Fabrication of Dense TiB$_2$/[ZrO$_2$-Al$_2$O$_3$] Composites with Both High Hardness (≥20 GPa) and Fracture Toughness (≥12 MPa·m$^{1/2}$) Simultaneously by Pulsed Electric-current Pressure Sintering

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ABSTRACT

In order to produce ceramic composites having both high Vickers hardness $H_v$ ≥20 GPa and high fracture toughness $K_{IC} ≥10$ MPa·m$^{1/2}$, dense TiB$_2$/[ZrO$_2$-Al$_2$O$_3$] composites have been fabricated using pulsed electric-current pressure sintering (PECPS) at 1873 K under 50 MPa for $6.0 × 10^3$ s in Ar. As the former starting materials, two kinds of TiB$_2$ powders were adopted; i) mono-modal particle size ($P_s$) distribution with an average particle size $<P_s>$ of 3.24 μm and ii) bi-modal $P_s$ distribution with $<P_s>$ of 3.06 μm, composed of the small $P_s$ of 0.58 and the large $P_s$ of 3.27 μm. On the hand, the latter was the mixed powders composed of ZrO$_2$(2.5 mol%Y$_2$O$_3$) solid solution (ss) and α-Al$_2$O$_3$ powders: each primary $P_s$ was 0.1–0.2 μm. Thus fabricated composites consisting of TiB$_2$, tetragonal/monoclinic ZrO$_2$ and α-Al$_2$O$_3$ with relative densities more than 99.0% showed improved mechanical properties, especially bi-modal TiB$_2$/[ZrO$_2$-Al$_2$O$_3$] composites revealed high $H_v$ of 22.3 GPa and $K_{IC}$ of 12.8 MPa·m$^{1/2}$. These high-mechanical behaviors might be explained in terms of i) better powder particle configuration, ii) high chemical stability of TiB$_2$, iii) the most proper composition, with adoption of iv) bi-modal TiB$_2$ powder and v) the most suitable sintering condition.

KEY WORDS

- titanium boride, partially stabilized ZrO$_2$, α-Al$_2$O$_3$, vickers hardness, fracture toughness

1 Introduction

As shown in Table 1 which summarizes various kinds of physical properties of representative hard materials, up to now, mainly three kinds of engineering ceramics have been developed; oxide and non-oxide, such as carbides (2), nitrides (4), borides (5) and their composites. The former oxides, partially stabilized ZrO$_2$ (PSZ) (6) and Al$_2$O$_3$ (7) are representatives, show relatively high bending strength $\sigma_b$ and high fracture toughness $K_{IC}$ are which are originated from stress-induced transformation toughening (8), and high chemical stability in air at high temperatures. Therefore, dense monolithic or dual composite oxides have been studied; utilizing high $K_{IC}$ of a small amount of Y$_2$O$_3$ added tetragonal ZrO$_2$ (YTZ) (9) and high hardness of Al$_2$O$_3$ (10). And controlling the microstructure, both high $\sigma_b$ more than 1.0 GPa and toughness $K_{IC}$ ≥15 MPa·m$^{1/2}$ at the same time have been achieved (11-14). The second non-oxides, such as carbides (SiC, TiC (20)), nitrides (Si$_3$N$_4$, TiN (21), Ti-C-N (22)) and borides (B$_4$C, TiB$_2$) (23) had been studied and widely used. Among them, two nitrides, TiN and Ti-C-N, had been utilized as the thin films which were formed on the hard metal based materials (tool steel, tungsten carbide) for cutting tools because it was very difficult to fabricate bulk materials due to their poor sinterability originated from covalent bonding. The third materials now have been being developed intensively since 2010; oxide-carbide, such as Al$_2$O$_3$-TiC (17-18), ZrO$_2$-SiC (19), Al$_2$O$_3$-ZrO$_2$-TiC (20), oxide-borides, ZrO$_2$-TiB$_2$ (21-23), ZrO$_2$-ZrB$_2$ (24), with the aim of utilizing the chemical stability and sinterability of oxides and high Vickers hardness $H_v$ of non-oxides.

