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The effect of Fe addition on processing and mechanical properties of reaction infiltrated boron carbide-based composites

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Abstract Dense metal-ceramic composites based on boron carbide were fabricated using boron carbide and Fe powders as starting materials. The addition of 3.5–5.5 vol% of Fe leads to enhanced sintering due to the formation of a liquid phase at high temperature. Preforms, with about 20 vol% porosity were obtained by sintering at 2,050 °C even from an initial boron carbide powder with very low sinterability. Successful infiltration of the preforms was carried out under vacuum (10^{-4} torr) at 1,480 °C. The infiltrated composite consists of four phases: $B_{12}(C, Si, B)_3$, SiC, $FeSi_2$ and residual Si. The decrease of residual Si is due to formation of the $FeSi_2$ phase and leads to improved mechanical properties of the composites. The hardness value, the Young modulus and the bending strength of the composites fabricated form a powder mixture containing 3.5 vol% Fe are 2,400 HV, 410 GPa and 390 MPa, while these values for the composites prepared form iron free B_4C powder are 1,900 HV, 320 GPa and 300 MPa, respectively. The specific density of the composite was about 2.75 g/cm^3. The experimental results regarding the sintering behavior and chemical interaction between B_4C and Fe are well accounted for by a thermodynamic analysis of the Fe–B–C system.

Introduction

Boron carbide is a low density ceramic with elevated hardness and Young modulus values that make it a valuable candidate for light armor applications. Fully dense boron carbide can be fabricated by hot pressing at a relatively high temperature (2,150–2,200 °C) [1]. An alternative approach for fabrication of dense boron carbide-based material is the so-called ''reaction bonding boron carbide (RBBC)'' process. According to this approach a mixture of B_4C powder and free carbon (or carbon bearing materials) is compacted and subsequently infiltrated with molten silicon [2–4]. Molten silicon reacts with free carbon and, possibly, with carbon that originated in the boron carbide to form the SiC phase. The final composites are fully dense and consist of the original B_4C particles, new SiC phase and some pockets of a residual unreacted Si. In order to decrease the amount of residual silicon and to improve the properties (in particular, to increase the hardness) of the composites, it has been suggested to infiltrate partially sintered boron carbide preforms with liquid Si. This variant of the process is denoted as the reaction infiltration approach [5].

One of the drawbacks associated with these approaches for the fabrication of the composites is the necessity of providing excess free carbon, which is added either in the form of pure carbon or in the form of carbon-rich organics. The latter carbon-containing compounds have to be pyrolyzed leaving behind free carbon that is more or less homogeneously dispersed throughout the compacted boron carbide particles. Pyrolysis is an environmentally unfriendly procedure, moreover, in many cases, residual free carbon instead of being dispersed uniformly forms agglomerates that react only partly with the molten silicon.

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An alternative approach for enriching the ceramic preforms with carbon is to induce the in-situ release of free carbon as the result of a chemical interaction between boron carbide and appropriate additions. Actually, such procedure would be even more beneficial, if these additions allowed improving the sinterability of the boron carbide preforms.

In the present study the effect of Fe addition on the processing and on the mechanical properties of the reaction infiltrated boron carbide composites was investigated. The motivation for using iron powder as an appropriate addition is based on the reaction between Fe and B_4C that leads to the release of free carbon and to the formation of the FeB phase. The relatively low melting point of FeB provides the conditions for liquid phase sintering of boron carbide at relatively low temperature. The effect of Fe on boron carbide sintering was reported by Lange and Munir [6]. The thermodynamic analysis of the ternary Fe–C–B system was conducted in order to explain the experimental observation related to various stages of the fabrication of the infiltrated composites.

