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Technical note

Reactive hot pressing of ZrB_2–ZrC_x ultra-high temperature ceramic composites with the addition of SiC particulate

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Abstract

Starting with non-stoichiometric Zr–B_4C powder mixture ZrB_2–ZrC matrix composites with SiC particulate addition have been made. It was found that variable amounts (5–25 vol%) of SiC could be incorporated and reactively hot pressed (RHPed) to relative densities of 97–99% at 1400–1500 °C. This technique has the potential to fabricate ZrB_2-based matrices at low temperatures with a variety of reinforcements whose composition and volume fraction are not limited by stoichiometric considerations. The hardness of the composites is in the range of 17–22 GPa.

Keywords: Borides; Carbides; Zirconium; Hot pressing; Densification

1. Introduction

Refractory transition metal borides (ZrB_2, HfB_2) in combination with SiC are candidates for use in oxidizing atmospheres at temperature in excess of 1900 °C.[1–10] While sintering temperatures of pre-synthesized powders have generally been in excess of ~1900 °C, in recent times reactive hot pressing (RHP) has been successfully adapted to produce ZrB_2–SiC composites at temperatures that have progressively reduced from 1900 to 1600 °C. The reactants and detailed process schedules vary[11–20] but a common feature in all low temperature processing is the use of elemental silicon and a source of carbon to produce SiC in situ. Such methods constrain the volume fraction of SiC to the stoichiometry of the reaction. In addition, changing to a different reinforcement would require separate optimization of the reaction.

In contrast, we have shown recently that ZrB_2–ZrC_x composites could be RHPed to high relative densities at 1200–1600 °C by exploiting the plasticity (transient or otherwise) of a carbon-deficient ZrC.[21,22] In particular, it was shown that as 'x' decreased from 1 to 0.67, the necessary process temperature reduced from 1600 to 1200 °C. The present work seeks to determine whether such a densifiable matrix can act as a host to particulate inclusions, in this case SiC, with a view to being able to fabricate composites wherein the size and volume fraction of the reinforcement can be easily changed.

2. Experimental procedure

Starting with Zr–B_4C powder mixtures the ZrB_2–ZrC_x–SiC_p (0–25 vol%) composites with different amounts of SiC_p are fabricated according to the following reaction:

$$3.5Zr + B_4C + SiC(040\text{–}25\ \text{vol\%}) \rightarrow 2ZrB_2 + 1.5ZrC_{\sim 0.67} + SiC(041\text{–}25\ \text{vol\%}) \quad (1)$$

The volume fractions of ZrB_2 and ZrC_x according to reaction (1) are ~62% and 38%, respectively when SiC is absent and the theoretical density of the composite is 6.26 g/cm^3. As the SiC content increases from 0% to 25%, the theoretical density of the composite reduces from 6.26 to 5.53 g/cm^3.

2.1. Materials, processing and characterization

The details of raw materials, powder processing and hot pressing schedules have been extensively reported earlier[21,23] and are only briefly reproduced here. Powders used were: Zr of 2–10 μm (M/s Yashoda Special Metals, Hyderabad, India),

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Table 1
Experimental conditions, density and hardness of the ZrB_2–ZrC_x–SiC_p composites.

Sl no.	Experimental conditions (MPa/°C/min)	Phases	Lattice parameter of ZrC (Å)[a]	Density-g/cm^3 (% RD)	Hardness (GPa)
ZrB_2–ZrC_x–SiC_p ($ZBCSC_p$-C)					
1	40/1400/30 – (1 wt% Ni)	ZrB_2, ZrC_x	4.682	6.20 (99.9)	22 ± 1.0
2	40/1400/30 – 5 vol% SiC (1 wt% Ni)	ZrB_2, ZrC_x, SiC	4.686	6.10 (99.9)	22.3 ± 1.8
3	40/1400/30 – 10 vol% SiC (1 wt% Ni)	ZrB_2, ZrC_x, SiC	4.686	5.82 (97.8)	–
4	40/1400/30 – 15 vol% SiC (1 wt% Ni)	ZrB_2, ZrC_x, SiC	4.686	5.53 (95.4)	17.2 ± 2.9
5	40/1500/30 – 20 vol% SiC	ZrB_2, ZrC_x, SiC	4.686	5.48 (97.3)	17.4 ± 0.6
ZrB_2–ZrC_x–SiC_p ($ZBCSC_p$-F)					
6	40/1500/30 – 20 vol% SiC	ZrB_2, ZrC_x, SiC	4.686	5.61 (99)	17.4 ± 1.1
7	40/1500/30 – 25 vol% SiC	ZrB_2, ZrC_x, SiC	4.686	5.34 (97.5)	20.7 ± 1.3
8	40/1500/30 – 25 vol% SiC (1 wt% Ni)	ZrB_2, ZrC_x, SiC	4.687	5.33 (97)	–

