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Pressureless sintering and properties of αSiC–B_4C composite

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Abstract

Pressureless sintering process to obtain high density silicon carbide–boron carbide (5% vol) composite (BCSiC) was studied. Sintering behaviour of this material was investigated between 1950 and 2200°C and it was compared to SiC material doped with boron and carbon. Density up to 96% T.D. was reached at 2150°C. Microstructural investigation revealed that B_4C grains, having an average size of 2 μm, were well dispersed in the SiC matrix. Mechanical properties like fracture toughness, hardness, flexural strength were determined in the range RT-1500°C and compared to other SiC-based material. BCSiC material showed same fracture toughness of SSiC, higher hardness and higher flexural strength than SSiC also at high temperature; these properties make BCSiC a very interesting material for application in which high oxidation resistance is requested, e.g. ceramic heat exchanger.

Keywords: Composites; B_4C; Mechanical properties; Microstructure-final; SiC–B_4C; Sintering

1. Introduction

Silicon carbide is a very interesting ceramic material due to its properties like high hardness, low bulk density, high oxidation resistance which made SiC useful for a wide range of industrial application. Sintering of silicon carbide was first performed by Prochazka[1] by using boron and carbon as sintering-aids. These additives permitted to reach high density at temperature over 2000°C by means of reduction of the superficial energy of the grains (boron)[2] and reaction with residual silica (carbon)[2–4] presents on the SiC particle surface. Using β-SiC instead of α-SiC is more difficult to obtain high density because of at 1900–2000°C begins transformation β to α which causes porosity entrapping between grains due to the different morphology of β and α grains.[5] In this case, phase transformation could be controlled by using hot-pressing which allowed to reduce sintering temperature, grain growth and thus to enhance mechanical properties.[6]

Production of high performance components depends on the good control of microstructure; in fact is well known that mechanical properties of ceramic materials is strictly controlled by average grain size.[7] Several additives like Al–C, Al_2O_3–C and Al_2O_3–Y_2O_3[8–10] were tested as sintering-aid for silicon carbide powder to enhance sintering rate and control grain growth. These additives were used instead of boron together carbon or alone (alumina–yttria) and sintering mechanism was already explained for each of these aids; Al[8] and alumina[9] together carbon promoted silicon carbide sintering via solid-state mechanism (SSiC) at temperature over 2000°C, while alumina and yttria leaded to high density sintered sample via liquid-phase mechanism (LPSSC) below 2000°C.[10] We have already demonstrated[11] that alumina–yttria system was not useful for high temperature applications, e.g heat exchanger manufacturing, due to the oxidation of grain boundary phase (YAG) which caused a decreasing of mechanical properties (e.g. flexural strength). SSiC material is normally used for this type of application[12] because of it showed higher oxidation resistance.[13,14]

Our work, reported in this paper, was focused on determination of properties of silicon carbide-boron carbide (5% vol) composite obtained by means of pressureless-sintering process. More precisely, our objective was to investigate effects of boron carbide addition on SiC properties with the aim to define a SiC-based material with improved mechanical properties useful for application in the energy field.

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2. Experimental procedure

α-SiC powder (A20, H.C. Starck, Germany) was wet-mixed in ethanol with 5% vol B_4C (grade HS, H.C. Starck, Germany) and 1% wt carbon black (Corax N115, Degussa, Italy). In Table 1 are reported characteristics of SiC, boron carbide and carbon black powders. Mixing was performed by Turbula mixer using polyethylene bottle and SiC balls as grinding media. After drying and sieving, the powder was compacted by die pressing at 67 MPa and subsequently was pressed at 300 MPa by CIP.

Sintering was performed in a graphite elements furnace in flowing Ar at 1 atm. Sintering behaviour was investigated in the temperature range 1950–2200°C. Thermal cycle was characterised by heating and cooling rate of 22°C/min and by dwell time of 0.5 h at sintering temperature. Density was determined using Archimede's method. Microstructural investigation was performed by SEM (Leo 438VP — Leo) on polished surface. Homogeneity of boron carbide and graphite inclusions distribution were checked on polished surface by EDS microprobe (Oxford Link Isis 300). Microstructure was revealed by means of Murakami's etching and examined by optical microscope (Reichter-Jung).

