Microstructure and properties of $\text{ZrB}_2\text{-SiC}$ and $\text{HfB}_2\text{-SiC}$ composites fabricated by spark plasma sintering (SPS) using TaSi_2 as sintering aid

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Dense $\text{ZrB}_2\text{-SiC}$ and $\text{HfB}_2\text{-SiC}$ composites were fabricated at 1800°C by spark plasma sintering (SPS) using TaSi_2 as sintering aid. The volume content of SiC was 5–30% and that of TaSi_2 was 5% in the initial compositions. The additive of TaSi_2 contributed to the densification of composites by the decomposition and simultaneous solid solution of Ta atoms into boride grains which was probably associated with the decrease of activation energy of boride grain boundaries. With increasing SiC content, the electrical conductivity of $\text{ZrB}_2\text{-SiC}$ and $\text{HfB}_2\text{-SiC}$ composites decreased from 19.89 to 11.99 and 22.29 to $13.42 \times 10^5 \Omega^{-1}\cdot\text{m}^{-1}$ respectively. Generally, the thermal conductivity of composites showed an increasing tendency with increasing SiC content, indicating the maximum values of 49.93 and 118.39 W/m·K respectively for $\text{ZrB}_2\text{-SiC}$ and $\text{HfB}_2\text{-SiC}$ composites produced with 30 vol % SiC content in the initial compositions. Additionally, the Vickers hardness of composites increased with the increment of SiC content from 16.9 to 20.2 and 24.0 to 28.5 GPa for $\text{ZrB}_2\text{-SiC}$ and $\text{HfB}_2\text{-SiC}$ composites respectively. The fracture toughness of $\text{ZrB}_2\text{-SiC}$ composites showed an increasing tendency from 3.70 to 4.44 $\text{MPa}\cdot\text{m}^{1/2}$ with increasing SiC content while those of $\text{HfB}_2\text{-SiC}$ composites did not show a changing tendency and was in a range of 3.28–3.54 $\text{MPa}\cdot\text{m}^{1/2}$. The elastic moduli of composites declined from 464.8 to 453.2 and 494.4 to 481.9 GPa for $\text{ZrB}_2\text{-SiC}$ and $\text{HfB}_2\text{-SiC}$ composites respectively with increasing SiC content.

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1. Introduction

Transition metal borides ZrB_2 and HfB_2 , due to their high melting points, high Young's moduli, high hardness, and good thermal conductivities, have been considered as the promising thermal protective materials for reentry spacecrafts.^{1)–4)} However, due to their poor self-diffusivity and strong covalence in the crystals, it is difficult to densify them at a temperature below 2000°C. Generally, sintering additives were introduced to lower the densification temperature. There are three main kinds of sintering aids: carbon and carbides (carbon, B_4C , WC, VC, SiC),^{5)–9)} nitrides (Si_3N_4 , ZrN, AlN, HfN),^{10)–13)} and silicides (ZrSi_2 , MoSi_2 , Ta_5Si_3 , TaSi_2 , TiSi_2).^{14)–18)} When using TaSi_2 , Sciti et al.¹⁷⁾ proved that dense fine-grained ZrB_2 -based and HfB_2 -based composites containing 15 vol % TaSi_2 could be produced at 1850 and 1900°C respectively under 30 MPa by hot pressing. However, the introduction of TaSi_2 caused the appearance of core-shell structure in which the core was ZrB_2 or HfB_2 and the shell was the solid solutions containing Ta. It was believed that the decomposition of TaSi_2 and solid solution of Ta atoms into boride grains induced the formation of solid solution. Very recently, Hu et al.^{19),20)} reported that the additive

of 10–20 vol % TaSi_2 could effectively decrease the sintering temperature to 1600°C for $\text{ZrB}_2\text{-SiC}$ composites through spark plasma sintering. He considered that the Ta atoms from the decomposition of TaSi_2 probably decreased the ZrB_2 grain boundary activation energy which contributed to the formation of coherent structure of grain boundaries. In addition, Ta atoms entered the ZrB_2 grains to form solid solution. Interestingly, when the sintering temperature was increased to 1800°C, the core-shell structure disappeared due to the homogeneous diffusion of Ta atoms in the boride grains. It is known that spark plasma sintering is an advanced sintering technique with high energy activity.^{21)–29)} In comparison with hot pressing, spark plasma sintering could enhance sintering by activating one or more concurring mechanisms, such as surface oxide removal, electromigration and electroplasticity.²³⁾ Similarly, Gasch et al.³⁰⁾ produced dense $\text{HfB}_2\text{-SiC}$ composites with 5 vol % TaSi_2 additive at 1800–1900°C using field assisted sintering (FAS).

