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Preparation of reaction bonded silicon carbide (RBSC) using boron carbide as an alternative source of carbon

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Abstract

RBSC composites are fully dense materials fabricated by infiltration of compacted mixtures of silicon carbide and carbon by molten silicon. Free carbon is usually added in the form of an organic resin that undergoes subsequent pyrolysis. The environmentally unfriendly pyrolysis process and the presence of residual silicon are serious drawbacks of this process. The study describes an alternative approach that minimizes the residual silicon fraction by making use of a multimodal particle size distribution, in order to increase the green density of the preforms prior infiltration. The addition of boron carbide provides an alternative source of carbon, thereby eliminating the need for pyrolized organic compounds. The residual silicon fraction in the RBSC composites, prepared according to the novel processing route, is significantly reduced. Their mechanical properties, in particular the specific flexural strength is by 15% higher than the value reported for RBSC composites prepared by the conventional approach.

Keywords: Reaction bonded silicon carbide; Boron carbide

1. Introduction

Reaction bonded silicon carbide (RBSC) composites are attractive materials for light armor applications. A conventional approach for RBSC composites fabrication involves infiltrating a compacted SiC/carbon mixture with molten Si. Most commonly, free carbon is formed as a result of pyrolysis of an organic resin that had been added to the SiC powder. The reaction between molten silicon and free carbon leads to the formation of silicon carbide grains, which precipitate on the original SiC particles, interconnect them and form a continuous ceramic skeleton. The typical microstructure of RBSC composites consists of about 85% of inter-connected silicon carbide and free silicon as a residual balance.[1]

The main advantage of the RBSC composites fabrication process is its relatively low temperature (~1500 °C), as compared to pressure-less or hot pressing densification. Its disadvantages are: (a) the unfriendly nature of the pyrolysis process that releases toxic gases; (b) the presence of residual silicon that lowers the mechanical properties of the final composites. One approach that has been put forward in order to reduce the fraction of residual silicon is to use powder mixtures with an appropriate multimodal particle size distribution [2]. Such distribution leads to maximal volume filling by the initial ceramic particles prior infiltration and reduces the fraction of residual non-reacted silicon after infiltration. The importance of volume filling by a multimodal distribution of ceramic particles and the necessity of limiting the maximal size of the large particles has been pointed out in previous reports.[3–5] This approach allows to fabricate compacts with a high green density in the 75–80 vol.% range and to limit the amount of residual silicon to below 10 vol.%.

In order to eliminate the necessity of going through the environmentally unfriendly pyrolysis step it was suggested to use boron carbide as alternative source of carbon.

Boron carbide reacts with molten silicon and the formation of the ternary B–C–Si carbide phase takes place. Parameters of reaction bonded boron carbide (RBBC) composites fabrication without free carbon additions, microstructural and mechanical characteristics of the infiltrated composites were discussed in a previous study.[6]

In the present work we have combined these two features, in order to fabricate RBSC composites with a lower amount of residual silicon using the environmentally friendly processing approach.

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Table 1
The powder compositions and particle size distribution that were used.

	Particle size, D^{50} (μm)	Vol.% of different powders								
		RB-1	RB-2	RB-3	RB-4	RB-5	RB-6	RB-7	RB-8	RB-9
SiC	106	53	38	28	23	18	53	53	53	53
	50	10	10	10	10	10	10	10	10	10
	13	18	18	18	18	18	18	12	7	2
	3	19	19	19	19	19	4	0	0	0
B_4C	106	0	15	25	30	35	0	0	0	0
	13	0	0	0	0	0	0	6	11	16
	3	0	0	0	0	0	15	19	19	19
Porosity of green compact (vol.%)		24	25	23	23	22	22	23	21	21

2. Experimental procedures

2.1. *Fabrication of the composites*

A commercial coarse (~120 μm, 98% purity) silicon carbide powder consisting of a mixture of α and β SiC was ground and sieved in order to obtain the requested particle size distribution. A fraction in the SiC powder mixtures was replaced by fine or coarse boron carbide powders. Fine boron carbide powder (~1 μm, grade HS, 97.5% purity) was supplied by H.C. Starck and B_4C powders with average particle size of 13 and 100 μm (97% purity) were supplied by "Modan Jang" a Chinese Company. Nine different powder samples were prepared with various particle size distributions (Table 1). The first powder sample (RB1) had no boron carbide addition and was used as a reference sample. In four of these mixtures (RB-2, RB-3, RB-4 and RB-5) coarse boron carbide powder was added; fine boron carbide powder was added to the remaining three mixtures. The optimal size distribution was applied to all powder mixtures irrespective of the nature of the particles, boron or silicon carbide. This was achieved by following the approach described in Ref. [2]. The relative volume fraction of boron carbide in the mixture varied within the 15–35 vol.% range. Different boron carbide volume fractions were examined in order to determine the fraction that would provide the adequate amount of carbon necessary to react with the incoming molten silicon. Since the amount of carbon released depends on the surface to volume ratio of the boron carbide particles, it was also necessary to gain insight into the relative effect of the particle size, while maintaining at the same time a ratio of coarse to fine particles, consistent with maximum volume filling requirement.

