Fabrication of B₄C/TiB₂ Composite Ceramics Using Pulsed Electric Current Pressure Sintering

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ABSTRACT

Dense B₄C/TiB₂ composite ceramics have been fabricated from the amorphous B and C, and fine TiC powders (25 nm in size Pₓ), using pulsed electric current pressure sintering (PECPS) at 2173 K under 50 MPa for 6.0 × 10² s in a vacuum. During PECPS the solid-state reaction between B and C was induced around 1373 K and almost at the same time TiB₂ phase was gradually formed, followed by a continuous formation of B₄C matrix including TiB₂ particles. On the other hand as the reference, two kinds of B₄C/TiB₂ composites from the B/C mixes and TiB₂ powders (1.86 μm and 58 nm in Pₓ) were also fabricated as the same manner. The former composites using TiC showed high relative density ≥ 98.9% up to 11 vol% TiB₂ and improved mechanical properties, such as three-point bending strength σ_b of 650 MPa, Vickers hardness Hᵥ of 33.5 GPa and fracture toughness KIC around 5.45 MPa·m¹/² at the composition of B₄C/TiB₂ = 93/7 vol%, however, the latter composites revealed lower relative densities of 96.5% at 7 vol% TiB₂ composition and deteriorated mechanical behaviors as Pₓ of TiB₂ increased.

KEY WORDS

Boron carbide B₄C, titanium boride TiB₂, pulsed electric current pressure sintering, composite ceramics, mechanical property

1 Introduction

Boron carbide (B₄C) ceramics have been attracting much attention for the high-temperature structural applications because of their high melting temperature (T_m = 2723 K), high hardness (Vickers hardness Hᵥ ≥ 30 GPa) which is the third hardest material behind diamond and cubic boron nitride, high elastic modulus (E = 290–450 GPa), low density (Dᵥ = 2.515 Mg/m³, JCPDS:#35-0798), chemical inertness to corrosive media, and excellent high performance under neutron irradiation. B₄C has been used as wear-resistance components, abrasives with high hardness more than SiC (Hᵥ ~ 30 GPa), lightweight armor or protector and neutron radiation shields, etc.¹⁻³⁻¹.

However, it is very difficult to fabricate dense B₄C ceramics because it shows poor sinterability due to covalent bond even at a temperature higher than 2273 K with the sintering additives such as Al, Mo, C, h-BN, TiB₂ and Al₂O₃.⁴⁻⁶ The pining effect of secondary phases resulted in the inhibition of grain growth and enhancement of densification of B₄C. Among these composites, B₄C/TiB₂ system ceramics are thought to be one of the best composites that can hold the intrinsic properties of B₄C because i) TiB₂ has a higher T_m = 3253 K, suggesting high stability of B₄C/TiB₂ system ceramics at elevated temperatures, and ii) TiB₂ has a high Hᵥ of 25–32 GPa and moderate density of Dᵥ = 4.495 Mg/m³, JCPDS:#35-0741) promising high Hᵥ and low densities.⁵⁻¹¹

About the previous studies of B₄C/TiB₂ composite ceramics, hot-pressed composites fabricated by X. Y. Yue et al.¹² showed high bending strength σ_b and fracture toughness KIC of 506 MPa and 9.4 MPa·m¹/², respectively. However, the value of Hᵥ was only 23.6 GPa. In addition, other hot-pressed composites fabricated by S. G. Huang et al.¹³ reported a combined high mechanical properties of σ_b and Hᵥ of 867 MPa and 29 GPa, respectively, while the value of KIC was modest (4.5 MPa·m¹/²). This trade-off relation has been reported by other researchers; S. Yamada et al.¹⁴ reported high σ_b (866 MPa) and low KIC (3.2 MPa·m¹/²) for the reaction hot-pressed B₄C/TiB₂ composites. By using other additive of Ti₅SiC₂ to B₄C, P. He et al.¹⁵ have reported lately that moderate σ_b (592 MPa), high KIC (7.01 MPa·m¹/²) and high Hᵥ (31 GPa) are attained for B₄C/TiB₂ composite prepared from B₄C-10 mass% Ti₅SiC₂ starting powders.

