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Mechanical properties of hot-pressed ZrB_2–$MoSi_2$–SiC composites

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Abstract

The elastic moduli, hardness, fracture toughness, and flexural strength of a hot-pressed ZrB_2–$MoSi_2$–SiC composite were examined. The effects of $MoSi_2$ and SiC contents were assessed. The dense compacts of ZrB_2–$MoSi_2$–SiC were produced by hot-pressing at 1800 °C for 30 min under a pressure of 30 MPa in vacuum. Ten series compositions of ZrB_2–$MoSi_2$–SiC, with the range from 10 to 40 vol.% for $MoSi_2$ and 5 to 20 vol.% for SiC, were studied. The shear modulus of ZrB_2–$MoSi_2$–SiC was in the range of 190–216 GPa, and Young's modulus measured was in the range of 438–490 GPa. The ranges of hardness and fracture toughness values were measured to be 13.2–16.8 GPa, and 2.6–3.7 MPa $m^{1/2}$, respectively. The average flexural strength of ZrB_2–$MoSi_2$–SiC ranged from 369 to 863 MPa, depending on $MoSi_2$ and SiC contents. The highest strength was obtained for 5 vol.% SiC-containing ZrB_2–$MoSi_2$–SiC, having the value of 863 MPa.

Keywords: ZrB_2–$MoSi_2$–SiC; Elastic moduli; Hardness; Fracture toughness; Flexural strength

1. Introduction

Zirconium diborides (ZrB_2)-based composites have an extremely high melting point (>3000 °C), high thermal and electrical conductivities, chemical inertness against molten metals, and good thermal shock resistance.[1,2] These unique mechanical and physical properties have never been achieved by other ceramics materials. Recently, the ZrB_2-based composites are being considered for use as potential candidates for a variety of high-temperature structural applications, including furnace elements, plasma-arc electrodes, or rocket engines and thermal protection structures for leading-edge parts on hypersonic re-entry space vehicles at over 1800 °C.[3–5] However, the densification of ZrB_2 powder generally requires very high temperatures (>2100 °C) and external pressure because of covalent bond and low self-diffusivity.[6] To improve sinterability, nitrides are added to pure ZrB_2,[7–9] producing an intergranular liquid phase that aids the densification of ZrB_2. In addition, other major problem of ZrB_2-based composites involves high-temperature oxidation.[10,11] To improve oxidation resistance, SiC is added to ZrB_2,[11,12] producing the formation of a protective borosilicate glass at temperature above 1200 °C that enhances oxidation resistance of ZrB_2. Even with these additives, a sintering temperature of above 1900 °C is still required for obtaining near-fully dense ZrB_2-based ceramic composites.

Recently, $MoSi_2$-containing ZrB_2-based composites have been developed. Near-fully dense $MoSi_2$-containing ZrB_2-based composites were sintered by pressureless and/or by hot-press at temperature below 1850 °C.[13,14] Very recently, authors[15] have reported a near-fully dense hot-pressed ZrB_2–$MoSi_2$–SiC composite. The composite showed high thermal and electrical conductivities that depended on compositions. However, the mechanical properties of the ZrB_2–$MoSi_2$–SiC composite and the effects of $MoSi_2$ and SiC contents are not well known. Therefore, it is necessary for the ZrB_2–$MoSi_2$–SiC composites to become familiar with the mechanical properties and correlation to the compositions. In the present study, the ZrB_2-based composites with $MoSi_2$ and/or SiC were hot-pressed at 1800 °C for 30 min under a pressure of 30 MPa in vacuum. The elastic moduli of the composites were calculated using the longitudinal and transverse soundwave velocities measured, whereas the hardness and the fracture toughness of the composites were

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determined using an indentation crack measurement. The room temperature flexural strength of the composites were determined by fracture using four-point flexural. Also, the effects of $MoSi_2$ and SiC contents on these properties were examined.