The mixtures were dry mixed in a planetary mixer for 8 h. Preforms, 20 mm diameter and 5 mm high were uniaxially compacted under 180 MPa. The compacts were infiltrated with liquid silicon (98.4%, Alfa Aesar) at 1480 °C for 15 min in a furnace under 0.01 Pa vacuum.

2.2. *Characterization*

2.2.1. *Microstructure and composition*

The microstructure of the samples was studied using optical microscopy (OM, Zeiss Axiovert 25) and scanning electron microscopy (SEM, JEOL-35) with an energy dispersive spectrometer (EDS). The samples for the microstructural characterization were prepared using a standard metallographic procedure that included a last stage of polishing by 2.5 μm diamond paste. Image analysis, using the Thixomet software, was applied in order to determine the amount of residual silicon in the composites. The phase composition was determined qualitatively by X-ray diffraction (XRD).

2.2.2. *Mechanical properties*

The micro-hardness values were determined using a (Buehler-Micromet 2100) micro-hardness tester under 2000 g

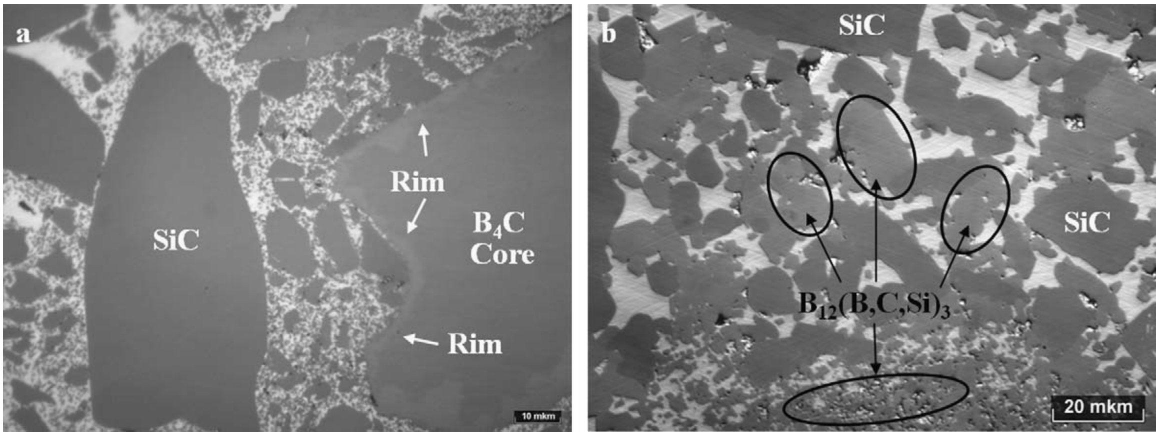

Fig. 1. The microstructure of the composites prepared by using: (a) coarse B_4C particles; a thin layer of the $(B_{12}(B,C,Si)_3$ rim phase surrounds the core of the particles; (b) fine B_4C particles that were converted into the $(B_{12}(B,C,Si)_3$ phase.

load. The flexural strength was measured with a LRX plus LLOYD machine (Lloyd Instruments, Fareham Hants, U.K.), on 1.5 mm × 2 mm × 20 mm samples. The elastic modulus of the composites was derived from ultrasonic sound velocity measurements using the “Pulse Echo” method. The density of the infiltrated composites was determined by the Archimedes method.

3. Results and discussions

3.1. Microstructure

The microstructure of the composites (Fig. 1a and b), prepared with the addition of coarse or fine boron carbide powder, consists of B_4C, $B_{12}(B,C,Si)_3$, SiC and residual silicon. A thin rim region surrounds the coarse boron carbide particles (Fig. 1a), while the fine boron carbide particles are almost completely converted into the ternary $B_{12}(B,C,Si)_3$ carbide (Fig. 1b). The presence of the $B_{12}(B,C,Si)_3$ grains with a gray color slightly lighter than the color of the SiC particles is clearly discernable. It is important to point out that the $B_{12}(B,C,Si)_3$ phase grains connect the ceramic particles and provide the continuous ceramic skeleton, similar to that of composites fabricated with free carbon addition. This observation is in a good agreement with the previously reported results for reaction bonded boron carbide composites.[6]