Based on the previous our study¹⁶ on CNF dispersed B₄C composites with sintering additive of 2.5 vol% Al₂O₃, having σ_b ~710 MPa, Hᵥ ~36 GPa, and KIC ~7.9 MPa·m¹/², and B₄C/CNF composites without sintering additive, having excellent high-temperature σ_b (~600 MPa) and toughness at 1723–1873 K¹⁷, we have tried to fabricate dense B₄C/TiB₂ composite ceramics from the mixture of amorphous B and C, and fine TiC powders (25 nm in particle size Pₓ), using pulsed electric current pressure sintering (PECPS)¹⁸ at
2173 K under 50 MPa for $6.0 \times 10^3$ s in a vacuum. During sintering the solid-state reaction between B and C was induced by PECPS around 1373 K and almost at the same time TiB$_2$ phase from TiC and B was gradually formed, followed by a continuous formation of B$_4$C matrix including TiB$_2$ particles. Thus obtained B$_4$C/TiB$_2$ composites showed high relative density $\geq 99\%$ up to 11 vol% TiB$_2$ and improved mechanical properties, such as three-point bending strength $\sigma_b$ of 650 MPa, Vickers hardness $H_v$ of 33.5 GPa and fracture toughness $K_{IC}$ around 5.45 MPa·m$^{1/2}$ at the composition of B$_4$C/TiB$_2$ = 93/7 vol%. These are balanced values in comparison with those of B$_4$C/TiB$_2$ composites previously reported. In the present study, their mechanical properties are investigated precisely in relation with the microstructure of thus fabricated composites.

2 Experimental procedure

Fig. 1 shows the flowchart for preparing B$_4$C/TiB$_2$ composites. High purity amorphous B powder (H.C. Starck-V Tech Ltd., average particle size $P_s$ of ~30 nm, purity of 98.5%, theoretical density $D_x$ of 1.73 Mg·m$^{-3}$)\(^{19}\), amorphous C powder (Mitsubishi Chemical Co. Ltd., Tokyo Japan, “Carbon Black #30”, $P_s$ of ~30 nm, 98.5%, $D_x$ of 1.80 Mg·m$^{-3}$)\(^{20}\), and titanium carbide TiC (Kojundo Chemical Laboratory Co. Ltd., Tokyo, Japan, $P_s$ of ~25 nm, 99.9%, $D_x$ of 4.911 Mg·m$^{-3}$)\(^{21}\) were used as starting materials. In addition to this, large TiB$_2$ (Japan New Metal Co. Ltd., Osaka, Japan, $P_s$ of 1.86 μm, 99.9%, $D_x$ of 4.495 Mg·m$^{-3}$) and small TiB$_2$ (Kojundo Chemical Laboratory Co. Ltd., $P_s$ of 58 nm, 99.9%) powders were also used as starting materials for comparison with nano-meter sized TiC. As will be described in the latter, sintered materials from amorphous B and C, and TiC showed B$_4$C/TiB$_2$ phases, i.e., TiC turned into TiB$_2$ due to the solid-state reaction with B. Therefore, based on the following equation; $(4 + \delta)\cdot B + (1 - \delta/2)\cdot C + \delta/2\cdot TiC \rightarrow B_4C + \delta/2\cdot TiB_2$, these powders were weighed into the final compositions of B$_4$C/TiB$_2 = 100/0$ to 89/11 vol%. For example, to fabricate B$_4$C/TiB$_2 = 93/7$ vol% composite, the $\delta$ value was determined to be 0.247. When the mixtures of B, C and TiB$_2$ powders were used as the starting materials, the sintered ceramics were also B$_4$C/TiB$_2$ composites. The weighed powders of boron B and carbon C were mixed in regent grade ethanol using an alumina mortar and pestle for $1.8 \times 10^3$ s (30 min). Before mixing TiC or TiB$_2$ with these (B and C) mixed powders, the TiC or TiB$_2$ powders were pre-dispersed into 2-propanol using an ultrasonic vibrating homogenizer with a power output of 300 W at frequency of 20 kHz (US-300T, Nihon-Seiki Ltd., Tokyo, Japan) for $1.8 \times 10^3$ s (30 min). After the mixed (B and C) powders were added into the TiC or TiB$_2$ dispersed solution, the mixed slurries with the compositions of B$_4$C/TiB$_2 = 100/0$~89/11 vol%, [here, the compositions are denoted as the final composite material], were homogenized using the same ultrasonic vibrator for $1.8 \times 10^3$ s (30 min). Then, the powder mixtures were prepared by drying the slurries with stirring at room temperature in air.