To date, the systematic investigation of $\text{ZrB}_2\text{-SiC}$ and $\text{HfB}_2\text{-SiC}$ composites fabricated by spark plasma sintering with TaSi_2 as sintering aid is rare. In this work, in addition to the research on low temperature densification of boride composites with 5–30 vol % SiC and 5 vol % TaSi_2 additive, the microstructure, physical, and mechanical properties of as-prepared materials were also evaluated.

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2. Experimental procedures

Commercial powders of ZrB_2 (99%, 2 μm) (Rare Metallic Co., Ltd., Japan), HfB_2 (99%, 2 μm) (Japan New Metals Co., Ltd., Japan), α -SiC (99%, 0.55 μm) (Yakushima Denko Co., Ltd., Japan), and TaSi_2 (99%, 2–5 μm) (Japan New Metals Co., Ltd., Japan) were used for fabricating the composites. The designed components contained 5–30 vol % SiC and 5 vol % TaSi_2 . These composites were named as ZS5–30 and HS5–30 respectively based on the initial SiC content. The powders were weighed with an electrical balance with an accuracy of 10^{-2} g. The weighed powders were mixed for 24 h in a SiC jar with ethanol as the dispersant. The milling media were silicon carbide balls. After milling, the slurry was dried in air and then sieved using a 125-mesh sieve. Then the mixture was put into a graphite die with a diameter of 20 mm for pre-compaction under a pressure of 5 MPa. A layer of flexible graphite paper (~ 0.2 mm thickness) was pre-set into the inner wall of die for lubricating and filling the gap between the punches and die, and the die was wrapped using a layer of carbon fiber for inhibiting the rapid heat diffusion. After that, the green body together with the die was heated in a spark plasma sintering apparatus (100 kN SPS-1050, Syntex Inc., Japan) in vacuum (10^{-2} Pa). Each pulse lasted 3.3 ms and the duty cycle was 12 pulses on and 2 pulses off. The temperature was measured by an optical pyrometer focusing on a hole in the wall of die. From ambient temperature to 700°C, it took 5 min to heat the sample. Then the temperature was increased up to 1800°C with a heating rate of 100°C/min. The holding time was 5 min. The sintering displacement versus temperature was recorded simultaneously and finally corrected using a known thermal expansion of graphite die. During sintering, the uniaxial pressure was increased to 30 MPa before 1000°C. After the power was turned off, the sample was cooled down to ambient temperature with the cooling rate of furnace. For comparison, milled pure ZrB_2 powder (ZT0) was sintered at 1800°C using the same procedure.

The contaminations on the surface of samples were removed using a diamond grinding wheel. All the samples were ground and polished down to 1.0 μm diamond grits. The densities of composites were measured with the Archimedes method. The phase compositions were examined by an X-ray diffraction (XRD) analyzer (JDX-3500, JEOL Ltd., Japan) with $\text{Cu K}\alpha$ radiation. The morphologies of polished and fracture surface of samples were investigated by a scanning electron microscope (SEM) (JSM-6500, JEOL Ltd., Japan) equipped with an energy dispersive spectroscopy (EDS) system. Vickers hardness measurement was conducted by a microhardness tester (MVK-E, Akashi Co., Japan) under a load of 9.8 N. For each sample, nine indents were measured. The evaluation of fracture toughness of samples was conducted by an indentation microfracture (IM) method. A hardness tester (AVK-A, Akashi Co., Japan) was adopted to produce the diagonal cracks. The applied load was 49 N. The lengths of diagonal cracks were measured by SEM. For each sample, at least six indents were examined. The elastic property was evaluated by an ultrasonic equipment (TDS 3034B, Tektronix Inc., USA). For each sample, three tests were conducted. The electrical conductivity was measured using a four-wire probe at room temperature. The applied constant current was 50 mA supplied by a DC precision current source (Model 6220, Keithley, Ohio). The current–voltage (IV) characteristics of samples were recorded using a digital nanovoltmeter (Model 2182, Keithley, Ohio). Additionally, thermal conductivity measurement was performed by a Xenon flash apparatus (LFA447

Fig. 1. Displacement of ZrB_2 -SiC composites versus sintering temperature during spark plasma sintering. ZS5–30 indicate the samples with different SiC content, and ZT0 is the sample of milled pure ZrB_2 powder.

