1500°C oxidation for 5 mol% boride dispersing composites. The degree of weight change varied with the dispersed borides. A few data points are remarkable; the weight gain of WB dispersed composites was lower than that of the boride free SiC matrix.

Table 3 summarizes the results of XRD analysis of the surfaces oxidized for 100 or 1000 h at 1500°C. Since the cristobalite “SiO₂” was detected on all surfaces, the following reaction can be occurred as usual boride free cases.¹¹

SiC + 3C = SiO₂ + CO(g)  (6)

Although ZrSiO₄ and HfSiO₄ were detected in each surface of sample containing ZrB₂ or HfB₂ no titanium oxide could be detected on the surface of sample TiB₂ dispersed. Though Ta₂O₅ was detected in every TaB₂ dispersion surfaces, Nb₂O₅ could be identified only in the surface of the 10 mol% NbB₂ dispersion oxidized for 100 h, in spite of the difficulty due to the appearance of Nb₂O₅ polymorphism. Nb₂O₅ must have been lost slowly from the oxidized surface. No vanadium, molybdenum and tungsten oxides could be detected in any surface. These results should arise from the difference of volatility at 1500°C, as shown in the following summary of the equilibrium vapor pressure data.¹²

MoO₃ > V₂O₅ > WO₃, SiO > B₂O₃ = 10⁺² Pa

10⁻² Pa = TiO > Nb₂O₅ > TiO₂ > SiO₂

= 10⁻³ Pa

10⁻⁸ Pa = ZrO₂, HfO₂, Ta₂O₅

Since the zirconium, hafnium and tantalum oxides have vapor pressures less than 10⁻⁸ Pa, such oxides remained on the surfaces by formation of ZrSiO₄, HfSiO₄ and Ta₂O₅, respectively. On the other hand, since the molybdenum, vanadium, tungsten and boron oxides have vapor pressures higher than 10⁺² Pa, such oxides vaporized and induced a weight gain reduction or a weight loss during the oxidation process. The titanium, niobium and silicon oxides have intermediate vapor pressures of the order of 10⁻³ Pa. In such cases, the oxidation behavior should vary with depending on both the amount of dispersed borides and the oxidation time.

As a result of the above considerations, it is clear that the overall weight change is not a preferable parameter for evaluating the oxidation resistance of SiC with additives of metallic borides because of the loss of heavy metals.

Figures 6 and 7 show photographs of samples exposed to static air for 1000 h at 1500°C. Boride free SiC matrixes showed excellent oxidation resistance. All samples with additives of metallic borides were more or less harmful for refractoriness. As shown in Figs. 6 and 7, the refractoriness of the individual samples was classified to be “Excellent”, “Good”, “Fair” and “Bad”.

On the other hand, the presence of oxide phase at 1500°C is different among the related oxides. The thermal properties of the related oxides are listed in Table 4.¹²

The refractoriness grades and the oxide phases at 1500°C are comparatively summarized for all the main compositions, as shown in Table 5.

The “Bad” grade of refractoriness seems to result from the additional solids of refractory metal oxides, TiO₂, ZrSiO₄, HfSiO₄ and Ta₂O₅. The formation of vapor phase of MoO₃ and liquid phase oxides only,
such as B₂O₃, V₂O₅, WO₃ and Nb₂O₅, seem to correspond to the refractoriness grade "Good" or "Fair".

Table 4. Melting point, boiling point and decomposing point of related oxides.¹²

<table>
<thead>
<tr>
<th>Related Oxide</th>
<th>Volume (cc/mol)</th>
<th>Melt. P. (°C)</th>
<th>Boil. P. (°C)</th>
<th>Congruent Melt. P. to SiO₂ (°C)</th>
<th>to SiO₂ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂O₃</td>
<td>37.7</td>
<td>470</td>
<td>9124</td>
<td>372</td>
<td>372</td>
</tr>
<tr>
<td>SiO₂</td>
<td>19.5</td>
<td>1720</td>
<td>2850</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>18.8</td>
<td>1970</td>
<td>3227</td>
<td>1550</td>
<td>450</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>22.1</td>
<td>2300</td>
<td>4000</td>
<td>1687</td>
<td></td>
</tr>
<tr>
<td>ZrSiO₄</td>
<td>21.0</td>
<td>2780</td>
<td>4600</td>
<td>1690</td>
<td>d</td>
</tr>
<tr>
<td>HfO₂</td>
<td>54.2</td>
<td>670</td>
<td>3652</td>
<td>661</td>
<td></td>
</tr>
<tr>
<td>Nb₂O₅</td>
<td>53.7</td>
<td>1450</td>
<td>2827</td>
<td>1448</td>
<td>450</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>50.6</td>
<td>1755</td>
<td>3227</td>
<td>1550</td>
<td>450</td>
</tr>
<tr>
<td>WO₂</td>
<td>30.8</td>
<td>1470</td>
<td>2827</td>
<td>1550</td>
<td>450</td>
</tr>
</tbody>
</table>

Table 5. Refractoriness and related oxide state for individual compositions at 1500°C.