[a] Error bar ± 0.001, RD- relative density.

B_4C of ~10 to 20 μm (M/s Boron Carbide India Ltd. Mumbai, India) and ~1 to 7 μm (M/s Alfa-Aesar, USA), β-SiC ~1 μm (M/s Alfa-Aesar, USA) and Ni of ~4 μm (M/s INCO, London, UK). The required amounts of powders were mixed in a rotatory ball mill in ethanol with ZrO_2-8 mol% Y_2O_3 milling media for 24 h in a plastic bottle and dried at ~100 °C for 5 h. The composites produced with coarse (10–20 μm) and fine (1–7 μm) B_4C powders are hereafter referred to as $ZBCSC_p$-C and $ZBCSC_p$-F, respectively. The dried powder mixtures were filled in a graphite die and RHP experiments were conducted at 40 MPa, 1400–1500 °C for 30 min. Standard procedures described earlier[21–23] were used to determine density, microstructural features and precision lattice parameters.

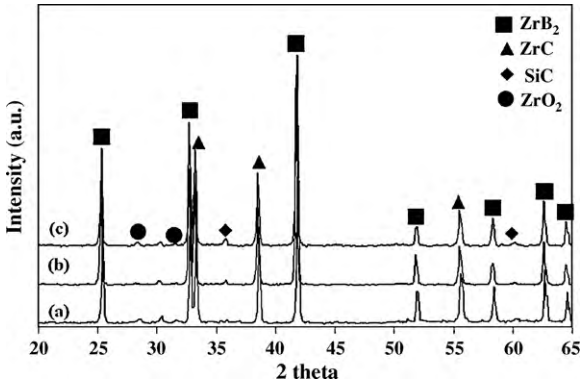

Fig. 1. The X-ray diffraction patterns of the $ZBCSC_p$-C composites with different fractions of SiC_p fabricated with 1 wt% Ni at 40 MPa, 1400 °C for 30 min: (a) 0 vol% SiC, (b) 5 vol% SiC and (c) 15 vol% SiC.

3. Results and discussion

The processing conditions, phases formed, lattice parameter of ZrC and densities of the composites are given in Table 1.

3.1.1. $ZBCSC_p$-C composites

The X-ray diffraction (XRD) patterns of the ZrB_2–ZrC_x–SiC_p (5–15 vol%) composites ($ZBCSC_p$-C) produced with 1 wt% Ni at 40 MPa, 1400 °C for 30 min are shown in Fig. 1. The peaks corresponding to ZrB_2, ZrC_x and SiC_p phases with very weak peaks of *m*-ZrO_2 are seen in all the composites. The lattice parameter of $ZrC_{x\sim0.67}$ in the composites is 4.686 ± 0.001 Å, which is slightly larger than that reported in our earlier work (4.682 Å) for ZrB_2–$ZrC_{x\sim0.67}$ composite[21] and for monolithic $ZrC_{x\sim0.67}$[22] produced by RHP. The relative density (RD) at 1400 °C reduces from 99.9% at 5 vol% SiC to 95.4% at 15 vol%. An increase in pressing temperature to 1500 °C results in a density of 97.3% with 20 vol% SiC.