Flexural strength was measured by four-point bend tests in the temperature range RT-1500°C. Samples as bars of 2×2.5×25 mm were prepared and tested in according to the standard EN 843-1 (crosshead speed 0.5 mm/min). Thirty samples were tested at RT and experimental results were fitted by means likelihood method to determine Weibull modulus. Hardness and fracture toughness were determined by means of Vickers indentation method (Durimet-Leitz) with a load of 98 N. Fracture toughness was calculated using equation proposed by Niihara[15] for median-crack:

$$K_{IC} = 0.203(c/a)^{-3/2}Ha^{1/2} \tag{1}$$

where c is the crack length, a the impression radius and H the hardness.

Superficial oxidation products were identified performing X-ray diffraction analysis (Rigaku–Miniflex CuK_{α} 1.54 Å) and EDS analysis on sample surface tested at 1500°C.

3. Results and discussion

3.1. Sintering and microstructure

Sintering behaviour of SiC–B_4C composite (BCSiC) was compared to that of the same SiC powder sintered

Table 1
Characteristics of starting powders

Powder	Purity (wt.%)	S.S.A. (m^2/g)	Particle size (μm)
α-SiC	> 97.5	20–23	0.6
B_4C	> 97.0	17–22	0.7–0.9
C		128	

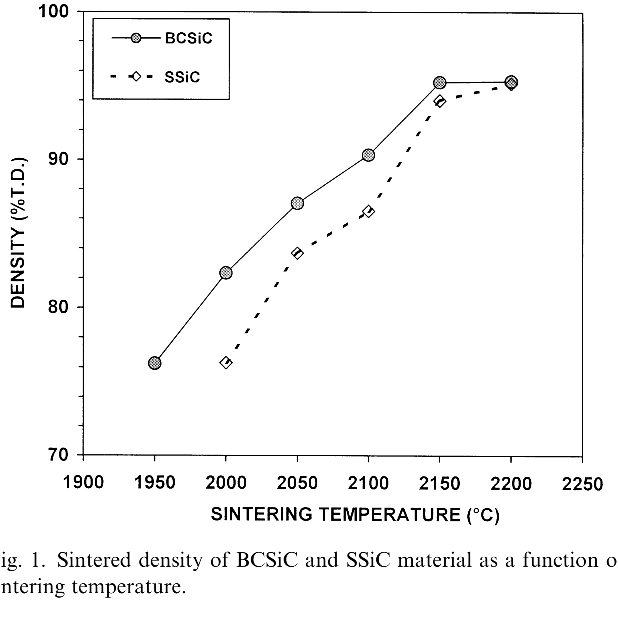

Fig. 1. Sintered density of BCSiC and SSiC material as a function of sintering temperature.

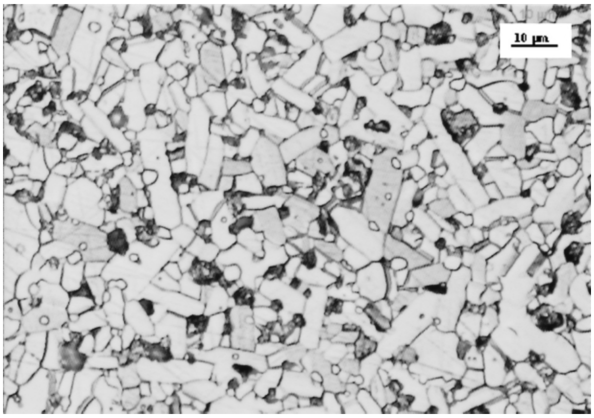

Fig. 2. Microstructure of BCSiC material (Murakami's etching).