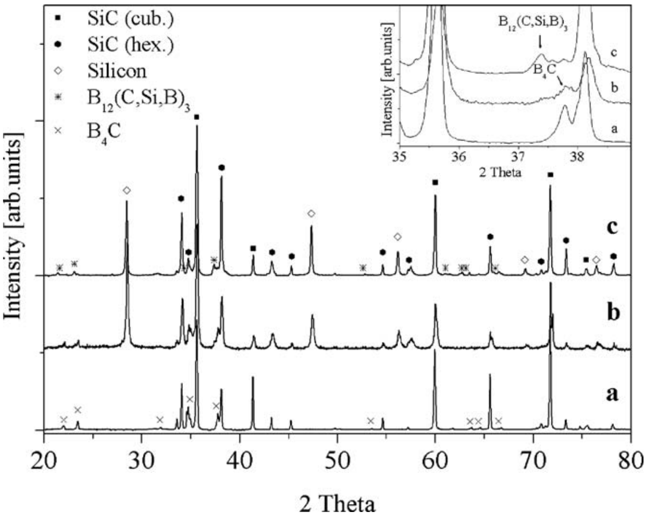

Fig. 2. XRD patterns of the composites. Spectrum (a) corresponds to the initial mixture of SiC with the 35 vol.% B_4C. Spectrum (b) stands for RBSC composite in which only coarse B_4C particles had been added. Spectrum (c) corresponds to the RBSC in which solely fine B_4C particles had been added. The insert shows at a higher resolution part of the spectrum and illustrates the absence of the (0, 2, 1) peak of B_4C and its replacement, at a slightly lower 2θ angle, by a peak corresponding to the ternary $B_{12}(C,Si,B)$ phase.

The diffraction spectra of the composites consist, in addition to the SiC peaks, of some low intensity peaks corresponding to the ternary boron containing compound. In the spectra of composites containing coarse B_4C particles, the diffraction peak of the ternary $B_{12}(B,C,Si)_3$ phase was identified as the low intensity shoulder adjacent to the (0, 2, 1) peak of B_4C (Fig. 2). In spectra of the composites prepared with the addition of fine boron carbide powder, only the peak associated with the ternary $B_{12}(B,C,Si)_3$ phase is present (in addition to the SiC and Si peaks), confirming that the initial fine boron carbide particles had been completely converted into the ternary $B_{12}(B,C,Si)_3$ phase. The low crystalline symmetry and the low volume fraction of the $B_{12}(B,C,Si)_3$ phase lowers the intensity of the peaks corresponding to this phase. In addition, the ternary phase is generated as the result of the interaction that takes place on the surface of the initial boron carbide particles with molten silicon. This interaction involves solid state diffusion within the boron carbide and results in the ternary compound displaying composition gradients. The non-uniform composition of this phase stands behind the broadened diffraction peaks.

We have previously reported that in reaction bonded boron carbide composites, fabricated in the absence of free carbon, the secondary SiC phase displays a plate-like morphology.[7] With boron carbide particles acting as the sole source of carbon, the gradual diffusion controlled release of carbon from within the boron carbide matrix favors the plate-like morphology of the

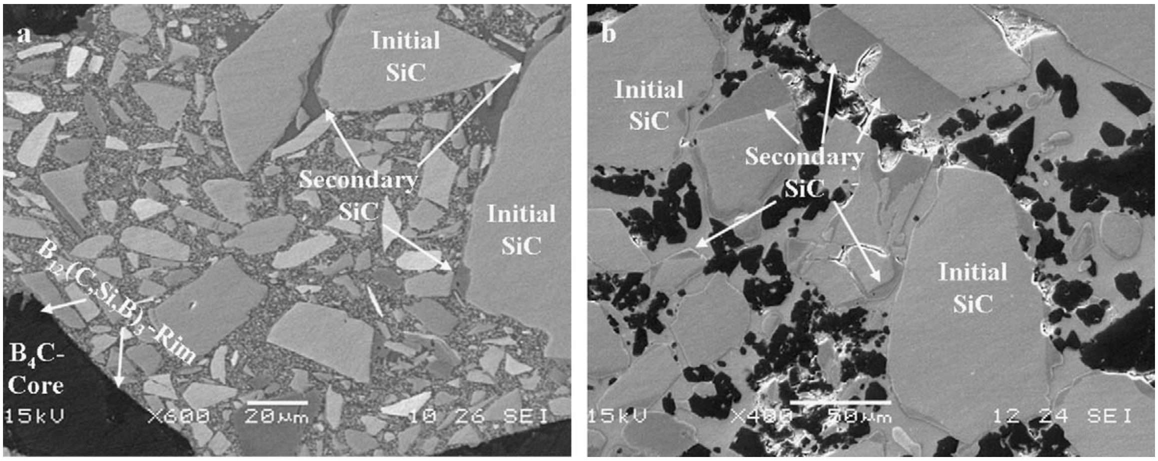

Fig. 3. SEM images of the infiltrated composites. (a) RBSC composite prepared by the addition of coarse B_4C particles. The ternary $B_{12}(C,Si,B)_3$ carbide is present as the brighter rim surrounding the coarse B_4C particle. Notice the low fraction of secondary SiC adjacent to the massive initial SiC particles; (b) RBSC prepared with the addition of fine B_4C particles giving rise to a larger fraction of secondary SiC attached to the initial SiC particles.

