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Short communication

Development of multi-phase B–Si–C ceramic composite by reaction sintering

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Abstract

A dense ceramic composite in the system B–C–Si has been synthesized by the reaction sintering technique based on infiltration of silicon melt at 1550 °C under vacuum into a porous compact made of boron carbide and petroleum coke powder. The final material is around 99% dense and microstructurally contains B_4C, SiC and Si as the major phases. The B_4C-phase reacted at its interface with Si-phase, which is explained in terms of dissolution of Si in the carbide phase.

Keywords: Multi-phase ceramic; B_4C–SiC–Si composite; Reaction sintering

1. Introduction

Dense B_4C is an important light-weight structural material because of its low specific weight, outstanding hardness, high melting point, good mechanical properties, adequate resistance to chemical agents and a high neutron absorption cross-section. For the last 50 years intensive studies were undertaken on the material for its development as a component in personal armor system. These initiatives lead to the improvement in its ballistic performance mostly through improvements in system design. No significant improvement of material aspects of B_4C as armor ceramics has been made. The problems of poor crack-propagation resistance and expensive methods of fabrication are still considered to be the prime issues. Boron carbide-based ceramic composite, e.g., SiC–B_4C ceramics, shows improved mechanical properties and raises interest [1]. Realization of the potential of the ceramic composite is hindered by processing difficulties. During consolidation of such a composite, an internal hydrostatic tensile stress occurs in presence of reinforcement phase which remains as a non-densifying inclusion and reduces sintering. Application of a small external force can compensate the internal tensile stress (hot pressing), but the processing becomes costly. A processing approach assuring non-shrinking crystalline matrix formation for B_4C-based composites becomes necessary. Reaction sintering technique based on condensed phase—condensed phase reaction is capable of forming non-shrinking matrices at low temperatures with short processing times. Although some initiatives have already been taken in this direction, the published works reported application of higher processing temperature (1900–2100 °C) [2], coarse grain structure for unacceptable microstructure [3] and uncontrolled Si–B reactions [4]. This paper reports the synthesis of B–C–Si multi-phase ceramic composites following reaction-sintering technique with an aim to examine these issues.

2. Experimental

Boron carbide (B_4C) (H.C. Starck, Germany), and petroleum coke powders were used as major raw materials. The powders were characterized for particle size distribution by laser technique (Mastersizer 2000, Malvern (UK)) and for surface area by BET method (Micromeritics (USA)). Monomodal distribution was observed in case of starting B_4C powder, as is shown in Fig. 1. The specific surface areas of B_4C and petroleum coke powders were of 0.71 and 5.36 $m^2\ gm^{-1}$, respectively, which indicated that the carbon powder was in sub-micrometer range. The dry powders were mixed as slurry in

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a suitable organic medium using a V-mixer. Careful addition of polyvinyl alcohol (PVA) was made in order to provide green strength and control of porosity level. After the mixing, organic solvent was allowed to evaporate and the remaining lumps were granulated by passing them through a sieve with a mesh size of approximately 1 mm. Any remaining organic solvent was driven off by suitably heating in an air oven. The granules were compacted into cylindrical pellets of about 20 mm diameter and 10 mm high using a die-set in a hydraulic press. The pellets were dried and measured for linear dimensions and green bulk density (B. D.). They were subsequently de-bonded by slow heating to about 350 °C and were reaction sintered by liquid Si infiltration (LSI) in a resistance heated graphite furnace at 1550 °C under vacuum. The pellets were allowed to cool slowly in the furnace. The as-sintered material was tested for measurement of linear dimension, bulk density (by water displacement method) and porosity (by boiling water method). X-ray diffraction (XRD) pattern was recorded by using a Philips (Holland) PW1710 diffractometer. Microstructural analysis was carried out with highly polished specimens (lapping and polishing were done using successively finer diamond pastes down to 1 μm size) using scanning electron microscopy (SEM) (SE-440, Leo-Cambridge, Cambridge, UK).

3. Results and discussion

Infiltration of molten silicon into green preform was found to be good and visibly no cracks were obtained either in the as-fired specimen or in the ground and polished samples (Fig. 2). The material properties obtained experimentally were summarized in Table 1. For a given preform density (ρ gm cm^{-3}) and weight fraction of carbon in the preform (y), mass balance defines volumetric relations between product phases. Assuming no carbon loss and no dimensional change occurring during complete reaction, the respective volume fractions of product phases of SiC, B_4C and Si can be predicted as

$$V_{SiC} = \frac{\rho y M_{SiC}}{M_C \rho_{SiC}} = 1.038y \quad (1)$$

$$V_{B_4C} = \frac{\rho(1-y)}{\rho_{B_4C}} = 0.3968\rho(1-y) \quad (2)$$

$$V_{Si} = 1 - (V_{SiC} + V_{B4C}), \quad (3)$$

where M_{SiC} (=40) and M_C (=12) represent the respective molecular weights of SiC and C; ρ_{SiC} (=3.21 gm cm^{-3}) and ρ_{B4C} (=2.56 gm cm^{-3}) are the respective densities of SiC and B_4C. For the starting formulation of powders used in the present study (ca. Table 1), the vol.% of the product phases of SiC, B_4C and Si could be estimated using above equations