For example, Al$_2$O$_3$-TiC composite (25) was developed at first for the substrate of thin-film magnetic heads for hard-disk drive and then have being being widely used for cutting tools because it showed high mechanical properties such as high hardness $H_v$ of 21.2 GPa (26), high-temperature strength, thermal shock resistance, and high chemical stability in air at elevated temperatures, and improved electrical conductivity; these physical and mechanical properties might be originated from those of Al$_2$O$_3$ and TiC. However, this composite also has a weak point of low $K_{IC}$ about 5.2 MPa·m$^{1/2}$ and low productivity using hot isostatic pressing (HIP) to densification.

Until now, high mechanical properties of simultaneous $H_v$ and $K_{IC}$ more than 20 GPa and 12 MPa·m$^{1/2}$, respectively, have not been achieved in the oxide based composite materials. However, we have attained higher mechanical properties just mentioned above...
by utilizing both high $K_{IC} \geq 15$ MPa·m$^{1/2}$ of PSZ-Al$_2$O$_3$ (PSZA) composites$^{12,13}$ and high $H_v$ of 33.3 GPa of TiB$_2$$^5$, and controlling their microstructures and crystalline phases by adopting the suitable powder particle configuration and sintering conditions.

In the present study, the improved mechanical behaviors of TiB$_2$/[ZrO$_2$-Al$_2$O$_3$] composites have been described precisely with relation to their microstructures.

### 2 Experimental procedure

#### 2.1 Fabrication of composites

Fig. 1 shows the flowchart for fabrication of TiB$_2$/[ZrO$_2$-Al$_2$O$_3$] composites. Two kinds of TiB$_2$ powders with mono- and bi-modal particle size ($P_s$) distributions (Japan New Metal Co. Ltd., Osaka, Japan; purity of 99.9%, theoretical density $D_x$ of 4.495 Mg·m$^{-3}$), as will be described later, and the mixtures of partially stabilized zirconium oxide ZrO$_2$ powder added with 2.5 mol% Y$_2$O$_3$, PSZ(2.5 mol%Y$_2$O$_3$), and $\alpha$-Al$_2$O$_3$ with the mixing ratio of PSZ(2.5Y)/$\alpha$-Al$_2$O$_3 = 77/23$ mol%, i.e., afterward abbreviated to PSZA, (Daiichi Kigenso Kagaku Kogyo Co., Ltd., Osaka, Japan; purity of 99.8%, average $P_s$ of around 0.1 μm, $D_x$ of 5.36 Mg·m$^{-3}$) were used as the starting materials. These powders, TiB$_2$ and PSZA, were weighed into the final compositions of TiB$_2$/PSZA = 100/0 to 0/100 vol%, at this stage we presumed that PSZ would have tetragonal ZrO$_2$ phase after pulsed electric-current pressure sintering (PECPS) at 1873 K for $6.0 \times 10^2$ s under 50 MPa in Ar. The weighed powders were mixed in regent grade ethanol 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. Then, the powder mixtures were prepared by drying the slurries with stirring at room temperature in air. After mixing with a small amount of polyvinyl alcohol aqueous solution (concentration of 7 mass%), the mixtures were uniaxially pressed into disks with a 16 mm diameter and a $\sim 5 \times 10^{-3}$ m thickness at 50 MPa and then cold isostatically pressed at 245 MPa for $6.0 \times 10^2$ s. The compressed powder compacts were wrapped with h-BN powder ($P_s$ of ~3 μm, >98% purity), then, they were put into a cylindrical mold (20 mmϕ-40 mmϕ-40 mm, high-density carbon) that was used for PECPS (SPS-5104A, SPS SYNTEX INC., Tokyo, Japan). Using this apparatus, sintering was performed at 1673 to 1873 K for $6.0 \times 10^2$ s under an uniaxial pressure of 50 MPa in Ar.
heating rate of 1.66 K·s$^{-1}$ and a cooling rate of $\sim 8.33 \times 10^{-3}$ K·s$^{-1}$, applying DC pulsed electric-current (on/off interval = 12:2). Heating temperature above $\sim 873$ K was monitored at the center position of the outside wall of carbon mold using a monochrome pyrometer. Sintering temperature of each composite was decided to give the highest relative density of correspondingly.