Typical scanning electron micrographs of the 5 vol% and 15 vol% SiC_p composites are shown in Fig. 2. The estimated volume fractions of SiC, according to image analysis of the 5% and 15% samples, are 4.7 ± 0.4 and 15.3 ± 1.2, while corresponding porosity estimated using optical micrographs (not shown) are ~1% and 5%, respectively. These are consistent with the density measurements and also indicate that there has not been significant loss of SiC by reaction with Zr. The grain sizes of the ZrB_2 and ZrC are ~1 to 2 μm, while SiC agglomerates of 0.83–6 μm were observed. The hardness of the composites decreased from 22 to 17 GPa as the RD of the composite decreased from 99.9% to 95.4%.

3.1.2. $ZBCSC_p$-F composites

The use of fine B_4C powder demonstrates (Fig. 3) that up to ~98% RD can be achieved with 25 vol% SiC. The XRD patterns and the lattice parameter of the ZrC_x are similar to those with coarse B_4C. Our earlier work[21] indicated addition of Ni to aid the completion of the reaction between Zr and B_4C, but without any effect on densification. Similarly there appears to be no change in densification (Fig. 3 and Table 1) when Ni is absent in the present experiment (25 vol% SiC_p, 1500 °C). Typical SEM micrographs of the 20 vol% and 25 vol% SiC_p composites shown in Fig. 4, indicate a reasonably uniform distribution of SiC_p though there is some tendency for particle clustering (0.14–6 μm) within the ZrB_2–ZrC matrix. The densities attained are comparable to those reported for ZrB_2–SiC–ZrC composites made by other routes that required temperatures ≥1600 °C.[15–18,20] The hardness of the 20 vol% and 25 vol% SiC_p composites is 17 and 20 GPa, respectively.

Thus, it is clear that RHP of non-stoichiometric Zr–B_4C powder mixture can be used to densify composites with variable SiC particulate content at a temperature that is low enough to avoid

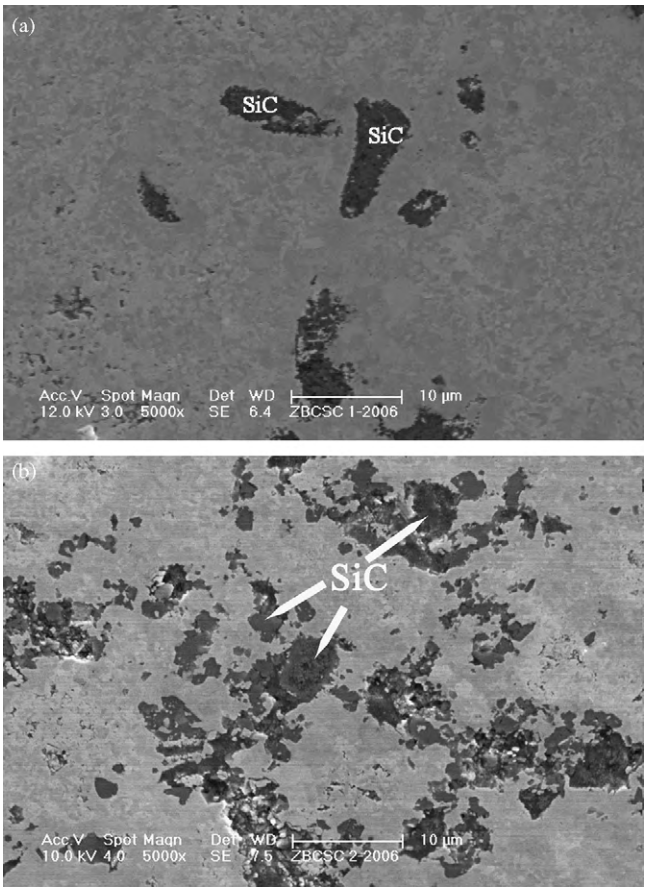

Fig. 2. Scanning electron micrographs of the $ZBCSC_p$-C composites produced with 1 wt% Ni at 40 MPa, 1400 °C for 30 min (a) 5 vol% SiC and (b) 15 vol% SiC. The grey clusters represent SiC particulates while the matrix reveals a darker ZrB_2 and a lighter ZrC_x phase.

degradation of the particulate. There is potential to exploit this sinterable matrix of ZrB_2–ZrC_x to include other reinforcements, such as suitably protected carbon fibres or other refractory carbides/borides.