Nanoflash, NETZSCH, Germany) at room temperature. A disk specimen with a dimension of $\Phi 10 \times 2$ mm² was used and tested for three times. A layer of graphite was coated on the surface of sample to enhance the absorption of Xenon light pulse energy and the emission of infrared radiation to the temperature detector.

3. Results and discussion

Figure 1 shows the displacement of ZrB_2 -SiC composites versus the sintering temperature during spark plasma sintering. It is seen that for composites when the sintering temperature is above 1100°C the displacement increases rapidly with the increment of temperature, which is possibly associated with the initial compaction of composites with decreasing porosity. On the other hand, at the temperature of 1400–1550°C, there is one stage of slight increase of displacement, which is probably ascribed to the decomposition and solid solution of Ta atoms into ZrB_2 grains. In previous investigation, it has been found that the core-shell structure existed in the ZrB_2 -SiC composites with 10 vol % TaSi_2 additive when sintered at 1600°C by SPS and no TaSi_2 could be examined in the dense composites.¹⁹⁾ It meant that TaSi_2 has decomposed completely before 1600°C. It is one evidence to describe the consumption of TaSi_2 at the temperature range of 1400–1550°C, which is associated with the continuous increase of displacement. Furthermore, when the sintering temperature is above 1550°C the displacement increases fast once again, which is due to the elimination of pores. The existence of Ta at the grain boundaries accelerates the formation of coherent structure among boride grains by decreasing the activation energy of grain boundaries.²⁰⁾ It seems that in present samples the additive of 5 vol % TaSi_2 could not lead to the full densification of composites at 1600°C. When the temperature reaches 1680°C, the displacement begins to approach a constant. This indicates that the samples are almost fully densified. In comparison with the composites, the displacement of milled pure ZrB_2 powder always shows an increasing tendency with increasing sintering temperature. It is concluded that the additive of TaSi_2 is propitious to the densification process of ZrB_2 matrix. In addition, the sintering displacement versus temperature of HfB_2 -SiC composites has the similar change tendency (not shown for brevity), which demonstrates the positive effect of TaSi_2 additive on densification.

Fig. 2. X-ray diffraction (XRD) patterns of composites sintered at 1800°C: (a) ZrB₂-SiC (ZS) and (b) HfB₂-SiC (HS).

Figure 2 shows X-ray diffraction patterns of ZrB₂-SiC and HfB₂-SiC composites sintered at 1800°C. No TaSi₂ diffraction peaks are observed in the diffraction spectra (Figs. 2(a) and 2(b)). It is believed that TaSi₂ phases have completely decomposed and Ta atoms entered boride grains to form solid solutions. With the increasing SiC content in the composites, the diffraction peaks of SiC become stronger. Additionally, a small amount of ZrO₂ and HfO₂ were detected in the composites, which is possibly ascribed to the ball milling process. Lee et al.³¹⁾ determined that the fresh surface of ZrB₂ particles during milling were easily covered by oxides, which is common in non-oxide particles.^{32),33)} **Figure 3** shows SEM micrographs of polished and fracture surface of ZrB₂-SiC and HfB₂-SiC composites. On the polished surface of composites, it is evident that there are not obvious pores (dark color) in the ZrB₂ and HfB₂ matrixes (grey color) with different content of SiC particles (grey-black color) (Figs. 3(a), 3(c), 3(e), and 3(g)). The measured densities of all of the composites are above 98.2% of the theoretical values. When the SiC content is low as 5 vol% in the initial compositions, the SiC particles distribute homogeneously and independently in the sintered ZrB₂ and HfB₂ matrixes (Figs. 3(a) and 3(e)). On the other hand, the higher SiC content in the initial compositions results in the connection of SiC particles as web structure in the dense samples (Figs. 3(c) and 3(g)). In the fracture surface of composites, both transgranular and intergranular fractures can be observed (Figs. 3(b), 3(d), 3(f), and 3(h)). In the fractured surface of HS5 and HS20, the transgranular fracture is the primary damage

Fig. 3. Scanning electron microscope (SEM) micrographs of polished and fracture surface of composites: (a) and (b) ZS5, (c) and (d) ZS30, (e) and (f) HS5, and (g) and (h) HS20.