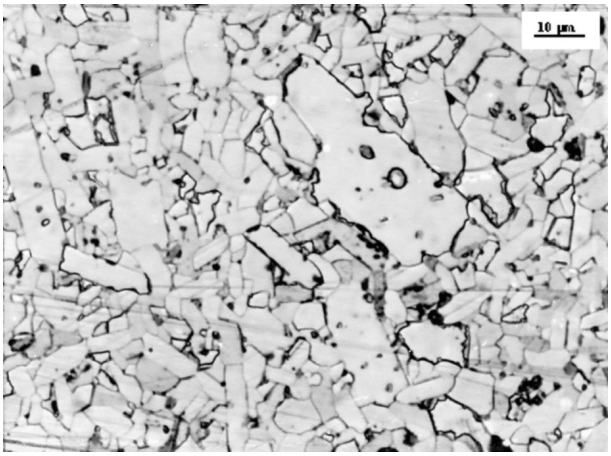

Fig. 3. Microstructure of SSiC material (Murakami's etching).

with boron (0.6% wt) and carbon (2% wt) (SSiC). Results are shown in Fig. 1. Density is reported as percentage of theoretical density assumed equal to 3.17 g/cm^3 for BCSiC (calculated by phase rule) and 3.2 g/cm^3 for SSiC. BCSiC showed higher density than SSiC at every temperature and the maximum value of density (96% T.D.) was reached at 2150°C. Therefore presence of boron carbide as secondary phase seems to improve sinterability of silicon carbide powder. Microstructural examination was performed on chemically etched surface (Murakami's etching: 60 g KOH, 60 g $K_3Fe(CN)_6$, 120 cc H_2O, $T=80°C$, $t=30$ min) using an optical microscope with the aim to determine average grain size. BCSiC microstructure reported in Fig. 2 was composed of SiC grains with average dimension of 8 μm with intergranular boron carbide particles of 2 μm. From the comparison of BCSiC microstructure reported in Fig. 2 with SSiC microstructure showed in Fig. 3, it was clear that BCSiC material showed a finer microstructure than SSiC. Furthermore, distributions of boron carbide particles and graphite inclusions inside the SiC matrix were checked by means of performing a superficial X-ray mapping of elements boron, carbon and silicon using EDS microprobe. B, C and Si X-ray maps of BCSiC sintered sample reported in Fig. 4a–d showed clearly that boron-rich phase particles (composed

