

Effect of ZrC and ZrO₂ Additions on the Microstructure and Properties of ZrB₂–SiC Ceramics

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Abstract—We have studied the effect of ZrC and ZrO₂ additions on the microstructure and properties of ceramic composites based on ZrB₂–5% SiC, produced by pressure-sintering mechanically activated powders at a temperature of 1600°C. The results demonstrate that the addition of ZrO₂ increases the density, hardness, and fracture toughness of ceramic composites based on ZrB₂–5% SiC. In particular, the K_{Ic} of the ZrB₂–5% SiC ceramic is 4.6 ± 0.3 MPa m^{1/2} and that of the composite containing 20% ZrO₂ is 7.3 ± 0.4 MPa m^{1/2}.

Keywords: zirconium diboride, densification, modulus of elasticity, fracture toughness, hardness

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INTRODUCTION

Zirconium and hafnium borides, ZrB₂ and HfB₂, have high electrical and thermal conductivity, wear resistance, and chemical inertness, in particular with molten metals, which makes them attractive for use in machines and apparatuses operating at high temperatures, under friction contact conditions, and in contact with molten metals [1–7]. However, the high chemical bond covalence; small Zr, Hf, and B self-diffusion coefficients; and high melting point impair the sinterability of single-phase ZrB₂ and HfB₂ ceramics. One effective approach to the densification of ceramics based on zirconium and hafnium diborides is to add other components, that is, to produce composite structures.

Moreover, the fabrication of a composite structure in ZrB₂- and HfB₂-based ceramics enables one to obtain novel service characteristics. For example, the high-temperature stability of ZrB₂–ZrC composites in an oxygen-containing atmosphere significantly surpasses that of single-phase ZrB₂ ceramics. ZrB₂- and HfB₂-based ceramic composites containing MoSi₂, SiC, TiC, and ZrO₂ additions have an appreciably higher fracture toughness than do single-phase ceramics [8–13].

Ceramic composites containing ZrB₂, ZrC, ZrO₂, and SiC are of interest from the viewpoint of practical application in engineering structures and friction pairs. Studies concerned with properties of such

ceramic composites are usually limited to a narrow range of component concentrations, which makes it impossible to carry out a complete analysis of the effect of composition on the structure and properties of composites.

The purpose of this work was to study the effect of composition on the microstructure and properties of ZrB₂–SiC–(ZrC/ZrO₂) ceramic composites.

EXPERIMENTAL

We studied ceramic composites based on ZrB₂–5% SiC with ZrO₂ and ZrC additions (5 to 20 vol %). The starting materials used to produce the ceramic composites were commercially available ZrB₂, 6H–SiC, ZrC, and ZrO₂ powders. Zirconia was stabilized with 3 mol % Y₂O₃ to give the tetragonal phase *t*-ZrO₂. All of the powders consisted of irregularly shaped particles. The average particle size of the ZrB₂ powder was $\langle d \rangle = 1.65$ μm ($\langle d_{90} \rangle = 4.14$ μm), that of the SiC powder was $\langle d \rangle = 2.2$ μm ($\langle d_{90} \rangle = 5.84$ μm), and that of the ZrC powder was $\langle d \rangle = 1.6$ μm ($\langle d_{90} \rangle = 3.3$ μm). The ZrO₂ powder had the smallest average particle size: $\langle d \rangle = 0.35$ μm ($\langle d_{90} \rangle = 0.7$ μm).

Powder mixtures were prepared and simultaneously activated by grinding for 3 min in an AGO planetary activator mill under ethanol at a vial rotation rate of 1820 rpm. Ceramic composites were produced by

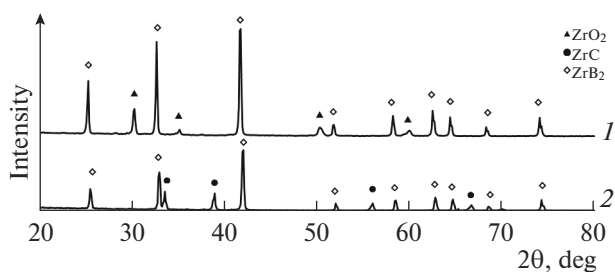


Fig. 1. X-ray diffraction patterns of the (1) ZrB₂-SiC-20 vol % ZrO₂ and (2) ZrB₂-SiC-20 vol % ZrC composite materials.

sintering the powder mixtures at a temperature of 1600°C and pressure of 30 MPa for 15 min in an argon atmosphere.