Experimental procedure

Boron carbide (5 μm mean particle size, Mudanjiang Abrasives And Grinding Tools Co, China) and Fe (particle size less than 10 μm, Alfa Aesar) powders were blended in planetary ball mill for 4 h. The B_4C powder and powder mixtures (3.5 and 5.5 vol% Fe) were uniaxially compacted under 30 MPa. The specimens (Ø20 mm) were sintered in the 2,000–2,100 °C temperature range for 30 min under argon atmosphere. The density of the preforms was determined by the liquid displacement method in distilled water. A dilatometric study of sintering kinetic (UNITHERM^{TM} 1,252 V, Anter Corporation) was conducted by heating up to 1,970°C. The porous preforms were infiltrated by liquid Si under vacuum (10^{-4} torr) at 1,480 °C. The microstructure of the infiltrated composites was examined by Optical Microscopy and Scanning Electron Microscopy (SEM) (JEOL®JSM-5600). Phase composition was determined by X-ray diffraction (XRD) (Rigaku RINT 2100). The amount of the different phases in the composite was evaluated by the Thixomet[1] image analysis software. Vickers hardness (2 kg load) was determined using a Buehler-Micromet 2100. Three points flexural strength was measured using samples with 20×6×3 mm dimensions. The elastic modulus of the composites was derived from ultrasonic sound velocity measurements.

Results and discussion

Interaction of boron carbide with solid Fe

The isothermal section of the ternary Fe–B–C phase diagram at 1,273 K (Fig. 1) was calculated using the ''Thermocalc'' software [7]. The overall composition of the mixture containing boron carbide and 5.5 vol%. Fe corresponds to point A and is located within the three phase (FeB–B_4C–graphite) region. Thus, interaction between boron carbide and Fe at 1,273 K results in the formation of FeB and of free C releasing, according to reaction:

$$B_4C + 4Fe = 4FeB + C \tag{1}$$

According to the XRD analysis (Fig. 2, pattern 1), the initial boron carbide powder contains some free carbon and unknown impurities. After the heat treatment of the powder at 1,173 K under vacuum at 10^{-4} torr, the diffraction peaks associated with the free carbon and the impurities were absent. The disappearance of the carbon peak is due to the oxidation of carbon by boron oxide, omnipresent in carbide powders, and by oxygen absorbed on the surface of the particles surface. Evaporation of the unknown impurities also takes place concomitantly. These conclusions are consistent with the 3% weight loss during the heat treatment. Surprisingly, only two phases, namely B_4C and FeB were detected after annealing the B_4C–Fe (5.5 vol%) mixture at 1,273 K for 2 h (Fig. 2, pattern 2). No peaks corresponding to carbon were detected in spite of is alleged presence according to Eq. 1. Only a slight bump can be discerned in the 20–30° region of the diffraction pattern. The carbon originated from the reaction (1) is present, probably, in an amorphous form. According to a stoichiometric calculation (the density of the amorphous carbon was taken as 0.7 g/cm^3), the amount of this carbon varies from 2 to 3 vol% for 3.5 and 5.5 vol% additions of Fe, respectively.

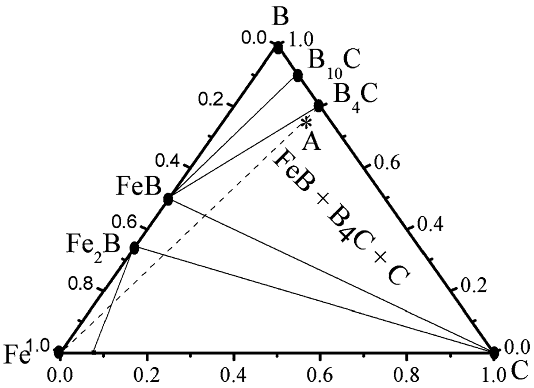

Fig. 1 Isothermal section of the ternary Fe–B–C diagram at 1,273 K

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[1] Image analysis program, developed at St. Petersburg State Polytechnic University, Department of Steel and Alloys.

