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Effects of processing temperature on microstructures and mechanical behaviours of reactive hot-pressed SiC(SCS-6)/Ti/ZrB_2–ZrC hybrid composites

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ABSTRACT

In this study, hybrid composites comprising SiC(SCS-6)/Ti composite and ZrB_2–ZrC ceramics were prepared by sandwiching Ti/SiC(SCS-6)/Ti sheets and Zr + B_4C powder layers, followed by reactive hot pressing (RHPing) between 1250 °C and 1400 °C. The effects of RHPing temperature on the microstructures and the mechanical behaviours of the composites were examined. For the samples prepared at 1250 °C and 1300 °C, a Ti-rich zone was observed in the matrix and around the fibres. However, for the sample prepared at 1400 °C, no Ti-rich zone was observed. In addition, the hybrid composites show non-catastrophic fracture behaviour, irrespective of RHPing temperature. Compared to the sample processed at 1400 °C, the samples processed at 1250 °C and 1300 °C exhibited higher flexural strength and greater damage tolerance. The lower strength and damage tolerance for the composite processed at 1400 °C are attributed to stronger interface bonding via significant degradation of the C-rich coating and to strength degradation of the fibres.

1. Introduction

Zirconium diboride (ZrB_2) is one of the most promising ultra-high temperature ceramic materials that include refractory transition-metal diborides, carbides, and nitrides [1,2]. It has a melting point above 3000 °C [1–4], high thermal and electrical conductivities [5–7] and chemical inertness against molten metals [8]. In addition, ZrB_2-based composite materials with various additives such as SiC, $MoSi_2$, ZrC and WC exhibit good ablation resistance [9], good oxidation resistance [3,10] and excellent strength at room and high temperatures [3,4,11]. The unique combination of the properties of both metallic and ceramic materials makes these additive-containing ZrB_2-based composite materials candidates for several high-temperature structural applications [1,2,12–14]. However, these ceramic materials exhibit high intrinsic brittleness and are sensitive to flaws. Therefore, in order to satisfy the strict constraints of such structural applications, ZrB_2 and ZrB_2-based composites require improved resistance to fracture through additional extrinsic toughening phase and/or microstructure design.

Overcoming this problem requires extrinsic toughening mechanisms. One of the most promising solutions for preventing catastrophic fracture of the monolithic ceramics is to apply continuous ceramic fibres to monolithic ceramics for fabricating fibre-reinforced ceramic matrix composites. Continuous ceramic fibre-reinforced ceramic matrix composites typically exhibit larger damage tolerance and higher resistance to failure because of crack deflection, fibre bridging, interface debonding/delamination and/or interface sliding [15,16]. Levine et al. previously reported an SiC(SCS-9a) fibre-reinforced ZrB_2–SiC composite with a fibre volume fraction (Vf) of 35% [17]; they prepared this composite using filament winding and slurry deposition, followed by hot pressing at 1300 °C. However, large matrix cracks and numerous pores were observed in the resulting composite [17]. The presence of these matrix cracks and pores is attributable to the thermal expansion mismatch between the fibre and the matrix and to the poor sinterability of the matrix at 1300 °C because the densification of ZrB_2–SiC generally requires a temperature $\geq$1650 °C [18–20]. As a result, the composite exhibited a flexural strength of only approximately 130 MPa [17]. In addition, we prepared a SiC(SCS-6) fibre-reinforced ZrB_2–ZrC matrix composite by RHPing at 1400 °C [21]. Unfortunately, the obtained SiC(SCS-6)/ZrB_2–ZrC composite exhibited catastrophic fracture behaviour and a flexural strength of only 100 MPa because of the strength degradation of the fibres due to an excessive interface reaction. Very recently, we successfully fabricated SiC(SCS-6)/Ti/ZrB_2–ZrC hybrid composites by sandwiching Ti/SiC(SCS-6)/Ti sheets and Zr + B_4C powder layers, followed

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by RHPing at 1300 °C [21,22]. The SiC(SCS-6)/Ti/ZrB_2–ZrC hybrid composites exhibited the flexural strengths of ≥440 MPa and non-catastrophic fracture behaviour. In addition, the strengths and the damage tolerance of the hybrid composites are improved with increasing the fibre content and the thickness of Ti layer. However, the effects of the processing temperature on the microstructures and the mechanical behaviours of the hybrid composites are not well understood.

In this study, hybrid composites comprising silicon carbide (SiC) fibre-reinforced Ti (SiC/Ti) composite and ZrB_2–ZrC ceramic were prepared through RHPing a preform consisting of Ti foils, SiC fibres and Zr + B_4C powder at different temperatures between 1250 °C and 1400 °C. The microstructures of the obtained hybrid composites were characterized by field-emission scanning electron microscopy and energy-dispersive spectroscopy. The mechanical behaviours of the hybrid composites were examined at room temperature. The effects of the processing temperatures on the microstructures and the mechanical behaviours of the hybrid composites were discussed.

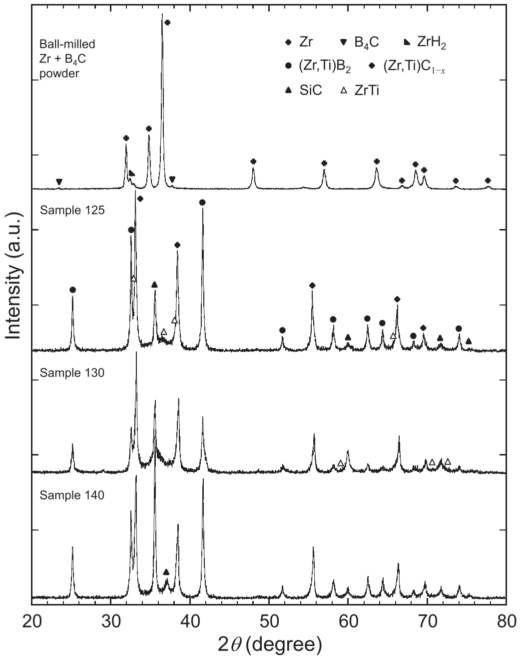

Fig. 1. XRD patterns of the ball-milled Zr + B_4C powder and the hybrid composites fabricated by RHPing at various temperatures.