The density of the ZrB₂-6H-SiC-ZrO₂ and ZrB₂-6H-SiC-ZrC composites was determined by hydrostatic weighing after their open porosity was closed with varnish. The theoretical density of the composites was calculated using the rule of mixtures.

The phase composition of the composites was determined by X-ray diffraction on a Shimadzu XRD 7000 diffractometer with CuK_α radiation ($\lambda = 1.5405 \text{ \AA}$).

Their hardness was determined on a polished sample surface by indenting a Vickers pyramid at a load of 98 N and dwell time of 10 s.

Fracture toughness was evaluated from the total length of cracks emanating from an indent using the relation $K_{Ic} = 0.16H_{1/2}(c/a)^{-3/2}$, where a is half the indent diagonal and c is the length of the cracks [14].

The modulus of elasticity of the ceramic composites was evaluated from the speed of ultrasound in the samples using a Tektronix TDS 220 oscilloscope (the United States) and a Panametrics 5800 pulser/receiver (Korea).

RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction patterns of the ceramic composites produced by us. According to the X-ray diffraction results, the phase composition of the composites includes the starting materials ZrB₂, 6H-SiC, ZrO₂, and ZrC. In the 95 vol % ZrB₂ + 5 vol % SiC + x vol % ZrO₂ composites, zirconia was present as the tetragonal phase t -ZrO₂.

The unit-cell parameters of the components of the composites were similar to those presented in the JCPDS Powder Diffraction File: $a = 3.167 \pm 0.002 \text{ \AA}$ and $c = 3.531 \pm 0.001 \text{ \AA}$ for ZrB₂ (JCPDS card no. 34-0423: $a = 3.168 \text{ \AA}$ and $c = 3.530 \text{ \AA}$); $a = 4.695 \pm 0.002 \text{ \AA}$ for ZrC (JCPDS card no. 65-0332: $a = 4.694 \text{ \AA}$); $a = 3.625 \pm 0.002 \text{ \AA}$ and $c = 5.198 \pm 0.001 \text{ \AA}$ for t -ZrO₂ (JCPDS card no. 89-7710: $a = 3.629 \text{ \AA}$ and $c = 5.197 \text{ \AA}$).

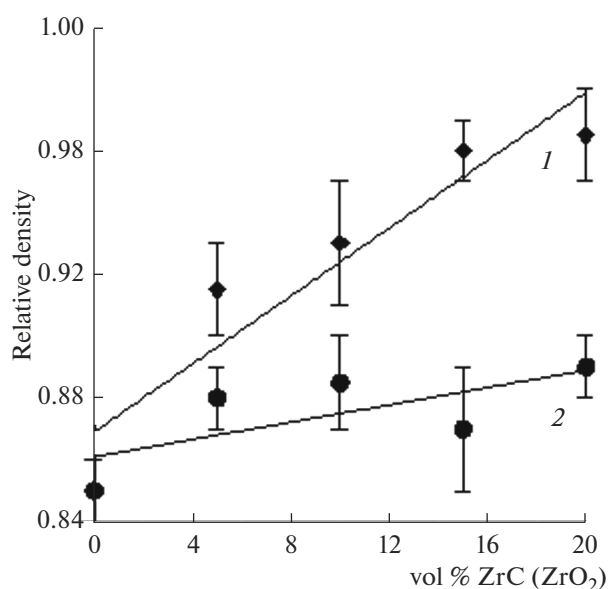


Fig. 2. Effect of ZrO₂ and ZrC additions on the relative density of the (1) ZrB₂-SiC-ZrO₂ and (2) ZrB₂-SiC-ZrC composites.

Because of the low intensity of the diffraction peaks of silicon carbide in the X-ray diffraction patterns of the composites, its unit-cell parameters were only determined for a powder 6H-SiC sample: $a = 3.072 \text{ \AA}$ and $c = 15.081 \text{ \AA}$ (JCPDS card no. 29-1131: $a = 3.073 \text{ \AA}$ and $c = 15.080 \text{ \AA}$).