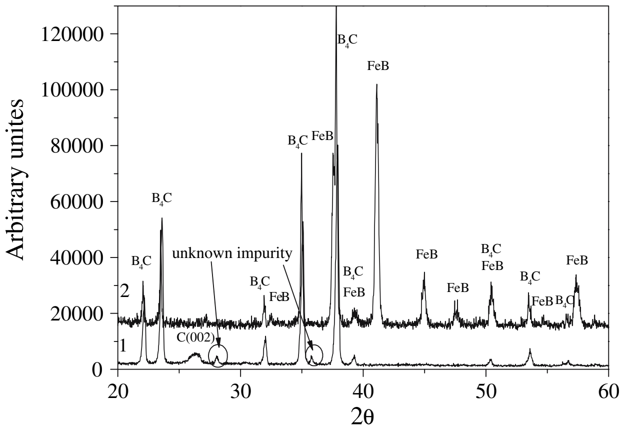


Fig. 2 XRD patterns of the starting B_4C powder (*1*) and B_4C + 5.5 vol% Fe mixture (*2*) after annealing at 1,273 K, for 2 h

Sintering of B_4C–Fe mixtures

The sintering procedure of the B_4C–Fe mixtures was performed by continuously heating to various temperatures in the 2,000–2,100 °C range and holding for 0.5 h. The residual porosity of various samples as a function of temperature is presented in Fig. 3.

In agreement with the results of Lange and Munir [6], improved sintering of the mixtures was observed in the present study. According to Sangsuwan et al. [8], successful infiltration may be achieved if the porosity of preforms is about 20–30 vol%. At a lower level of porosity, some of the pores are closed and only partial infiltration takes place. According to the experimental results, the desired porosity may be obtained by sintering the powder mixtures at relatively low temperature. This feature allowed using low cost boron carbide powder for composite fabrication. Usually the final density attained by sintering such boron carbide powder under these conditions is quite low.

Assuming that the rate of densification is a single thermally activated process in the temperature range over which the sintering study was carried out, the activation energy of the process for the powder mixtures was derived from the experimental points shown in Fig. 4. The activation energy for the single phase boron carbide powder is about 660 ± 20 kJ/mole (as compared to 717 kJ/mole reported in Skorokhod [9]). The activation energy for the densification of the Fe-containing mixtures is remarkable lower: 560 ± 80 kJ/mole for 3.5 vol% Fe and 450 ± 80 kJ/mole for 5.5 vol% Fe. The decreased activation energy by the addition of Fe is attributed to the apparition of a different mechanism of densification. Enhanced densification may be attributed to the presence of a liquid phase during the heat treatment. In order to further investigate the sintering mechanism, a dilatometric study was carried out and the results were related to the corresponding isothermal sections of the ternary phase diagram.

Sintering kinetics

The densification curves for the boron carbide powder and for its mixture with 5.5 vol% of Fe are shown in Fig. 5. Three calculated isothermal sections of the Fe–B–C phase diagram are presented in Fig. 6. The overall starting composition (point A) is located on the dashed lines that connect Fe corner with the point corresponded to B_4C. The experimental observations derived from the dilatometric curves were related to these diagrams.

The first indication of the densification of the powder mixture was detected at a temperature close to 1,200 °C (see Fig. 5) and at this temperature the first amount of liquid appears in the isothermal section (Fig. 6a). The

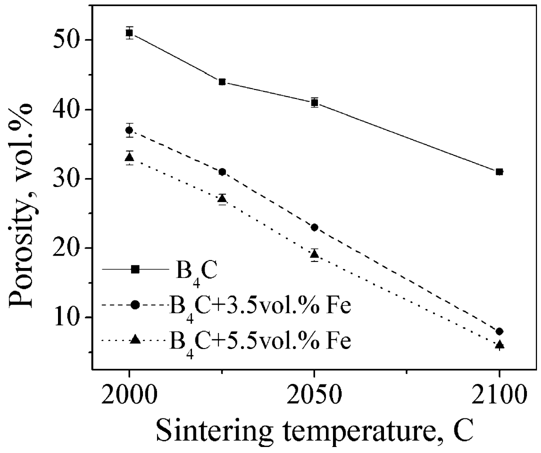


Fig 3 The effect of the mixture composition and temperature on the porosity of the sintered performs