Table 1
Characteristics of green preform and Si infiltrated specimen

Preform density (gm cm^{-3})	1.44
Preform carbon content (wt.%)	25
Ceramic density (gm cm^{-3})	2.73
Ceramic porosity (vol.%)	0.65
Post-infiltration change in linear dimension (%)	
Diameter wise	+1.25
Height wise	+1.56

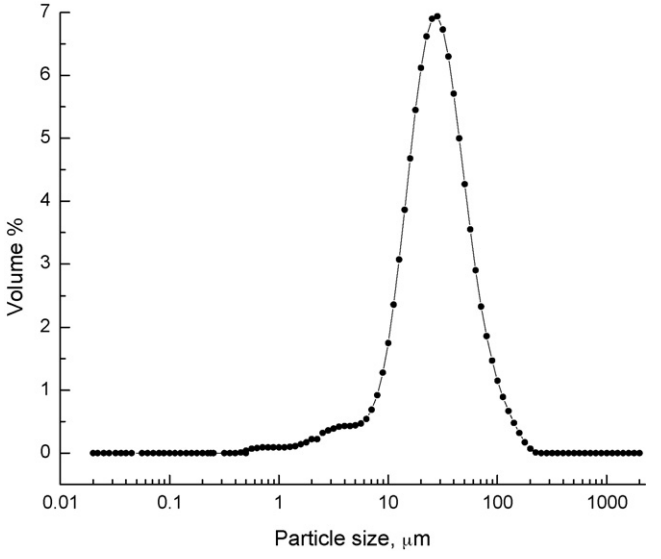

Fig. 1. Particle size distribution pattern of starting B_4C powder showing nearly narrow peak at around 23 μm.

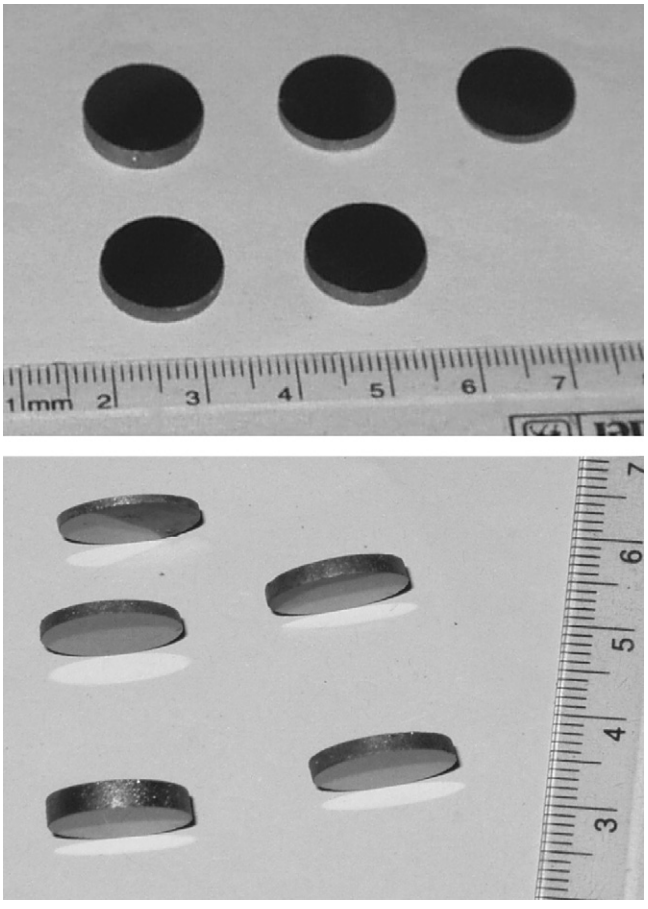

Fig. 2. Samples of multi-phase ceramic composite in the system B–C–Si, after polishing down to 1 μm finish without any sign of cracking of disintegration.