Figure 2 shows the relative density ρ_{rel} as a function of the volume percentage of ZrC for the ZrB₂-SiC-ZrC ceramic composites and as a function of the volume percentage of ZrO₂ for the ZrB₂-SiC-ZrO₂ composites. According to these data, the relative density of the ZrB₂-SiC-ZrO₂ composites increases in proportion to the increase in the volume fraction of zirconia. The ρ_{rel} of the ZrB₂-5 vol % SiC ceramic containing no zirconia is 0.85 ± 0.05 , whereas that of the composite containing 20 vol % ZrO₂ is $\rho_{rel} = 0.96 \pm 0.2$. Extrapolating ρ_{rel} as a function of the volume percentage of ZrO₂ to a pore-free state, we find that the density of a ZrB₂-SiC-ZrO₂ composite prepared by sintering at a pressure of 30 MP and temperature of 1600°C for 15 min will be similar to its theoretical density at a ZrO₂ content above 25 vol %. Zirconia is the lowest melting point component of the ZrB₂-SiC-ZrO₂ composites. Increasing the volume fraction of zirconia leads to a decrease in the melting point of ZrB₂-SiC-ZrO₂ mixtures (increase in the homologous temperature $\alpha = 1600^\circ\text{C}/t_m$) and, as a consequence, an increase in the density of the composites.

The relative density of the ZrB₂-SiC-ZrC samples exceeded that of the ZrB₂-5% SiC, but only