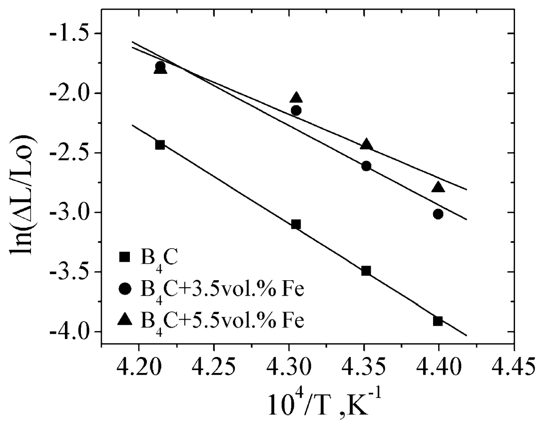


Fig 4 Determination of activation energies for densification of boron carbide powder and its mixtures with Fe

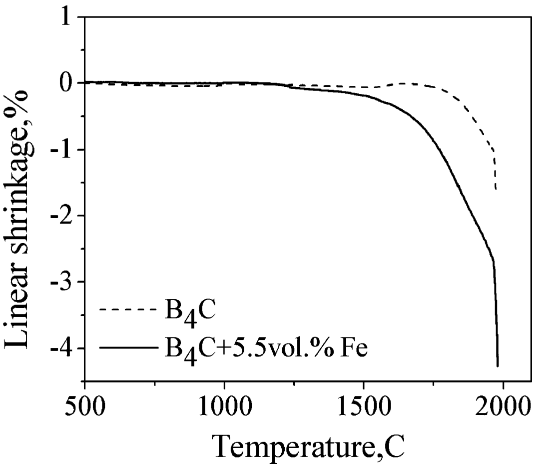


Fig. 5 Shrinkage of the powder compacts as a function of temperature

interaction of Fe and boron carbide particles leads to partly dissolution of the ceramic in the melt which consists of a liquid solution of carbon and boron in Fe with a significantly decreased melting temperature to below 1,200 °C. The amount of the liquid phase increases with further heating (see Fig. 6b). The liquid phase is, however, a transient phase, because up to melting point of FeB, only solid phases (boron carbide, FeB and carbon) coexist. At temperatures higher than 1,650 °C (Fig. 6c), the liquid phase becomes stable in contact with boron carbide and a remarkable increase of the rate of sintering takes place at this temperature (Fig. 5). This observation supports the conclusion, namely that the enhanced sintering of the B_4C–Fe mixture may be attributed to the presence of the liquid phase, which promotes mass transfer and leads to the decreased apparent activation energy of densification.

Enhanced sintering due to the Fe addition is clearly observed in Fig. 7. Only initial stages of sintering can be detected in the boron carbide powder (Fig. 7a), while it is much more pronounced in the B_4C + 5.5 vol% Fe mixture (Fig. 7b).

Infiltration of porous performs

Successful infiltration of the preforms with 20 and 30 vol% porosity was carried out under vacuum (10^{-4} torr) at 1,480 °C. SEM images of the infiltrated composites are shown in Fig. 8a, b.

No residual porosity is observed in the composites. According to EDS and XRD analysis (Fig. 9) the microstructure of the composites prepared using a B_4C–Fe mixture consists of four phases: $B_{12}(C, Si, B)_3$ (dark particles), residual Si (bright regions), polygonal SiC (gray particles) and $FeSi_2$ (brightest particles). The presence of $FeSi_2$ in the composites is a result of the interaction between liquid Si and FeB. This reaction leads to a remarkable decrease of the amount of residual silicon. According to the estimated amount of the SiC phase (Table 1) and the amount of initial free carbon for the composites, fabricated from B_4C–Fe mixture, some direct interaction between boron carbide and liquid Si also takes place. The boron released from the reactions of silicon with FeB and boron carbide dissolves in molten Si. This liquid solution, which contains also some amount of carbon, gives rise to a