2.2 Evaluation

Crystalline phases of the sintered materials were identified by X-ray diffraction (XRD) analysis (CuKα radiation, Rint 22000, Rigaku, Osaka, Japan). Microstructural observation on the morphology and elemental distributions, as well as the fractured or polished surfaces of sintered composites, was conducted using a both field emission-type scanning electron microscopy (FE-SEM, JSM-7001FD; JEOL, Tokyo, Japan) equipped with an energy-dispersive spectroscope (EDS, JED-2300/F; JEOL). Bulk densities ($D_{\text{obs}}$) of mixed powder compacts, i.e., green densities, were estimated by measuring the weights and dimensions of powder compacts; and $D_{\text{obs}}$ of sintered materials also 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 into 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 $\sigma_b$ was evaluated with a crosshead speed of $8.33 \times 10^{-3}$ m·s$^{-1}$ and an 8.0 × 10$^{-3}$ m-span length using WC jigs. Vickers hardness $H_v$ and fracture toughness $K_{IC}$ were evaluated with an applying load of 196 N and a duration time of 15 s for the former, and the indentation fracture method (IF) with Niihara’s equation$^{27}$ for the latter.

3 Results and discussion

3.1 Starting powders

In the present study, as based on the idea that bi-modal particle-size ($P_s$) distribution powder might give the higher densities of powder compacts and sintered materials than those of mono-modal $P_s$ distribution powder, then mono- and bi-modal TiB$_2$ powders were adopted and compared. Fig. 2 shows the $P_s$ distributions and SEM images of TiB$_2$: (a) mono- and (b) bi-modal TiB$_2$ powders. The former showed an average $P_s$ of 3.24 μm and on the other hand, that of latter was 3.06 μm; the small $P_s$ of 0.58 μm and the large $P_s$ of 3.27 μm from the $P_s$ distribution data. S. Yerazunis, et al.$^{28}$, reported that packing density of binary mixed spheres was much depend on both the ratio of large $P_s$/small $P_s$ and the content of small $P_s$ powder. The higher ratio, the better relative density at the content of small $P_s$ powder around 30%. In the present study, bi-modal TiB$_2$ powder, the ratio of large $P_s$/small $P_s$ = 3.27/0.58 = 5.63, and a roughly estimation of the content of small $P_s$ powder from the height of each peak was 15%. From these, it could be estimated that the packing density of bi-modal TiB$_2$ powder compact had a relative density $D_r$ around 70%, on the other hand that of mono-modal TiB$_2$ had the $D_r$ around 63%$^{28}$, thus it was thought that bi-modal distribution would give us about 7% higher density than mono-modal.

Furthermore, the counter part of starting materials, PSZA powder was characterized using a SEM equipped with EDS. Fig. 3
shows SEM images of mixed powder with the composition of \( \text{ZrO}_2(2.5 \text{ mol}\% \text{Y}_2\text{O}_3)/\text{Al}_2\text{O}_3 = 77/23 \text{ mol}\% \): taken under (a) low, (b) middle and (c) high magnifications, right (d) and (e) showing elementary analysis of white and gray particles corresponding to \( \text{ZrO}_2(2.5 \text{ mol}\% \text{Y}_2\text{O}_3) \) and \( \text{Al}_2\text{O}_3 \), respectively. At a glance, SEM images suggested that PSZA powder was spray-dried spherical balls with 3~5 μm in diameter, consisted of fine \( \text{ZrO}_2(2.5 \text{ mol}\% \text{Y}_2\text{O}_3) \) solid solution particles (\( P_s \): 0.1~0.2 μm), which is proved by XRD analysis, and also fine α-\( \text{Al}_2\text{O}_3 \) powder.