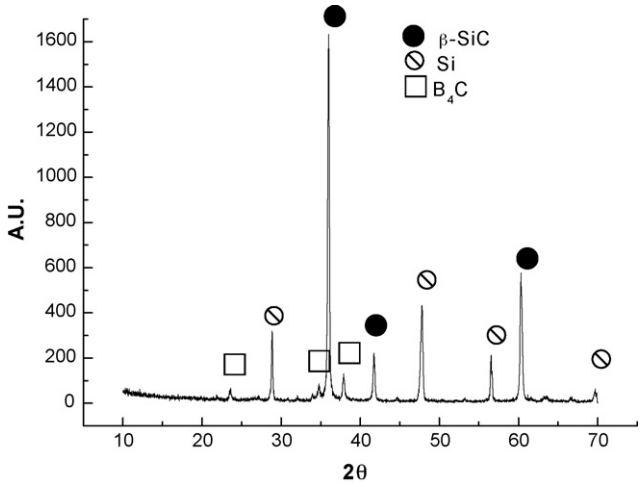

Fig. 3. XRD scan of the Si infiltrated specimen showing the presence of β-SiC, B_4C and Si as the product phases.

and found to be 37.37, 42.86 and 19.77%, respectively, which gave a value of theoretical density to be 2.74 gm cm^{-3}. The material properties obtained in the present study (ca. Table 1) revealed that the infiltrated specimen was >99% dense with respect to theoretical density. The presence of SiC, B_4C and Si as the product phases was also supported by XRD analysis as shown in Fig. 3. Si and SiC phases were found to have cubic symmetry with cell parameters $a = 5.4028$ Å and 4.3524 Å, respectively. The boron carbide phase has rhombohedral symmetry and larger lattice parameters with $a = 5.63401$ Å and $c = 12.31611$ Å. The values of weight % of crystalline phases were estimated from X-ray diffraction line profile using Reitveld analysis by X'pert High Score Plus software (PANalytical). The values of cell parameters and the quality of fitting were assessed from various numerical criteria of fit, viz., the profile residual factor (R_p), the weighted residual factor (R_{wp}), the expected residual factor (R_{exp}), weighted-statistics (D_{ws}) and the goodness of fit (GOF). In the present study the reliability parameters were found to be $R_{wp} = 11.228$, $R_p = 11.120$, $R_{wp} = 13.84$, $D_{ws} = 0.6263$ and GOF = 1.520, which are related to good fitting. The vol.% of phases obtained from the corresponding weight per cents for SiC, B_4C and Si could be found to be 32.34, 57.16 and 10.48%, respectively, which gave a value of sintered density (2.745 gm cm^{-3}) nearly equal to the experimentally measured density. Compared to the vol.% of phases predicted, a notable increase in the vol.% of B_4C and a decrease in vol.% of Si were obtained. This fact coupled with the larger cell parameters for B_4C particularly in *c*-direction indicates the possible dissolution of Si in B_4C lattice [5]. The microstructure of reaction-sintered specimen also shows the presence SiC, B_4C and Si-phases (Fig. 4). The B_4C-phase is shown to have reacted at its interface with Si-phase due to dissolution of Si. Further detailed examination of the interface is needed which is beyond the scope of the present study. The % linear dimension change on reaction sintering was found to be nearly 1%, which indicates that near-net shape processing is possible in the case of reaction sintering of B–C–Si multi-phase ceramic composite.

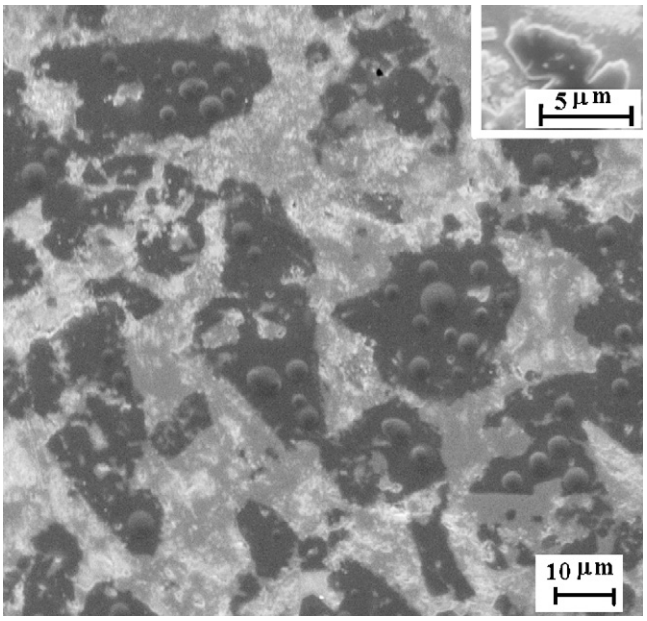

Fig. 4. SEM photomicrograph of the Si infiltrated specimen showing the presence of B_4C (deep black), SiC (dark grey) and Si (bright grey) phases; sign of reaction at the B_4C/Si boundary probably due to dissolution of Si in the carbide is shown in the inset.

4. Conclusions

The present study demonstrated the possibility of net-shape production of B–C–Si multi-phase ceramic composite by reaction sintering at 1550 °C via infiltration of Si-melt into a porous preform containing B_4C and C. The final material has negligible porosity, around 99% dense, and contains B_4C, SiC and Si as the major phases. The B_4C phase has found to have reacted at its boundary with Si-phase which is explained in terms of dissolution of Si in the carbide phase.

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