2. Experimental procedure

Zr powder (D_{50} = 10 μm, 98% purity, Kojundo Chemical Laboratory Co., Ltd., Japan) and B_4C powder (D_{50} = 0.8 μm, 98% purity, H.C. Starck GmbH, Germany) were mixed in a 4:1 molar ratio to prepare a homogeneous Zr + B_4C powder mixture, which was used to synthesize the ZrB_2–ZrC ceramic matrix through RHPing at less than or equal to 1400 °C [23]. The designed composition resulted in the presence of excess Zr (~10 vol%) in the synthesized ZrB_2-ZrC matrix [23]. SiC fibre (SCS-6, Avco Specialty Materials, Lowell, MA, USA) was used as a reinforcement phase. The SiC fibre was ~140 μm in diameter continuous β–SiC fibre with an outermost coating layer of ~3.6 μm called SCS coating that was richer in C than the stoichiometric SiC fibre [24,25]. The C-rich SCS coating was designed to protect the fibre from strength degradation by reducing the stress concentration at the defects present on the fibres' surface [25,26]. Typical properties of the SiC fibres at room temperature include an elastic modulus of 400 GPa, a tensile strength of 3400 MPa and a failure strain between 0.8% and 1.0%. In addition, a 10-μm-thick Ti foil (99.9% pure, Rikazai Co., Ltd., Kawasaki, Japan) was used to produce Ti/SiC(SCS-6)/Ti composite sheets.

The SiC fibres were wound into a mat with a spacing of 200 μm and held by an acrylic binder. The fibre mat was then intermediated between two Ti foils to obtain a Ti/SiC(SCS-6)/Ti composite sheet. The hybrid composite green bodies were formed by sandwiching the Ti/SiC(SCS-6)/Ti composite sheets and the (Zr + B_4C) powder layers. The hybrid composite green bodies consisted of 8-ply Ti/SiC(SCS-6)/Ti composite layups and 9-ply Zr + B_4C powder layups. The detailed fabrication procedure of the hybrid composite has been reported elsewhere [21,22], which was schematically drawn in Supplementary Fig. S1 in the online version at DOI: 10.1016/j.jeurceramsoc.2016.06.009. Subsequently, the green bodies were hot pressed in graphite dies lined with graphite foil and coated with BN. A hot-pressing apparatus with high-frequency heating (NEW-HP5, Nissin Giken Co., Ltd., Saitama, Japan) was used herein to consolidate the composites. Green bodies were heated under a vacuum to 950 °C at a rate 10 °C/min. When the die temperature reached 950 °C, a uniaxial pressure of 20 MPa was applied. After the hot press was held 950 °C for 15 min, it was backfilled with argon and heated at 25 °C/min to the setpoint temperature under 20 MPa and flowing Ar atmosphere. The final consolidation of the matrix was performed at 1250 °C, 1300 °C and 1400 °C, respectively. After holding time of 10 min, the hot press was cooled at 20 °C/min to 1000 °C. After 15 min, the load was removed, the sample was cooled to 500 °C at 10 °C/min and the electric power was then switched off, resulting in tablets averaging 40 mm × 25 mm × 3 mm in size with Vf ≈20%. Hereafter, the SiC(SCS-6)/Ti/ZrB_2–ZrC hybrid composites consolidated at 1250 °C, 1300 °C and 1400 °C were denoted as sample 125, sample 130 and sample 140, respectively. Field emission scanning electron microscopy (FE-SEM) equipped with an energy-dispersive spectroscopy (EDS) was used for the microstructural observations. The quantitative compositional analysis of the interface reaction zone between the fibres and the matrix and the matrix reaction zone within the matrix which were formed during RHPing was preformed through EDS.

Specimens with average dimensions of 25 mm × 3.5 mm × 2 mm were cut from the composite plates using a diamond grinding wheel. The surfaces of the specimens were ground with an 800-grit diamond wheel. The flexural strength of the specimens was measured using a four-point bending test fixture (inner span = 10 mm; outer span = 20 mm) at room temperature. The bending tests were performed using an Autograph testing system (AG-X/R, AG-100KND, Shimadzu, Kyoto, Japan) with a crosshead speed of 0.5 mm/min. At least five specimens were used for each measurement. After the bending tests, the fracture surfaces of the samples were examined by FE-SEM.

3. Results and discussion

3.1. Effects of RHPing temperature on microstructures

Fig. 1 shows the XRD patterns of the ball-milled Zr + B_4C powder mixture and the hybrid composites prepared at various temperatures. Before RHPing, α–Zr and B_4C are the primary crystalline phase present in the Zr + B_4C powder mixture, in addition to a trace amount of ZrH_2 which originated from raw Zr powders [23]. On the other hand, for the hybrid composites obtained after RHPing, the main intensity peaks of ZrC were observed in the wide range $33° < 2\theta < 70°$ and not only in the range $33° < 2\theta < 34°$; this suggests that zirconium carbide formed might be ZrC_{1-x}. In addition, the lattice parameters of the formed ZrB_2 and ZrC_{1-x} phases were determined: a = 3.169–3.173 Å and c = 3.525–3.529 Å for ZrB_2 and

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