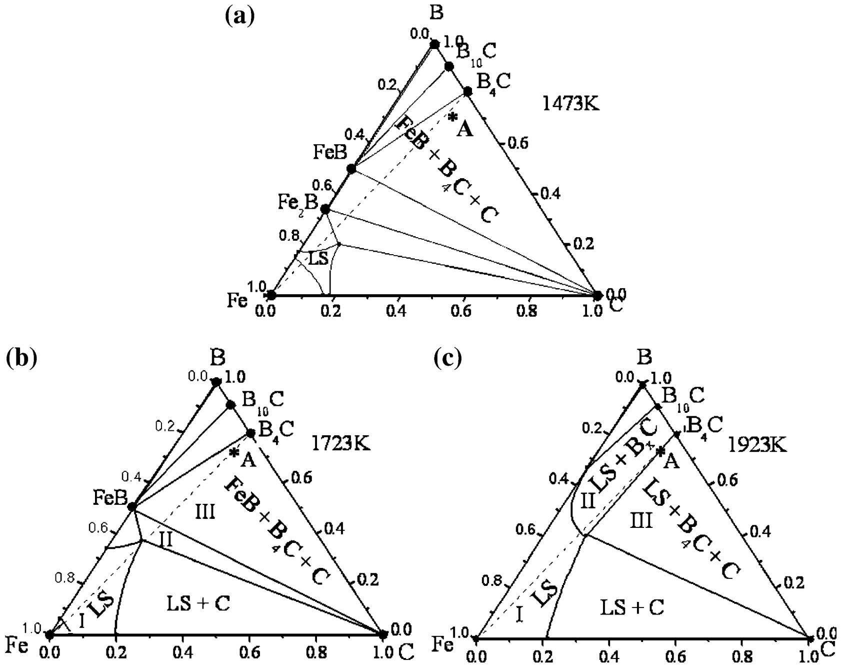


Fig 6 Isothermal sections of the Fe–B–C system: (**a**) 1,200 °C, (**b**) 1,450 °C, (**c**) 1,650 °C, LS noted the Fe–B–C liquid solution

Fig. 7 SEM images (secondary electrons) of B_4C (**a**) and B_4C + 5.5 vol% Fe (**b**) samples sintered at 2,025 °C

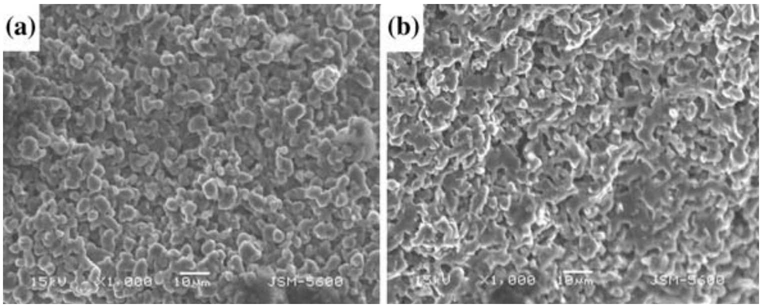
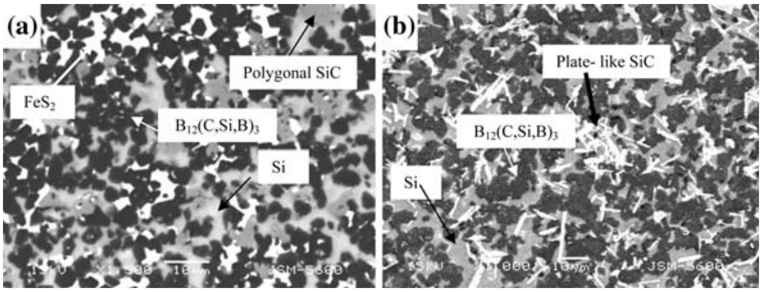


Fig. 8 SEM images of the infiltrated composites. The preforms sintered at 2,000 °C: (**a**) B_4C + 5.5 vol% Fe, (**b**) B_4C without additives