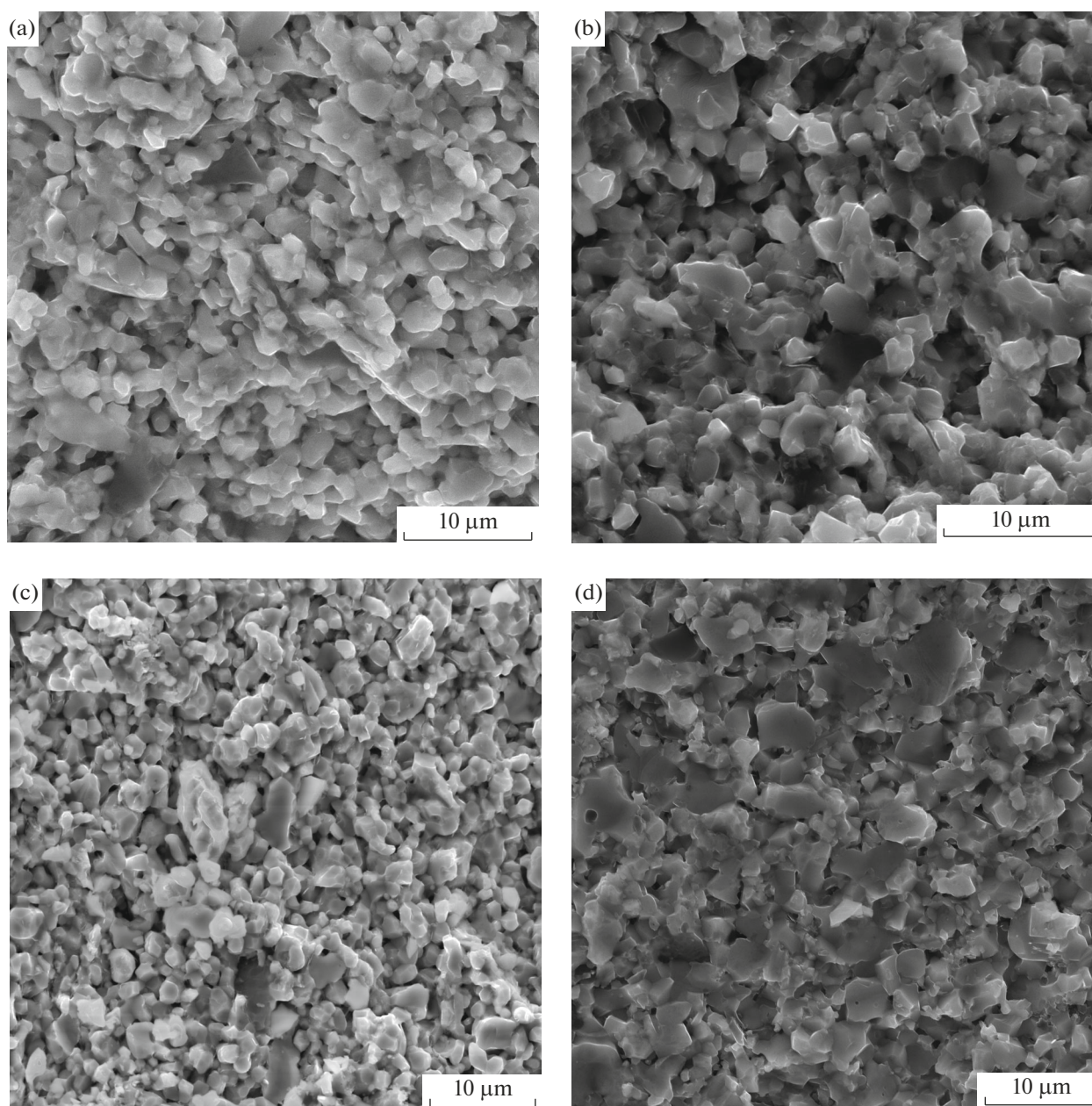


Fig. 3. Microstructures of the (a) $\text{ZrB}_2\text{-SiC-5\% ZrO}_2$, (b) $\text{ZrB}_2\text{-SiC-15\% ZrO}_2$, (c) $\text{ZrB}_2\text{-SiC-5\% ZrC}$, and (d) $\text{ZrB}_2\text{-SiC-15\% ZrC}$.

slightly. The relative density of the composites containing more than 5% ZrC was on average 0.88 ± 0.05 .

Figure 3 illustrates the microstructure of the $\text{ZrB}_2\text{-SiC}$ based composites at different ZrC and ZrO_2 contents. An increase in the volume fraction of ZrC or ZrO_2 in the composites was accompanied by an increase in grain size. The average grain size was determined by the line intercept method using images of the microstructure of the composites [15]. In particular, the average grain size was $2.5 \mu\text{m}$ in the $\text{ZrB}_2\text{-SiC-5\% ZrO}_2$ ceramic and $4.2 \mu\text{m}$ in the composite

containing 15% ZrO_2 . In the $\text{ZrB}_2\text{-SiC-ZrC}$ composite with the lowest ZrC concentration, the average grain size was $2.57 \mu\text{m}$; at 15% ZrC, the average grain size was $5.2 \mu\text{m}$.

The modulus of elasticity E evaluated from the speed of ultrasound in the $\text{ZrB}_2\text{-SiC}$ ceramic was $373 \pm 25 \text{ GPa}$. At the same time, the modulus of elasticity calculated for the $\text{ZrB}_2\text{-SiC}$ composite using the additivity rule is 458 GPa . The discrepancy between the experimentally determined and calculated moduli

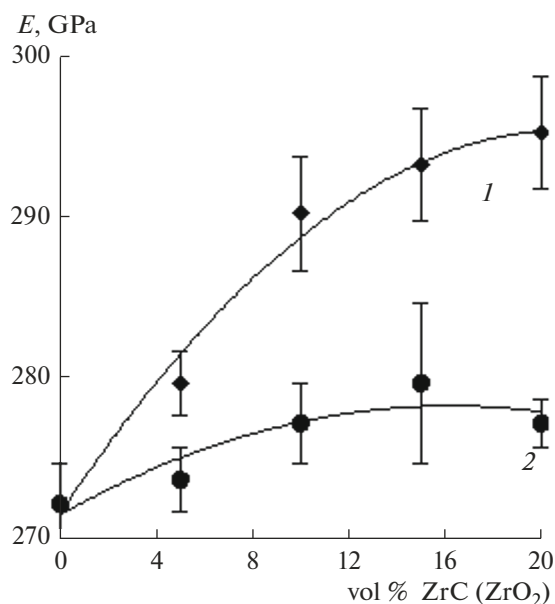


Fig. 4. Effect of ZrO₂ and ZrC additions on the E of the (1) ZrB₂-SiC-ZrO₂ and (2) ZrB₂-SiC-ZrC composites.

of elasticity is primarily due to the residual porosity in the ZrB₂-SiC ceramic.

The addition of ZrC to a ZrB₂-SiC ceramic matrix had no significant effect on the modulus of elasticity of the composites (Fig. 4). The modulus of elasticity of the ZrB₂-SiC-ZrO₂ composites was found to increase with increasing zirconia content. In particular, the composite containing 5% ZrO₂ had $E \approx 387 \pm 5$ GPa. Since the modulus of elasticity of ZrO₂ is lower than those of ZrB₂ and SiC, it is clear that the main cause of the observed increase in the modulus of elasticity of the ZrB₂-SiC-ZrO₂ composites is the reduction in porosity [16–18].