The mixtures were uniaxially pressed into disks with a 20 mm diameter and a ~5 mm thickness at 50 MPa and then cold isostatically pressed at 245 MPa or 1 GPa for $1.8 \times 10^3$ s (3 min). Their green densities were 1.13 Mg·m$^{-3}$ after 245 MPa-CIPing for mixed powder (B and C) corresponding to the final compound B$_4$C, 1.44-1.49 and 1.56-1.58 Mg·m$^{-3}$ for mixed powder (B and C)/TiC corresponding to the final composition of B$_4$C/TiB$_2$ = 90/10 vol% powders after 245 MPa and 1.0 GPa-CIPing, respectively. These values corresponded to 64.5% (B and C), 66.3~68.5% and 71.2~72.5% [(B and C)/TiC] of the theoretical densities $D_x$ (1.745 and 2.181 Mg·m$^{-3}$) which were calculated using the $D_x$ of 1.73 for...
amorphous B\(^{30}\), 1.80 for amorphous C\(^{30}\), and 4.911 Mg m\(^{-3}\) for TiC (PDF\#32-1383). From this, it is clear that the relative densities increased gradually from 64.5 to 66.3–68.5% under 245 MPa-CIP\(\text{ing}\) with addition of 25 nm TiC powder and also increased from 66.3–68.5% to 71.2–72.5% with increasing CIP\(\text{ing}\) pressure. The latter is a new finding because in the ceramics powder compacts it has been believed that higher CIP\(\text{ing}\) pressure than around 200 MPa could not improve the densities.