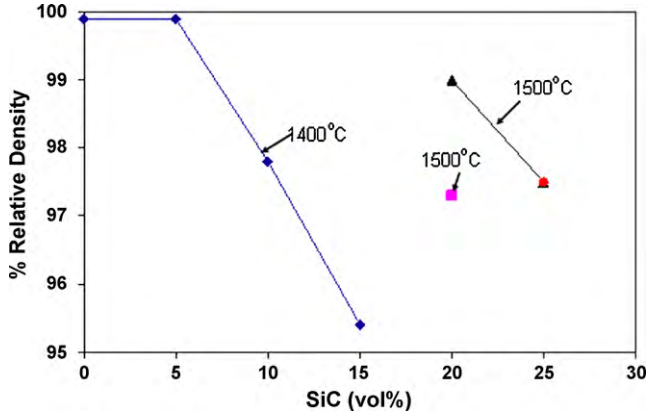

Fig. 3. The relative density (%) versus SiC_p content plot of the composites ($ZBCSC_p$-C: (♦) 1400 °C with 1 wt% Ni, (■) 1500 °C without Ni and $ZBCSC_p$-F: (▲) 1500 °C without Ni and (●) with 1 wt% Ni).

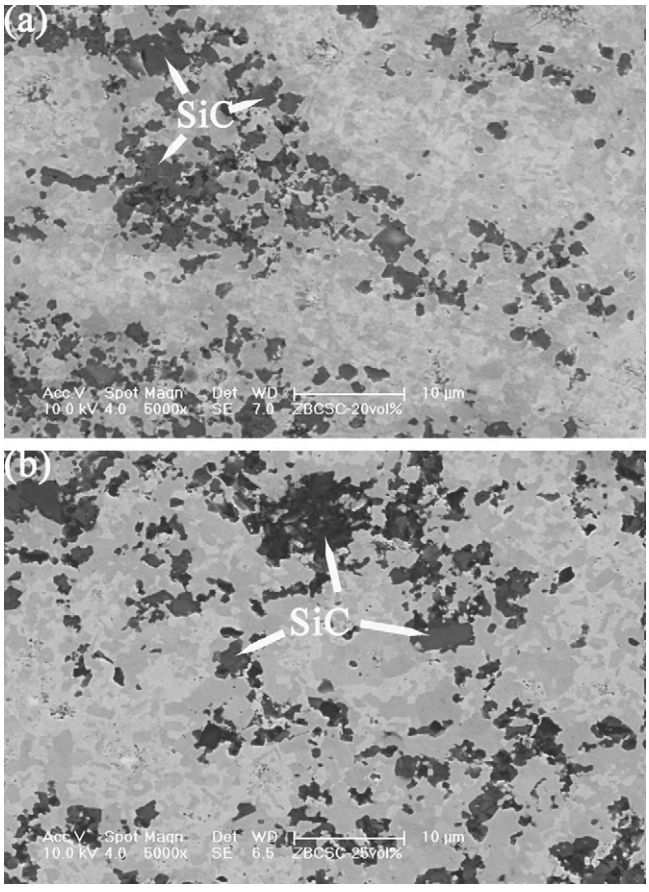

Fig. 4. SEM micrographs of the $ZBCSC_p$-F (composites produced without Ni at 40 MPa, 1500 °C for 30 min: (a) 20 vol% SiC and (b) 25 vol% SiC.

4. Conclusions

It is possible to produce ZrB_2–ZrC_x–SiC_p composites at temperatures as low as 1500 °C using non-stoichiometric Zr–B_4C powder mixtures with up to 25 vol% SiC particulates. For any given powder mixture, final relative densities of the composites decreased monotonically with particulate content. Fine reactant powders promote higher relative densities. The hardness of the composites is in the range of ∼17 to 22 GPa.

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