Fig. 4. Crack propagation on the polished surface of ZS and HS composites. The arrow shows the propagating direction.

mode. While in the fractured surface of ZS30, the intergranular fracture controls the crack propagation. Further work about crack propagation on the polished surface of composites also proved this, as shown in **Fig. 4**. Obviously, the cracks on the polished surface of both ZS5 and ZS30 are deflected by the SiC particles. Because that in ZS5 the SiC content is low, the crack mainly traverses the boride grains. It seems that more introduced SiC particles in the ZrB₂ matrix benefit the larger energy dissipation by crack deflecting, which probably contributes to the enhancement of fracture toughness. However, the cracks on the polished

Table 1. Typical physical and mechanical properties of ZrB₂-SiC (ZS) and HfB₂-SiC (HS) composites fabricated at 1800°C by spark plasma sintering

Samples	Electrical conductivity ($\times 10^5 \Omega^{-1} \cdot \text{m}^{-1}$)	Thermal conductivity (W/m·K)	Vickers hardness (GPa)	Fracture toughness (MPa·m ^{1/2})	Young's modulus (GPa)
ZS5	19.89 $\pm$ 5.16	41.94 $\pm$ 0.41	16.9 $\pm$ 1.0	3.70 $\pm$ 0.66	464.8 $\pm$ 1.2
ZS10	17.87 $\pm$ 3.56	39.53 $\pm$ 0.30	17.2 $\pm$ 0.9	3.87 $\pm$ 0.92	460.8 $\pm$ 0.9
ZS20	15.15 $\pm$ 1.20	43.28 $\pm$ 0.26	19.0 $\pm$ 1.3	3.91 $\pm$ 1.03	458.8 $\pm$ 1.0
ZS30	11.99 $\pm$ 1.84	49.93 $\pm$ 0.48	20.2 $\pm$ 0.8	4.44 $\pm$ 0.91	453.2 $\pm$ 0.8
HS5	22.29 $\pm$ 1.66	77.91 $\pm$ 0.16	24.0 $\pm$ 1.3	3.36 $\pm$ 0.49	494.4 $\pm$ 0.8
HS10	18.99 $\pm$ 2.53	89.92 $\pm$ 0.35	24.8 $\pm$ 1.0	3.54 $\pm$ 0.38	486.3 $\pm$ 1.3
HS20	18.51 $\pm$ 1.46	86.87 $\pm$ 0.29	26.3 $\pm$ 1.0	3.35 $\pm$ 0.20	483.3 $\pm$ 0.9
HS30	13.42 $\pm$ 2.15	118.39 $\pm$ 0.66	28.5 $\pm$ 1.2	3.28 $\pm$ 0.36	481.9 $\pm$ 1.1

surface of HS5 and HS30 go through both the boride and SiC particles. It is known that the thermal expansion coefficients of ZrB₂, HfB₂, and α -SiC are 5.7, 5.2, and $4.4 \times 10^{-6} \text{K}^{-1}$ respectively.^{34),35)} The thermal mismatch might cause inner residual stresses in ZS and HS composites during the cooling process.³⁶⁾ According to the Selsing's model of a single spherical inclusion imbedded within an infinite isotropic elastic matrix,³⁷⁾ the estimated micro internal stresses are about -0.79 and -0.49 GPa in ZS and HS composites respectively. The boride grains are under the tensile stress in the tangential direction and compressive stress in the radial direction. Correspondingly, the SiC particles are under the compressive stress, which induces the crack propagation towards SiC particles. Additionally, only in ZS composites, the crack is prone to propagate around the SiC particles, which is probably due to the weaker bonding of coherent structure at the ZrB₂-SiC interfaces in comparison with that in HS composites.

Table 1 lists the typical physical and mechanical properties of as-prepared ZrB₂-SiC (ZS) and HfB₂-SiC (HS) composites. It is seen that for ZS and HS composites the electrical conductivity decreases with increasing SiC content. It is easy to be understood that SiC is a semiconductor which has the high electrical resistivity.³⁸⁾ A larger introduction of SiC is corresponding to the relatively decreased content of conductive boride in the composites. For ZS5–30, the electrical conductivity of composites decrease from 19.89 to 11.99 $\times 10^5 \Omega^{-1} \cdot \text{m}^{-1}$; and for HS5–30, those decline from 22.29 to 13.42 $\times 10^5 \Omega^{-1} \cdot \text{m}^{-1}$. In comparison with ZS composites, HS composites show the higher electrical conductivity with the same SiC content. It was reported that the electrical conductivity of ZrB₂ (about $4.55 \times 10^6 \Omega^{-1} \cdot \text{m}^{-1}$) was lower than that of HfB₂ (about $9.09 \times 10^6 \Omega^{-1} \cdot \text{m}^{-1}$).^{39),40)} The high electrical conductivity of prepared composites suggests the possibility of machining complex shapes by electrical discharge method (EDM), which can reduce the cost compared to traditional diamond machining. Additionally, the thermal conductivity of composites were measured and compared. It is clear that with the increasing content of SiC the thermal conductivity generally indicates an increasing tendency, which may be due to the reason that SiC has the higher thermal conductivity than ZrB₂ and HfB₂.⁴¹⁾ Zimmermann et al.³⁹⁾ has determined that at room temperature ZrB₂-30 vol % SiC composite possessed the higher thermal conductivity (62 W/m·K) than single phase ZrB₂ (53 W/m·K). The abnormal decrease of thermal conductivity of ZS10 in ZS composites and HS20 in HS composites is unclear now. Anyhow, when the SiC content is increased to 30 vol % in the initial compositions, ZS30 and HS30 possess the highest thermal conductivity of 49.93 and 118.39 W/m·K respectively in their