The mixed powder compacts with the final composition of TiB\(_2\)/PSZA = 65/35 vol% were sintered using pulsed electric-current pressure sintering (PECPS). Fig. 4 shows the shrinkage profiles of (a) mono- and (b) bi-modal TiB\(_2\)/PSZA powders compacts. The drastic shrinkages around 1323 K are very interesting; i) the shrinkage starting-temperature \( T_{\text{s,ink}} \) for mono-modal TiB\(_2\)/PSZA compact is about 1165 K, on the other hand, \( T_{\text{s,ink}} \) for bi-modal TiB\(_2\)/PSZA shifts to lower temperature (1100 K) than that of the former by 65 K, and ii) the degree of shrinkage \( \Delta l/l_o \) between the top at 1100~1165 K and bottom at 1323~1345 K are 0.34 and 0.39 for the former and the latter, respectively. As will be described later, the bulk density of mixed powder compact, \( D_{\text{green}} = 2.78 \) and \( D_{\text{green}} = 3.12 \text{ Mg·m}^{-3} \) for mono- and bi-modal TiB\(_2\)/PSZA powder compacts, respectively, and high shrinkage \( \Delta l/l_o \) degree for the latter, the sinterablity of PSZA might be enhanced by the small TiB\(_2\) particles contained in bi-modal powder; here, the authors presumed the shrinkages from 1100 to 1345 K might be originated from fine PSZA sintering. Then the microstructure of both sintered samples were observed. Fig. 5 displays SEM images taken under low [(a), (c)] and high [(b), (d)] magnifications for mono- and bi-modal TiB\(_2\)/PSZA compacts = 65/35 vol% composites, respectively; they were sintered at 1323 K for \( 6.0 \times 10^2 \) s under 50 MPa in Ar. It is clear that low magnified SEM images prove the finer grains surrounded by bi-modal TiB\(_2\) particles and high magnification images display the smaller voids are distributed in the latter composites, i.e., bi-modal TiB\(_2\)/PSZA = 65/35 vol% composites. These phenomena might be explained by the fact that the many smaller TiB\(_2\) particles could suppress the grain growth of PSZA during sintering and occupied the vacant space formed by large TiB\(_2\) particles in the powder compact. And also crystalline phases of powder compacts were
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Fig. 5  SEM photographs taken under low [(a),(c)] and high [(b),(d)] magnifications for mono-modal and bi-modal TiB2/PSZA = 65/35 vol% composites, respectively; they were sintered at 1323 K.

Fig. 6  XRD patterns of TiB2/PSZA = 65/35 vol% composites from mono-modal TiB2 and PSZA powders fabricated at various temperatures: (a) 1673 K, relative density \(D_r = 92.4\%\), (b) 1773 K, \(D_r = 98.1\%\), and (c) 1873 K, \(D_r = 99.6\%\) for 6.0 \(\times\) 10\(^2\) s under 50 MPa in Ar. At low sintering temperature of 1673 K, the composite consisted of only TiB2 and PSZA phases, however, with increasing sintering temperature, such as, 1773 and 1873 K, in addition to two phases the other B\(_6\)O\(_{0.787}\) (DB card #01-087-2286) appeared in the composites. On the other hand, the bi-modal TiB2/PSZA composite showed that they consisted of only two phases even sintered at 1873 K as shown in Fig. 7. From the fact that i) bulk densities of powder compacts, \(D_{\text{green}}\) (mono-modal TiB2/PSZA) = 2.78 Mg m\(^{-3}\), and \(D_{\text{green}}\) (bi-modal TiB2/PSZA) = 3.12 Mg m\(^{-3}\), ii) simple crystalline phases of 1873 K-sintered composites consisting of only TiB2 and PSZA, and iii) bulk density of sintered composite \(D_{\text{bulk}}\) (mono-modal TiB2/PSZA) = 4.79 Mg m\(^{-3}\) (\(D_r: 99.6\%\)) and \(D_{\text{bulk}}\) (bi-modal TiB2/PSZA) = 4.80 Mg m\(^{-3}\) (\(D_r: ≥99.9\%\)), bi-modal TiB2 powder gave the higher microstructural properties, such as two-phase composites, and high bulk density, hereafter, bi-modal TiB2 powder was used for the experiments in the present study.