Table 2
Properties of the RBSC composite samples.

	RBSC[a]	RB-1	RB-2	RB-3	RB-4	RB-5	RB-6	RB-7	RB-8	RB-9
Density (g/cm^3)	2.85–3.10	2.92	2.86	2.83	2.81	2.79	2.89	2.86	2.84	2.83
Young's Modulus (GPa ± 3)	320–340	344	346	348	349	352	343	345	351	353
Flexural strength (MPa ± 18)	190–250	204	207	183	171	179	255	256	237	270
Hardness (Hv)	1500–2200	1534 ± 202	1562 ± 186	1607 ± 185	1630 ± 197	1652 ± 211	1673 ± 262	1835 ± 262	1928 ± 307	1963 ± 331
Residual Si (vol.%)	15–35	23.4	19.5	17.5	14.5	12.4	19.4	15.6	12.0	10.6
Weibull modulus	–	9.44	12.08	7.71	8.39	9.17	15.55	8.93	12.4	16.1
Specific Young's modulus, (GPa/(g/cm^3))	110	118	121	123	124	126	119	121	124	125
Specific flexural strength, (MPa/(g/cm^3))	81	70	72	65	61	64	88	90	83	95
Specific hardness, (Hv/(g/cm^3))	–	525 ± 69	546 ± 65	568 ± 65	580 ± 70	592 ± 75	579 ± 91	642 ± 92	679 ± 108	694 ± 117

[a] Range of the composite properties values reported in literature.[1,8,9]

resulting secondary SiC. In contrast, in RBSC fabricated according to the conventional route in the presence of free carbon, no such plate-like SiC phase was observed. In the present case, even though the source of carbon is in the B_4C phase, no plate-like SiC particles were found, due to the presence of the initial SiC particles on the surface of which heterogeneous nucleation of the secondary SiC took place. It is also noteworthy that in composites with coarse B_4C powder addition, the newly formed SiC layer (Fig. 3a) that surrounds the original SiC particles is thinner than in the composite fabricated with the fine boron carbide addition (Fig. 3b). The difference underlines that the fine particles with a higher surface to volume ratio are a more effective carbon source than the coarse particles.

3.2. Mechanical properties

The mechanical and the physical properties of the composites that were fabricated with different fractions of B_4C are summarized in Table 2. The specific mechanical properties are also reported in order to emphasize the changing density effect.

The density of the different composites reflects the amount of added boron carbide (2.52 g/cm^3) that decreases the density and of the fraction of newly formed SiC (3.21 g/cm^3) that increases density. A striking feature is the significantly reduced residual silicon fraction in the composites having both a relatively high boron carbide content and a high fraction of fine boron carbide powder, e.g. samples RB-4, RB-5, RB-8 and RB-9.The relatively high residual silicon fraction of RB-2 and RB-6 is attributed to their low boron carbide content, insufficient apparently to release enough carbon to react with the incoming molten silicon. The decreased free silicon implies an increased SiC fraction and stands behind the increased hardness values. As expected, the Young modulus does not depend on the particle size of the added boron carbide but increases with increasing boron carbide volume fraction. The flexural strength depends on the boron carbide particle size and is higher for the composites fabricated with the addition of fine particles. Table 2 also presents the specific mechanical properties. Noteworthy is the increased specific flexural strength of the composites, prepared according the novel approach. This increase is essentially due to the lower density of the relatively large boron carbide content of these composites.

The Weibull modulus for the composites with fine boron carbide powder addition displays a higher value as compared to the samples prepared with coarse boron carbide particles and reflects the higher level of micro-homogeneity of the former.

4. Conclusions

RBSC composites were fabricated using various fractions of boron carbide as an alternative source of carbon. The main advantage of the novel approach is the significantly reduced residual silicon fraction. A further advantage is the increased specific mechanical properties associated with the lower density of the composites fabricated with the addition of the low density boron carbide. These composites display improved mechanical properties as compared to RBSC fabricated by conventional processing. Boron carbide additions in the form of fine particles are a more effective carbon source than the coarse particles. The RBSC composites fabricated with a fine B_4C powder addition also display a relatively higher reliability as shown by their increased Weibull modulus. Finally, the suggested novel approach is environmentally friendly and avoids the formation of toxic organic compounds.

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