The compressed powder compacts were pre-heat-treated for 3.6 \(\times\) 10\(^3\) s (2 h) at 1223 K (950°C) under reduced pressure to eliminate a small amount of water and oxygen adsorbed on the surfaces of amorphous (B and C), and TiC nano-powders without particle-sintering during heating\(^{30}\). After elimination of adsorbed gas and wrapping with \(h\)-BN powder \((\rho, \text{ of } \sim 3 \mu\text{m}, > 98\% \text{ purity})\), they were put into a cylindrical mold \((20 \text{ mm} \times 40 \text{ mm} \times 40 \text{ mm}, \text{ high-density graphite carbon})\) that was used for PECPS (SPS-5104A, SPS SYNTEx INC., Tokyo, Japan). Using this apparatus, sintering was performed at 2173 K (1900°C) for 6.0 \(\times\) 10\(^3\) s (10 min) under an uniaxial pressure of 50 MPa in a vacuum (\(~10\) Pa) with a heating rate of 1.66 K s\(^{-1}\) (100°C min\(^{-1}\)) and a cooling rate of \(-8.33 \times 10^{-5}\) K s\(^{-1}\) (\(-50^\circ\text{C} \text{ min}^{-1}\)), applying DC pulse electric current \((\text{on/off interval } = 12:2)\). Heating temperature above \(~873\) K (600°C) was monitored at the center position of the outside wall of carbon mold using a monochromate pyrometer. Sintering temperature was decided on the fabrication of monolithic B\(_4\)C. From the results of the preliminary experiments, a 2173 K (1900°C)-sintering gave a high density (relative density of 99.9%) of single-phase B\(_4\)C ceramics and high mechanical properties of Vickers hardness \(H\) of 33.5 GPa and fracture toughness \(K_{IC}\) of 4.98 MPa m\(^{1/2}\) which value was determined by IF method\(^{32}\); Crystalline phase of the sintered materials were identified by X-ray diffraction (XRD) analysis (Cu\(K\alpha\) radiation, Rint 22000, Rigaku, Osaka, Japan). Hereafter, TiC(TiB\(_2\))-dispersed B\(_4\)C composites were also sintered at the same sintering conditions of 2173 K/6.0 \(\times\) 10\(^3\) s/50 MPa/vacuum (1900°C/10 min/50 MPa/vacuum). Microstructural observation of the morphology and elemental distributions, as well as of the fractured or polished surfaces of sintered composites, were conducted using a both field emission-type scanning electron microscope (FE-SEM, JSM-7001FD; JEOL, Tokyo, Japan) and transmission electron microscope (FE-TEM, JEM-2100F; JEOL) equipped with an energy-dispersive spectrooscope (EDS, JED-2300/F; JEOL). The latter transmission electron microscope was utilized to observe the morphology, analyze the elemental lines on the nanoregions of the composites. Before TEM observation, the specimens were made thinner using a focused ion beam (FIB, FB-2200; Hitachi High-Tech Fielding) equipped with a micro-sampling system. Bulk densities of sintered materials were measured by Archimedes’ method. After phase identification, test bars for mechanical-property measurements were cut from the sintered materials with a diamond cutting-blade and then their two (upper and lower) surfaces were polished to mirror surface with a diamond paste (nominal particle size 1–3 μm); the left two sides were grinded with a diamond abrasive tool containing #400 grid-pass diamond particles. And then three-point bending strength \(\sigma\) was evaluated with a cross-head speed of \(8.33 \times 10^{-5}\) mm s\(^{-1}\) (0.5 mm min\(^{-1}\)) and an 8 mm-span length using WC jigs. Vickers hardness \(H\) and fracture toughness \(K_{IC}\) were evaluated with an applying load of 19.6 N and a duration time of 15 s for the former, and the indentation fracture method (IF)\(^{33}\) with Niihara’s equation\(^{33}\) for the latter.

### 3 Results and Discussion

#### 3.1 Characteristics of powder compacts and their shrinkage profiles

Fig. 2 shows an XRD pattern of powder compact consisting of amorphous (B and C), and nanometer size (25 nm) TiC, heated at 1173 K (900°C) for 6.0 \(\times\) 10\(^3\) s (10 min) under 50 MPa in a vacuum, with the composition corresponding to B\(_4\)C/TiB\(_2\) = 93/7 vol%; this corresponding expression is used afterward because this powder compact turns into B\(_4\)C/TiB\(_2\) composite after PECPS as will be described. This XRD pattern reveals only sharp diffraction peaks attributed to TiC (PDF\#32-1383) without other peaks, indicating that there is no solid state reactions among amorphous (B and C), and TiC even at 1173 K (900°C). However, as shown in Fig. 3 (A) which presents the shrinkage profiles of powder compacts during PECPS with the final compositions of B\(_4\)C/TiB\(_2\) = (i) 100/0, (ii) 95/5 and (iii) 89/11 vol%, a little drop in thermal expansion curves \((\Delta l / l_{0}, \text{ here } \Delta l \text{ is a shrink in length of powder compact and } l_{0} \text{ the length before sintering})\) are observed around 1473 K (1200°C) for all compacts. After this temperature, powder compacts revealed a weak steady expansion up to around 2023 K (1750°C) of (i) 100/0 monolithic and a sudden drop at 2173 K (1900°C) for all, suggesting that macroscale densification has started. Fig. 3 (B) presents the crystalline phases of the samples with the final composition of B\(_4\)C/TiB\(_2\) = 93/7 vol%, which were taken after PECPS heating to each desired temperature; (I) B, (II) B\(_4\)C and (III) TiB\(_2\) curves represent their mass fraction in each sample. As will be described in Fig. 5, from room temperature to near 1173 K the