Fig. 7  XRD pattern of TiB2/PSZA = 65/35 vol% composites from bi-modal TiB2 and PSZA powders fabricated 1873 K for 6.0 \(\times\) 10\(^2\) s under 50 MPa in Ar.

Fig. 8 shows SEM (BEI) images of the microstructures of 65/35 vol% composites fabricated from; (a) ~ (c) mono-, and (d) ~ (f) bi-modal TiB2 mixed with PSZA powders. Sintering was performed at 1873 K for 6.0 \(\times\) 10\(^3\) s under 50 MPa in Ar. At a glance, SEM images of mono-modal TiB2 based composites, (a) and (b) taken under low magnifications, indicate large-localized white-island-shaped regions (PSZA matrix) consisting a small grey particles, i.e., TiB2, however, those of bi-modal TiB2 based composites, (d) and (e) under the same magnifications as (a) and (b), do not show little island-shaped regions. There is a little difference between higher magnified SEM images (c) and (f) in a small partially area. Therefore, big difference in
the microstructures between mono- and bi-modal TiB₂ derived composites was that, the former tended to segregate the PSZA island-shaped regions than the latter. This phenomenon implied the decrease in mechanical properties of the former composites.

Then the microstructures of other composites derived from bi-modal TiB₂ were observed. Fig. 9 shows SEM (BEI) images of the microstructures with various compositions fabricated using PECPS for $6.0 \times 10^3 \text{s}$ under 50 MPa in Ar. TiB₂/PSZ23A=: (a) 20/80 vol% (1723 K), $D_r = 99.8\%$, (b) 40/60 (1723 K), 99.9\%, (c) 60/40 (1873 K), 99.9\%, and (d) 80/20 (2173 K), 97.0\%.

Dense composites composed of a lot of PSZA powders, such as (a) 80 and (b) 60 vol% can be fabricated by relatively low sintering temperature of 1723 K; this might be due to both sinterable PSZA powder and PECPS which could densify the materials at low temperatures\(^{12}\), however, with decreasing fine PSZA powder, the composites required higher sintering temperatures from 1873 to 2173 K to fabricate dense materials, and then this brought the grain growth of TiB₂.