<table>
<thead>
<tr>
<th>Refractoriness</th>
<th>Main Composition</th>
<th>Solid Phase</th>
<th>Liquid Phase</th>
<th>Vapor Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent</td>
<td>SiC</td>
<td>SiO₂</td>
<td>O₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Poor</td>
<td>SiC + TiB₂</td>
<td>SiO₂</td>
<td>O₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Poor</td>
<td>SiC + ZrB₂</td>
<td>SiO₂</td>
<td>O₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Poor</td>
<td>SiC + HfB₂</td>
<td>SiO₂</td>
<td>O₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Poor</td>
<td>SiC + V B₂</td>
<td>SiO₂</td>
<td>O₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Poor</td>
<td>SiC + NbB₂</td>
<td>SiO₂</td>
<td>O₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Poor</td>
<td>SiC + TaB₂</td>
<td>SiO₂</td>
<td>O₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Poor</td>
<td>SiC + MoB</td>
<td>SiO₂</td>
<td>O₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Poor</td>
<td>SiC + W B</td>
<td>SiO₂</td>
<td>O₂</td>
<td>O₂</td>
</tr>
</tbody>
</table>

3.4 Evaluation method of refractoriness

Some evaluation methods for the effect of addition of the metallic borides on oxidation resistance were investigated in order to clarify the cause of the difference between "Good" and "Fair" and to narrow analytically down the most preferable metallic boride for a refractory composite. The amount of cristobalite, \( W(g/cm²) \), on the oxidized surface is generally marked as the absolute scale for oxidation resistivity of SiC–B–C system. Initially, the authors roughly assume that some depth from the surface was oxidized uniformly whatever the composition and the micro-structure were. The oxidation reactions of weight loss were postulated as following reaction by the results in Table 3.

\[
VB₂ + 4O₂(g) = V₂O₅(g) + B₂O₃(g); \\
-72.56 g/mol \quad (10)
\]

\[
NbB₂ + 4O₂(g) = Nb₂O₅(g) + B₂O₃(g); \\
-114.53 g/mol \quad (11)
\]
The weight change on the right hand side of each equation was calculated from each atomic weight section. Next, "W" was estimated from the measured weight change "w(g/cm²)" according to the following equation.

\[
W = w \times \frac{(2M_O - M_C)}{(1-x)(2M_O - M_C)} - (M_{me} + yM_B)
\]

(14)

\(M_O, M_C\), and \(M_B\): Atomic weights of O, C, and B element

\(M_{me}\): Atomic weight of metal, such as V, Nb, Mo, and W

\(x\): mol% of dispersed metallic boride in SiC matrix

\(y\): 1 or 2 for mono-boride or di-boride, respectively

On the other hand, the ratios of "((101)SiO₂/(102)6HSiC" in the XRD peak intensities were also evaluated 4 times per sample. This ratio is a semi-quantitative scale for the amount of cristobalite on an oxidized surface.

Both results are summarized in Table 6. As seen in Table 6, both results showed a good agreement in the order of the amount of surface SiO₂. Therefore, the both methods seem to appropriately evaluate the oxidation resistivity for the composite, and the order is reliable.

Sintered bodies with additive of MoB and VB₂, which are the sources for relatively higher vapor pressure oxides MoO₃ and V₂O₅, induce a more drastic increase of the cristobalite layer with increase of dispersed amount from 10 to 20 mol%. On the other hands, sintered bodies containing NbB₂ and WB as additives, which are the sources for relatively lower vapor pressure oxides Nb₂O₅ and WO₃, showed the little formation of cristobalite layer. It is considered that the equilibrium vapor pressures of formed liquid oxides as low as that of SiO₂ is more preferable for the refractoriness of boride dispersing SiC composites.

NbB₂ and WB are considered to have the brightest prospect for developing a refractive composite toughened with dispersing particles.

4. Summary

TiB₂, ZrB₂, HfB₂, VB₂, NbB₂, TaB₂, and WB were found to be dispersible particles to achieve the fully densified composites.

By dispersing the above metallic borides into SiC up to 20 mol%, the fracture toughness of the composite increased linearly from 3.2 MPa·m¹/₂ to about 5 MPa·m¹/₂. The dispersed boride for the most effective toughening was not yet clariefied due to the large standard deviation of the experimental data and the large differences in particles size.

TiB₂, ZrB₂, HfB₂, and TaB₂, which formed oxides of TiO₂, ZrSiO₄, HfSiO₄, and Ta₂O₅ through an oxidation reaction, induced severe corrosion. On the other hand, VB₂, NbB₂, MoB, and WB, which formed liq-
uid phase of oxides such as V_2O_5, Nb_2O_5, and WO_3, or gas phase such as MoO_3 at 1500°C, showed a somewhat mild corrosion. The more preferable metallic borides seemed to be NbB_2 and WB which formed lower equilibrium vapor pressure oxides only than VB_2 and MoB.

In conclusion, NbB_2 and WB seem to have bright prospects for developing new SiC composite ceramics that simultaneously realize sintering, toughening, and the least degrading in corrosive oxidation at 1500°C.

References