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![Fig. 2 XRD pattern of the mixture of amorphous B and C, and TiC corresponding to B\(_4\)C/TiB\(_2\) = 93/7 vol% composite.](image-url)
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The powder compact consisted of amorphous B, C and a small amount of TiB₂, and between 1173 and 1973 K the mixture of amorphous B and C turned into B₄C by the solid state reaction gradually. However, over around 1973 K the chemical reaction has been enhanced to form B₄C, at the same time B phase disappeared at 2173 K. It should be noted that the shrinkage profile in Fig. 3 (A) corresponds much to the phase formation curves in Fig. 3 (B) at each stage, such as low 1373 and high 1973 K temperatures.

In order to investigate the microstructural development in powder compacts, the samples were taken during PECPS from 1173 to 2173 K every 200 K and observed using SEM. Fig. 4 shows their fracture surfaces of powder compacts taken at i) 1173, ii) 1323, iii) 1573, iv) 1773, v) 1973 and vi) 2173 K for 6.0 × 10² s (10 min) under 50 MPa in a vacuum. In addition, their crystalline phases

![Graph of Shrinkage profile](image)

Fig. 3 (A) Shrinkage profile of the powder compact corresponding to B₄C/TiB₂ = 93/7 vol% composite, (B) mass fraction of (i) B, (ii) B₄C and (iii) TiB₂ in the same powder compact during PECPS treatment.

![SEM photographs of fracture surfaces](image)

Fig. 4 SEM photographs of the fracture surfaces of the powder compacts corresponding to B₄C/TiB₂ = 93/7 vol% during PECPS; heated at (i) 1373, (b) 1573, (c) 1773, (d) 1973 and (e) 2173 K for 6 × 10² s under 50 MPa.

![XRD patterns](image)

Fig. 5 XRD patterns of the powder compacts corresponding to B₄C/TiB₂ = 93/7 vol% during PECPS; heated at (i) 1373, (b) 1573, (c) 1773, (d) 1973 and (e) 2173 K for 6 × 10² s under 50 MPa.
were also investigated using the same samples; their XRD patterns are displayed in Fig. 5. In the sample heated at 1173 K (900°C), only TiC diffraction peaks are observed in Fig. 2, however, the sample at (a) 1373 K in Fig. 5 presented an appearance of TiB₂ (PDF#35-0741) and at the same time of TiC phase. At higher temperature, for example, the XRD patterns of sample at (b) 1573 K indicates the embryonic formation of B₄C from amorphous B and C by the solid-state reaction, strong diffraction peaks of TiB₂ and disappearance of TiC. It is easily observed that with increasing temperature from (c) 1773, (d) 1973 to (e) 2173, both B₄C and TiB₂ phases became strong and TiC perfectly diaphraged. Here, strong BN diffraction peaks (PDF#45-1171) might be derived from the BN powder adhered to the samples surface during high temperature under high pressure of 50 MPa. These data are summarized and shown in Fig. 3 (B). Based on the shrinkage profiles (Fig. 3 (A)), the microstructures of samples (Fig. 4) and the XRD patterns (Fig. 5), it is clear that a little drop around 1473 K in shrinkage curves correspond to the formation of TiB₂ from TiC and B, and up to 2173 K the microstructure development gradually proceed and then around 2173 K sudden shrinkage results the densification of powder compact followed by the development of B₄C matrix and perfect TiB₂ appearance as white small particles in Fig. 4 vi).