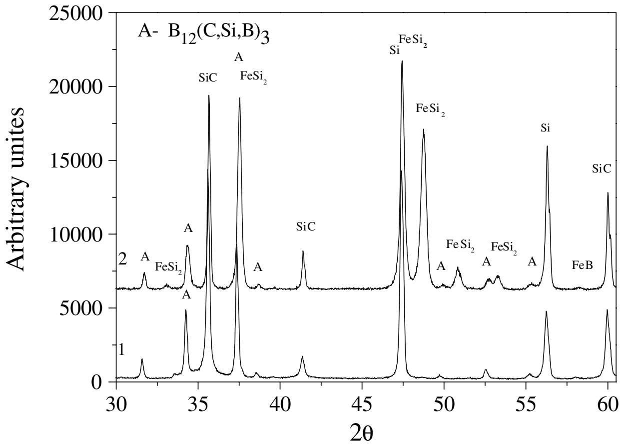


Fig. 9 XRD analysis of the Si infiltrated composites fabricated using B_4C powder (*1*) and B_4C–Fe mixture (*2*). *A* notes the peaks corresponded to the $B_{12}(C, Si, B)_3$ phase

Table 1 Phase composition of the infiltrated composites

Starting powder	Amount of the phases in the infiltrated composites			
	SiC	$FeSi_2$	Si	B_xC
B_4C	22 ± 3	–	28 ± 2	50 ± 5
B_4C + 5.5 vol% Fe	25 ± 5	9 ± 2	14 ± 1	52 ± 5

dissolution precipitation process that leads to the formation of the ternary $B_{12}(C, Si, B)_3$ carbide, according to the mechanism, described in previous study [10].

The microstructure of composites prepared from boron carbide without Fe additions (Fig. 8b) consists of $B_{12}(C, Si, B)_3$, residual silicon and plate-like SiC. The mechanism of the plate-like SiC particles formation has been also discussed in Hayun et al. [10].

Mechanical properties of the infiltrated composites

The hardness of the infiltrated composites (Fig. 10) increases with decreasing initial porosity and the increasing amount Fe addition. High hardness of the composites may be attributed to a lower fraction of residual silicon.

Young modulus of the infiltrated composites (Table 2) strongly depends on the porosity of the preforms, which in turn depends on the amount of Fe addition.

Three-point bending tests were conducted for the composites fabricated from the preforms (3.5 and 5.5 vol% Fe) with close to 30 vol% porosity. Flexural strength values of

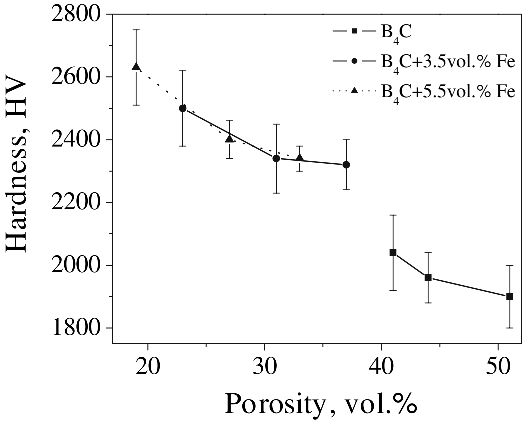


Fig. 10 Hardness of the infiltrated composites

Table 2 Young modulus of the infiltrated composites

Fe addition, wt%	Porosity, % vol	Young's moduli, GPa
0	50	315 ± 10
15	32	350 ± 20
0	42	320 ± 10
15	20	410 ± 10

350 ± 20 and 390 ± 20 MPa were obtained for the composites fabricated using B_4C–Fe mixtures with 3.5 and 5.5 vol% Fe, respectively. The enhanced mechanical properties of the composites may be attributed to the decreasing fraction of residual silicon.

Conclusions

The effect of Fe addition on the processing and mechanical properties of the reaction infiltrated boron carbide composites was investigated. Fe additions improve the sinterability of the boron carbide powder and the desired porosity for successful infiltration of the preforms is attained by sintering at about 2,050 °C. The experimental results regarding the sintering behavior and chemical interaction between B_4C and Fe are well accounted for by a thermodynamic analysis of the Fe–B–C system. The infiltrated composites fabricated from the B_4C–Fe mixture consist of $B_{12}(C, Si, B)_3$, SiC, $FeSi_2$ and residual silicon. A remarkable decrease of the fraction of the residual silicon allows improving the mechanical properties of the composites.

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