Table 1 presents the hardness (H_V) and fracture toughness (K_{Ic}) data for the composites. According to these data, increasing the percentage of zirconium carbide in the ZrB₂-SiC-ZrC composites had no significant effect on their hardness. For example, the H_V of the ZrB₂-SiC ceramic was 12.7 ± 0.2 GPa and that

of the ZrB₂-SiC-20% ZrC was 13.5 ± 0.4 GPa. On the whole, the hardness of the ZrB₂-SiC-ZrC composites obtained in this study was lower than would be expected, which was due to the residual porosity.

The hardness of the ZrB₂-SiC-ZrO₂ composites was found to increase with increasing ZrO₂ content. Zirconia has lower hardness than do the other components of the composites—silicon carbide and zirconium boride—so the observed increase in hardness is attributable to the densification of the composites with increasing ZrO₂ content.

Fracture toughness K_{Ic} evaluated for the ZrB₂-5% SiC ceramic from the total length of cracks emanating from a Vickers indent is 4.6 ± 0.3 MPa m^{1/2}, which is comparable to the fracture toughness of the composites richer in silicon carbide (the K_{Ic} of ZrB₂-20% SiC is ≈ 4 –6 MPa m^{1/2}) and exceeds the K_{Ic} of monolithic ZrB₂ ceramics [19–21]. The main mechanism behind the increase in the fracture toughness of the ceramic composites containing finely dispersed inclusions is the change in crack propagation trajectory at interfaces [22, 23]. It is reasonable to assume that the high K_{Ic} of the ZrB₂-5% SiC ceramic (with a low concentration of silicon carbide inclusions) is due to the residual porosity: pores hinder crack propagation.

The ZrB₂-SiC-ZrC composites differing in ZrC content differed rather little in K_{Ic} . For example, the fracture toughness of the composite containing 5% zirconium carbide was 4.5 ± 0.3 MPa m^{1/2}, and that of the composite containing 20% zirconium carbide was 4.7 ± 0.3 MPa m^{1/2}.

Increasing the percentage of zirconia in the ZrB₂-SiC-ZrO₂ composites led to an increase in their K_{Ic} . For example, the fracture toughness of the composite containing 20% ZrO₂ was 7.3 ± 0.4 MPa m^{1/2}. Owing to their lower porosity, these composites had higher fracture toughness. The increased fracture toughness of the composites containing finely dispersed inclusions of tetragonal zirconia, which undergoes a martensitic transformation under the effect of a mechanical load, can be due to not only crack deflection at interfaces but also crack energy dissipation through

Table 1. Hardness H_V and fracture toughness K_{Ic} of the ZrB₂-SiC-ZrO₂ and ZrB₂-SiC-ZrC composites

Composite	H_V , GPa	K_{Ic} , MPa m ^{1/2}	Composite	H_V , GPa	K_{Ic} , MPa m ^{1/2}
ZrB ₂ -SiC	12.7 ± 0.2	4.6 ± 0.3	ZrB ₂ -SiC	12.7 ± 0.2	4.6 ± 0.3
ZrB ₂ -SiC-5% ZrO ₂	13.4 ± 0.3	3.1 ± 0.3	ZrB ₂ -SiC-5% ZrC	12.5 ± 0.2	4.5 ± 0.3
ZrB ₂ -SiC-10% ZrO ₂	14.2 ± 0.3	4.5 ± 0.4	ZrB ₂ -SiC-10% ZrC	12.8 ± 0.3	4.3 ± 0.3
ZrB ₂ -SiC-15% ZrO ₂	14 ± 0.4	5.8 ± 0.3	ZrB ₂ -SiC-15% ZrC	13 ± 0.4	4.1 ± 0.2
ZrB ₂ -SiC-20% ZrO ₂	14.3 ± 0.4	7.3 ± 0.4	ZrB ₂ -SiC-20% ZrC	13.5 ± 0.4	4.1 ± 0.3

the tetragonal-to-monoclinic phase transition of the *t*-ZrO₂ particles [24–26].

CONCLUSIONS

The addition of ZrC to a ZrB₂–5% SiC ceramic composite prepared by pressure sintering at a temperature of 1600°C has been shown to cause no appreciable increase in the density of the material and have no significant effect on its properties. In contrast, the addition of ZrO₂ helps increase the density, hardness, and fracture toughness of ceramic composites based on ZrB₂–5% SiC. In particular, the *K*_{IC} of the ZrB₂–SiC ceramic is 4.6 ± 0.3 MPa m^{1/2} and that of the composite containing 20% ZrO₂ is 7.3 ± 0.4 MPa m^{1/2}.

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