Thermodynamics of solid state reactions above mentioned can be explained as follows:

\[
\begin{align*}
\text{Ti} + 2\text{B} &= \text{TiB}_2 + \Delta H (315.9 \text{ kJ·mol}^{-1}) \\
\text{Ti} + \text{C} &= \text{TiC} + \Delta H (184.1 \text{ kJ·mol}^{-1}) \\
4\text{B} + \text{C} &= \text{B}_4\text{C} + \Delta H (62.7 \text{ kJ·mol}^{-1})
\end{align*}
\]

From (1) − (2) + (3); \(6\text{B} + \text{TiC} = \text{B}_4\text{C} + \text{TiB}_2 + \Delta H (194.5 \text{ kJ·mol}^{-1})\)

Thus, \((4 + \delta) \text{B} + (1 - \delta/2) \text{C} + \delta/2 \text{TiC} = \text{B}_4\text{C} + \delta/2 \text{TiB}_2\) each value of formation enthalpy of chemical compound is described elsewhere²⁴.

As shown in Fig. 6, all powder compacts after sintering at 2173 K revealed each corresponding B₄C/TiB₂ compositions; B₄C/TiB₂ = (a) 93/7, (b) 91/9 and (c) 89/11 vol% without any other phase. Their microstructures was observed using SEM (Fig. 7 (a)−(d)), proving that the dense B₄C/TiB₂ composites could be fabricated from amorphous (B and C) and fine TiC powders, in which composites fine TiB₂ particles dispersed into dense B₄C matrix homogeneously. Bulk densities of these composites were measured by Archimedes method. Table 1 summarized the bulk \(D_{\text{obs}}\), theoretical \(D_x\) and relative \(D_{\text{obs}}/D_x\) densities as a function of the TiB₂ content; \(D_{\text{obs}}/D_x\) of higher than 98.9% is achieved even the compositions of 89/11 vol%.

3.2 Mechanical properties of composites

Their mechanical properties, such as, three-point bending strength \(\sigma_b\), Vickers hardness \(H_v\), and fracture toughness \(K_{IC}\) were measured; the latter two properties were evaluated using Vickers hardness tester and IF method²², respectively. Fig. 8 displays (a) \(\sigma_b\) (b) \(H_v\) and (c) \(K_{IC}\) of B₄C/TiB₂ composites as a function of TiB₂ content;
the previous data that we already reported at the Spring Conference of Jpn. Powder and Powder Metallurgy in 2016 are also presented. The \( \sigma_s \) values changed like a sine wave; they are low (around 450 MPa) between 1 and 5 vol\% TiB\(_2\) compositions, however, it increased rapidly to 650 MPa at 7 vol\% and decreased gradually to 350 MPa at 11 vol\%. This behavior could not be explained accurately yet, however, compression stress induced in the matrix might play much important role on this matter as will be described.

The other important property of this composite ceramics, \( H \) values increased gradually from 32.5 (pure B\(_4\)C) to 38.0 GPa at 11 vol\% through 33.5 GPa at 7 vol\% TiB\(_2\), although a little drop around 5 vol\%. On the other hand, \( KIC \) values decreased a little from 5.0 to 4.5 MPa·m\(^{1/2}\) through 5.45 MPa·m\(^{1/2}\) at 7 vol\% TiB\(_2\) almost monotonously. The \( KIC \) values determined by the IF method has been investigated and compared with international standardized fracture toughness test reported by Quinn et al\(^{23}\). They used the Standard Reference Material SRM2100 and showed the difference in \( KIC \) values among various IF technique (Niihara\(^{23}\), Miyoshi\(^{26}\) and Anstis\(^{27}\)) as a function of indentation load; up to indentation load of 100 N, Niihara’s eq. tends to give higher \( KIC \) values than those of SRM2100, however, Miyoshi’s eq. is that 96.7% (TiB\(_2\) = 27 nm) and 99.8% (93/7 vol\% TiB\(_2\) = 25 nm in diameter) powders using pulsed electric current pressure sintering at 2173 K (1900°C) for 10 min under 50 MPa in a vacuum; B\(_4\)C/TiB\(_2\) = 93/7 vol\% composite also fabricated using amorphous B and C, and TiB\(_2\) (1.86 μm and 58 nm in diameters).