systems. Surely, HS composites have the higher thermal conductivity compared to ZS composites under the same SiC content, which is probably associated with the higher thermal conductivity of HfB₂ (107 W/m·K).⁴²⁾

In order to evaluate the mechanical properties of composites, the Vickers hardness, fracture toughness, and elastic modulus were examined. For the Vickers hardness, it is observed that the hardness values increase with increasing SiC content in ZS and HS composites. The Vickers hardness increases gradually from 16.9 to 20.2 GPa in ZS composites and that of HS composites increases from 24.0 to 28.5 GPa. It is known that the hardness values of α -SiC, ZrB₂, and HfB₂ are 32, 17.9, and 21.2 GPa respectively.^{35),43)} The additive of SiC into borides undoubtedly contributes to the enhancement of hardness. Owing to the higher intrinsic hardness of HfB₂, HS composites show the higher Vickers hardness in comparison with ZS composites with the same SiC content. In addition, the fracture toughness of ZS and HS composites show the different changing tendency. For ZS composites, the fracture toughness increases gradually from 3.70 to 4.44 MPa·m^{1/2} with the increment of SiC content. In combination with the observation of crack propagation on the polished surface of ZS composites (Fig. 4), it seems that the deflection effect of SiC particles in the boride matrix on the crack propagation contributes to the toughness enhancement. However, the fracture toughness of HS composites do not show an increasing tendency with increasing SiC content, which is probably ascribed to the fact that only transgranular fracture of boride and SiC particles exists in the HS composites, i.e., no obvious crack deflection effect. The fracture toughness of HS composites are in a range of 3.28–3.54 MPa·m^{1/2}. For the Young's modulus, the modulus values of composites decrease with increasing SiC content. In ZS5–30 composites, the elastic moduli decrease from 464.8 to 453.2 GPa; and in HS5–30 composites, those decline from 494.4 to 481.9 GPa. This decreasing tendency obeys the mixture rule developed by Reuss⁴⁴⁾ because of the lower elastic modulus of SiC (415 GPa) in comparison with those of ZrB₂ (491 GPa) and HfB₂ (502 GPa).^{35),45)} Also, the elastic moduli of HS composites show the higher value compared to those of ZS composites under the same SiC content, which is associated with the higher elastic modulus of matrix.

4. Conclusions

Dense ZrB₂-SiC and HfB₂-SiC composites were produced at 1800°C by SPS using TaSi₂ as the sintering aid. The volume content of SiC was 5–30% and that of TaSi₂ was 5% in the initial compositions. The additive of TaSi₂ contributed to the densification of composites by the decomposition and simultaneous solid solution of Ta atoms into boride grains which probably

resulted in the decrease of activation energy of boride grain boundaries. With increasing SiC content, the electrical conductivity of ZrB₂-SiC and HfB₂-SiC composites decreased from 19.89 to 11.99 and 22.29 to 13.42 $\times 10^5 \Omega^{-1} \cdot \text{m}^{-1}$ respectively. Generally, the thermal conductivity of composites showed the increasing tendency with increasing SiC content, indicating the maximum values of 49.93 and 118.39 W/m·K respectively for ZrB₂-SiC and HfB₂-SiC composites synthesized with 30 vol % SiC in the initial compositions. Additionally, the hardness of composites increased with the increment of SiC content from 16.9 to 20.2 and 24.0 to 28.5 GPa for ZrB₂-SiC and HfB₂-SiC composites respectively. The fracture toughness of ZrB₂-SiC composites showed the increasing tendency from 3.70 to 4.44 MPa·m^{1/2} with increasing SiC content while those of HfB₂-SiC composites did not show the changing tendency and were in the range of 3.28–3.54 MPa·m^{1/2}. The elastic moduli of composites declined from 464.8 to 453.2 and 494.4 to 481.9 GPa for ZrB₂-SiC and HfB₂-SiC composites respectively with increasing SiC content.

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