Fig. 9 represents mechanical properties of bi-modal TiB₂/PSZA composites as a function of TiB₂ content: (a) bending strength $\sigma_b$, (b) Vickers hardness $H_v$, and (c) fracture toughness $K_{IC}$. Bending strength $\sigma_b$ gradually decreases with increasing the PSZA content, showing that high $\sigma_b$ has been much depend on PSZA content. On the other hand, Vickers hardness $H_v$ shows a plateau up to 50 vol%
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TiB₂, however, the graph revealed a peak value of 22.3 GPa around 65 vol% TiB₂ composition. This must be explained by their microstructure, such as relative density, and grain sizes of TiB₂ and PSZA as shown in Fig. 9 (d). In Fig. 10, previous data reported on TiB₂(1%CoB-6%TaB₂)/ZrO₂ = 82.6/17.4 vol% composite shown in black rhombic (Hᵥ: 18 GPa, KᵥC: 8 MPa·m⁻⁰.⁵)⁹ and TiB₂/ZrO₂(Y₂O₃) = 82.6/17.4 vol% composites in white quadrate (Hᵥ: 21 GPa, KᵥC: 5-6 MPa·m⁻⁰.⁵)²⁰ are also plotted. Fracture toughness KᵥC values are presented in Fig. 10 (c). Both Hᵥ and KᵥC reveal the nearly same plateau between 10 and 50 vol% TiB₂ and then mounted a hill, showing the peak values of Hᵥ: 22.3 GPa and KᵥC: 12.8 MPa·m⁻⁰.⁵. These could be explained in term of achieving a delicate balance between the TiB₂/PSZA composition and the microstructure, as already described. Then the effect of microstructure on both Hᵥ and KᵥC were investigated. In Fig. 11, Vickers hardness Hᵥ and fracture toughness KᵥC of TiB₂/PSZA = 65/35 vol% composites with various t-ZrO₂ (vol%) ratios, which were obtained by controlling sintering temperature, and discrimination of TiB₂, i.e., mono- or bi-modal powders are also displayed. It should be noted that both peak values of Hᵥ and KᵥC are achieved at nearly the same t-ZrO₂ (vol%) of around 23% and the highest t-ZrO₂ (vol%) value of 94% did not give the higher values, even for KᵥC which was much depend on t-ZrO₂ phase content. This means that in these composites stress induced transformation toughening mechanism of ZrO₂ from tetragonal to monoclinic did not play an important role. Then other toughening mechanism was investigated. Fig. 12 shows SEM photographs of Vickers impressions formed under the condition of 196 N for 1.5 × 10⁻⁵ s: (a)-I to (a)-III and (b)-I to (b)-III for the mono- and bi-modal TiB₂/PSZA = 65/35 vol% composites, respectively; among them (a)-II & (a)-III and (b)-II & (b)-III show each crack propagation pathway on their surface under moderate and high magnifications, respectively. At a glance on (a)-I and (b)-I, it is very interesting that the shape of impressions is much different between mono- and bi-modal TiB₂ derived composites; the former has a quadrilateral and the latter asteroid with 4 legs. However, when we observed the latter we found the same thin quadrilateral impression around the asteroid; this distorted impression might be originated from the small TiB₂ particles with higher hardness (Hᵥ: 32-33 GPa)⁵ than that (Hᵥ: 14-15 GPa)¹¹,¹² of PSZA. And these crack deflections in the propagation pathway could increase KᵥC values, because from our previous study¹¹ the ZrO₂ transformation toughening required higher t-ZrO₂ ratio than 60 vol% in bulk material, however, the t-ZrO₂ ratios in these composites with high KᵥC were only 20~25% as shown in Fig. 11. Then the microstructures of these composites were observed and investigated precisely. Fig. 13 and 14 present SEM images and EDS analyses of mono- and bi-modal TiB₂/PSZA = 65/35 vol% composites, respectively, those were fabricated under the condition of (1873 K/6.10 × 10⁻⁵ s/50 MPa/Ar); (a)~(c): BEI images taken under various magnifications, (d)~(e): EDS line-analysis along with red lines and (f): EDS positioning analysis. In each Figs, tables summarized the elemental atomic contents at the position identified by corresponding numbers in Fig. (f). Among these images there is not so much difference, however,
some coagulates are found in Fig. 13 (a) and (b), which correspond to ZrO$_2$-Al$_2$O$_3$ grains from brighter images (heavy element, i.e., Zr) and EDS line-analysis. And when we compare the images between Fig. 13 (d) and Fig. 14 (d), especially, in the latter white brighter regions are easily distinguished, indicating ZrO$_2$ grains are surrounded by a little gray belt, α-Al$_2$O$_3$; that is, segregation of α-Al$_2$O$_3$ from the PSZA powder is clear, however, in the former the degree of segregation is not so high. In this way a little difference might have much effect of increasing $K_{IC}$.

### 4 Conclusions

By adopting the suitable composition and controlling the microstructure through good selection of the starting materials, such as mono-modal or bi-modal TiB$_2$ powders, and utilization of
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rapid sintering, i.e., pulsed electric-current pressure sintering, both high Vickers hardness \( H_v \) (22.3 GPa) and high fracture toughness \( K_{IC} \) (12.8 MPa·m¹/²) have been achieved simultaneously in the dense TiB₂/[ZrO₂(2.5 mol%Y₂O₃)-23 mol%Al₂O₃] = 65/35 vol% composites. These high mechanical properties have not been reported before in the ceramics. Thus fabricated composites could be a candidate materials for high-performance working tool in future.

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