### Table 1

<table>
<thead>
<tr>
<th>Composition (B(_4)C/TiB(_2)) (vol%)</th>
<th>( D_{obs} ) (Mg/m(^3))</th>
<th>( D_e ) (Mg/m(^3))</th>
<th>( D_{obs}/D_e ) (%)</th>
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<tbody>
<tr>
<td>100/0</td>
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<td>2.654</td>
<td>99.8</td>
</tr>
<tr>
<td>93/7 (58 nm)</td>
<td>2.57</td>
<td>2.654</td>
<td>96.7</td>
</tr>
<tr>
<td>93/7 (1.86 μm)</td>
<td>2.57</td>
<td>2.654</td>
<td>96.7</td>
</tr>
<tr>
<td>91/9</td>
<td>2.68</td>
<td>2.713</td>
<td>98.9</td>
</tr>
<tr>
<td>89/11</td>
<td>2.73</td>
<td>2.733</td>
<td>99.9</td>
</tr>
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</table>

*\( D_e \): Calculated using \( D(B_4C) = 2.515 \text{ Mg/m}^3 \) (PDF: # 35-0798) and \( D(TiB_2) = 4.495 \text{ Mg/m}^3 \) (PDF: # 35-0741).*

will be considered again and corrected. It is easily recognized the smaller \( P_r \), the higher \( H_r \) and \( KIC \); \( H_r \) and \( KIC \) increased rapidly even in the same composition from 27 to 35.5 GPa and from 3.8~4.1 to 5.45 MPa·m\(^{1/2}\), respectively; this should be noted. However, the relative densities \( D_e \) of these composites should be considered and mentioned, especially these mechanical properties. The values of \( D_e \) are that 96.7\% (TiB\(_2\) = 1.86 μm), 96.7\% (TiB\(_2\) = 58 nm) and 99.8\% (TiB\(_2\) = 27 nm\(^3\) from TiC: 25 nm\(^3\)) as shown in Table 1 and their microstructures are also shown in Fig. 10. These SEM photographs reveal that the large starting TiB\(_2\) powder resulted in more porous (Fig. 10 (a)) and the grain sizes \( G \) of TiB\(_2\) in the composites are large in comparison with those (Fig. 10 (b): TiB\(_2\) = 58 nm\(^3\)) and (Fig. 10 (c): TiB\(_2\) = 27 nm\(^3\)).