2. Experimental procedure

The starting powders used in this study were: ZrB_2 powder (Grade F, Japan New Metals, Tokyo), average particle size ≈2.1 μm, $MoSi_2$ powder (Grade F, Japan New Metals), average particle size ≈3.1 μm; and α-SiC powder (Grade UF-15, H.C. Starck, Berlin, Germany), average particle size ≈0.5 μm. In order to examine the effect of composition on mechanical properties, 10 series of ZrB_2–$MoSi_2$–SiC compositions were prepared in this study. The detailed compositions are shown in Table 1. The powder mixtures were ball-milled in a SiC media using ethanol as a solvent for 24 h and the resulting slurry was then dried. The obtained powder mixtures were hot-pressed (FVHP-1-3, Fuji Electric Co. Ltd., Tokyo, Japan) in the graphite dies at 1800 °C for 30 min under a pressure of 30 MPa in vacuum in tablets averaging 21 mm × 25 mm × 3.5 mm in size. The detailed sintering process has been reported elsewhere.[15] The densities, ρ, of the hot-pressed composite compacts were measured using Archimedes method with distilled water as medium. The theoretical densities of the composites were calculated according to the rule of mixtures. Microstructure of the composites was observed by field emission scanning electron microscopy (FE-SEM). The grain size, d, was determined by measuring the average linear intercept length, d_m, of the grains in FE-SEM images of sintered ZrB_2 ceramics, according to the relationship of $d = 1.56\, d_m$ which was given by Mendenlson.[16]

The elastic moduli measurements of the composites were performed using an ultrasonic equipment (TDS 3052B, Tektronix Inc., Beaverton, OR, USA) with a fundamental frequency of 20 MHz. The shear modulus, G, Young's modulus, E, and Poisson's ratio, ν, were calculated using the longitudinal and transverse soundwave velocities measured in the composite specimens. The detailed calculations were reported elsewhere.[17] On the other hand, the hardness and the fracture toughness, K_{IC}, of the composites were determined using an indentation crack size measurement. The indentation tests were performed on the polished surface of the specimens by loading with a Vickers indenter (AVK-A, Akashi, Co. Ltd., Yokohama, Japan) for 15 s in ambient air at room temperature. The corresponding diagonals of the indentation and crack sizes were measured using an optical microscope attached to the indenter. The indentation load of 98 N was used, and five indents were made for each measurement. The fracture toughness, K_{IC}, of composites were calculated from the Anstis equation.[18] In addition, the ZrB_2–$MoSi_2$–SiC composite plates were cut into a rectangular shape bending test specimen with dimensions of ∼25 mm × 2 mm × 2.5 mm for measuring fracture strength. The surfaces of the specimen were ground with a 800-grit diamond wheel and the tensile surface was polished by diamond paste down to 1.0 μm. The edges of the specimen were then chamfered at 45°. The room temperature fracture strength of the composites was determined by fracture, using four-point flexure (inner span 10 mm, outer span 20 mm). The bend test was performed using a testing system (Autograph Model AG-50KNI, Shimadzu Co. Ltd., Kyoto, Japan) with a crosshead speed of 0.5 mm/min. At least five specimens were used for each measurement. After the bend testing, the fracture surfaces of specimens were examined by FE-SEM.

3. Results and discussion

3.1. Densification and microstructure

The measured densities and relative densities of the hot-pressed ZrB_2–$MoSi_2$–SiC composites are summarized in Table 1. From the table, it can be seen that near-fully dense composites to theoretical densities were hot-pressed at 1800 °C under a pressure of 30 MPa with holding time of 30 min for ZrB_2–$MoSi_2$ powder, regardless of $MoSi_2$ amount. This indicated that the addition of $MoSi_2$ significantly improved sinterability of ZrB_2 ceramic and promoted densification of pure ZrB_2 phase at lower temperature. Improvement of densification due to addition of $MoSi_2$ is documented in the literature. Sciti et al.[13] and Bellosi et al.[14] showed that near-fully dense (relative density >98%) ZrB_2-based ceramics with 15 vol.% $MoSi_2$ were obtained by hot-press at 1750 °C under a pressure of 30 MPa with holding time of 45 min, as a result of the presence of intergranular liquid phase. They concluded that the addition of $MoSi_2$ produces an intergranular liquid phase that favors the process of grain rearrangement as well as improves the packing

Table 1
Compositions, densities and relative densities of the hot-pressed ZrB_2–$MoSi_2$–SiC composites

Materials	Compositions (vol.%)			Theoretical density (g/cm^3)	True density (g/cm^3)	Relative density (% TD)
	ZrB_2	$MoSi_2$	SiC			
ZMS-1	90	10	0	6.10	6.08	99.7
ZMS-2	80	20	0	6.12	6.11	99.8
ZMS-3	70	30	0	6.14	6.13	99.8
ZMS-4	60	40	0	6.15	6.13	99.7
ZMS-5	75	20	5	5.98	5.98	100
ZMS-6	70	20	10	5.83	5.79	97.3
ZMS-7	60	20	20	5.55	5.39	94.6
ZMS-8	55	40	5	6.01	6.01	100
ZMS-9	50	40	10	5.86	5.81	99.1
ZMS-10	40	40	20	5.58	5.34	95.7