In order to investigate the effect of small TiC (25 nm\(^3\)) particle addition on the mechanical properties of composites, the unit cell volume \( (v) \) of B\(_4\)C phase was measured precisely at room temperature using high-purity Si as an internal standard. Fig. 11...
shows the $v$ values as a function of TiB$_2$ content (vol%); when the content increased more than around 5 vol%, $v$ value decreased gradually, suggesting the high compression stress on B$_4$C grains, which stress originates from the difference in thermal expansion coefficient: $\alpha$ (TiB$_2$) = 8.1 $\times$ 10$^{-6}$ K$^{-1}$ and $\alpha$ (B$_4$C) = 6.53 $\times$ 10$^{-6}$ K$^{-1}$, and Young’s modulus: $E$ (TiB$_2$) = 370~565 GPa and $E$ (B$_4$C) = 290~450 GPa. Based on this experimental result as shown in Fig. 11, and in addition to the dependence of relative density, the improvement of both $H_v$ and $K_{IC}$ might be explained due to high compression stress on the B$_4$C matrix. Furthermore, the effect of fine TiC particle addition on the mechanical properties was investigated from the microstructural viewpoints using FE-TEM. Fig. 12 shows the TEM image of the microstructure of B$_4$C/TiB$_2$ = 93/7 vol% composite, focusing on the fine TiB$_2$ particle within the B$_4$C matrix; (i) and (ii) images display the particle morphology and elemental analysis on the selected area inside and outside the different “TiB$_2$” particles. In (i), a table indicates the elemental mass fractions in each area and also the chemical compositions derived from this analysis, Ti(B$_{0.74}$C$_{0.26}$) and B$_4$C are inside and outside, respectively. Another (ii) also indicates Ti(B$_{0.79}$C$_{0.21}$) and B$_4$C within and without the “TiB$_2$”. These results proved that these “TiB$_2$” particles are TiB$_2$ solid solution (ss) that contained a small amount of carbon. In Fig. 12 (iii) and (iv), the results of line elemental analysis conducted crossing the TiB$_2$ (ss) particles those are estimated to be around 650 nm are shown. Elemental mass fraction of each position on the line is summarized in table of (iii) and elemental line profiles are displayed along the line in (iv). From these results, it is cleared that TiB$_2$ has a core-shell structure, inner portion is TiB$_2$ (ss) and outer portion is boron carbide solid solution that is deviated from the stoichiometric B$_4$C to B less compositions; totally the chemical compositions of TiB$_2$ (ss) might be TiC:TiB$_2$ = 51~56/49~44 mol%. However, the precise determination of their lattice parameters is difficult due to too small. Then the grain boundary between TiB$_2$ (ss) and B$_4$C matrix was observed precisely using HR-TEM; black upper side region is TiB$_2$ (ss) and lower side B$_4$C. In TiB$_2$ (ss) region, crystalline lattices, (101) and (100) could be distinguished in the black lattices and indicated outside by the lines with circled numbers. The reported XRD data for TiB$_2$ (PDF#35-0741), lattice distance $d$(100) and $d$(101) are 0.26247 and 0.230370 nm, respectively. However, $d$(100) and $d$(101) determined from TEM image are 0.263~0.261 and 0.196~0.198 nm respectively. The former $d$(100) consists with
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Fig. 13  High-resolution TEM photograph on the grain boundary between TiB₂ (left black region) and B₄C (right white region). In TiB₂ (left black region), distance between (100) planes, d(100), and distance between (101) planes, d(101), are determined from TEM image are 0.263–0.261 and 0.196–0.198 nm respectively.

TiB₂: 835-0741, d(100)=0.26247 nm, d(101)=0.20370 nm
that of pure TiB₂ on the other hand, the latter \(d(101)\) of the present TiB₂, \(\langle ss\rangle\) is a little smaller than that pure TiB₂. Considering the smaller atomic radius of carbon (0.77 nm) vs. boron (0.88 nm), boron in the (101) planes might be replaced with carbon.

4 Conclusions

Dense B₄C/TiB₂ composite ceramics have been fabricated from the mixture of amorphous B and C, and fine TiC powders (25 nm in particle size \(\langle s\rangle\), using pulsed electric current pressure sintering (PECPS) at 2173 K under 50 MPa for \(6.0 \times 10^3\) s in a vacuum. During sintering the solid-state reaction between B and C was gradually formed, followed by a continuous formation of B₄C matrix including TiB₂ particles. Thus formed TiB₂ particles have a core-shell structure with the thin surface consisting of B deficient boron carbide and core of TiB₂ solid solution (\(\langle ss\rangle\)) having a small amount of carbon. The present B₄C/TiB₂ (\(\langle ss\rangle\)) = 93/7 vol% composites revealed high bending strength of 650 MPa, Vickers hardness \(H_v\) of 33.5 GPa, and fracture toughness \(K_{IC}\) around 5.5 MPa m\(^{1/2}\) at room temperature. The present composite fabrication method using self-propagating high-temperature synthesis (SHS) and pulsed electric current pressure sintering (PECPS) might become the new process adopted in the next generation.

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29) ibid. Table 223. Young’s modulus of ceramics, p. 762.

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