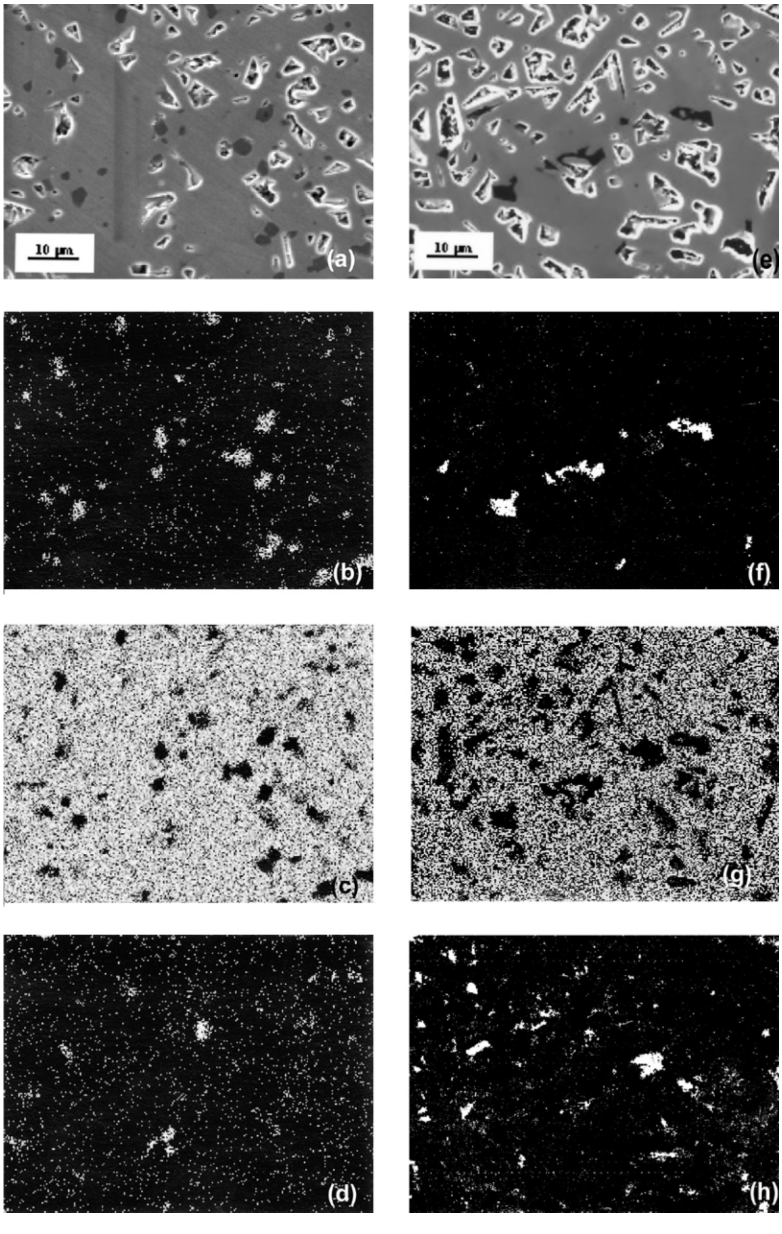

Fig. 4. SEM micrograph of (a) BCSiC polished surface and (e) SSiC polished surface together to EDS X-ray maps of (b) boron, (c) silicon and (d) carbon in BCSiC and of (f) boron, (g) silicon and (h) carbon in SSiC.

by boron carbide as resulted from EDS microprobe analysis, Fig. 5b) distribution was homogeneous and free graphite inclusions (distinguishable from C contained in SiC both by means of comparison C and Si X-ray maps and performing EDS analysis on C-rich phase particles, Fig. 5a) were very small compared to inclusions contained in the SSiC microstructure and revealed by means of EDS X-ray maps (Fig. 4e–h). As reported by Hamminger,[4] dimension and distribution of graphite inclusion were a very important parameters which should have controlled to ensure high density reaching. In BCSiC, with the addition of boron carbide, it was possible to cut in half the C quantity which must be used as sintering aid; in this way higher density than SSiC could be obtained.

3.2. Mechanical properties

Evaluation of mechanical properties of BCSiC sintered sample was made in comparison with two types of SSiC material: one commercial (Hexoloy SA-Carborundum), one manufactured by ourselves. Fracture toughness and hardness values, determined by means of Vickers indentation method with a load of 98 N, are reported in Table 2. BCSiC material showed same value of fracture toughness, while hardness was slightly increased with boron carbide as secondary phase. These properties makes BCSiC an interesting material for application where high wear resistance is requested.

BCSiC flexural strength was determined in the temperature range RT-1500°C. Thirty samples as bar were

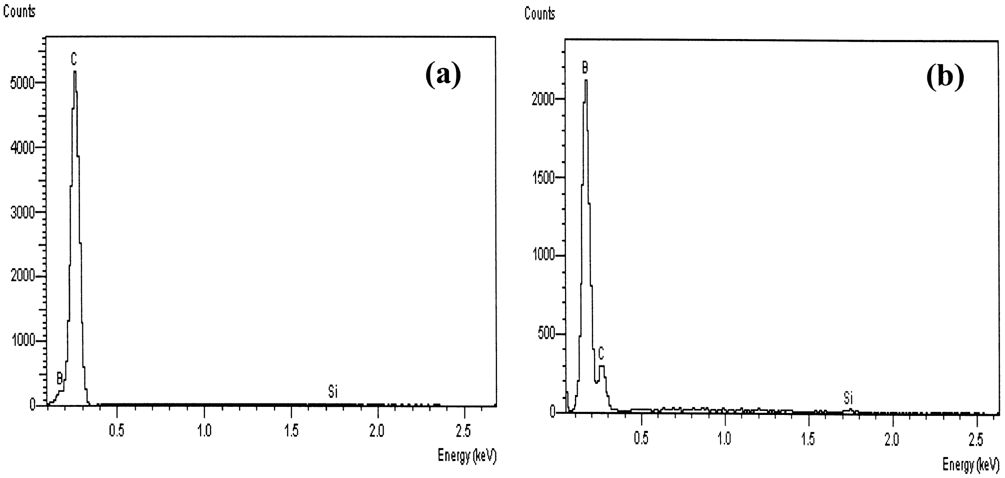

Fig. 5. EDS analysis of (a) carbon-rich inclusion and (b) boron-rich particle.

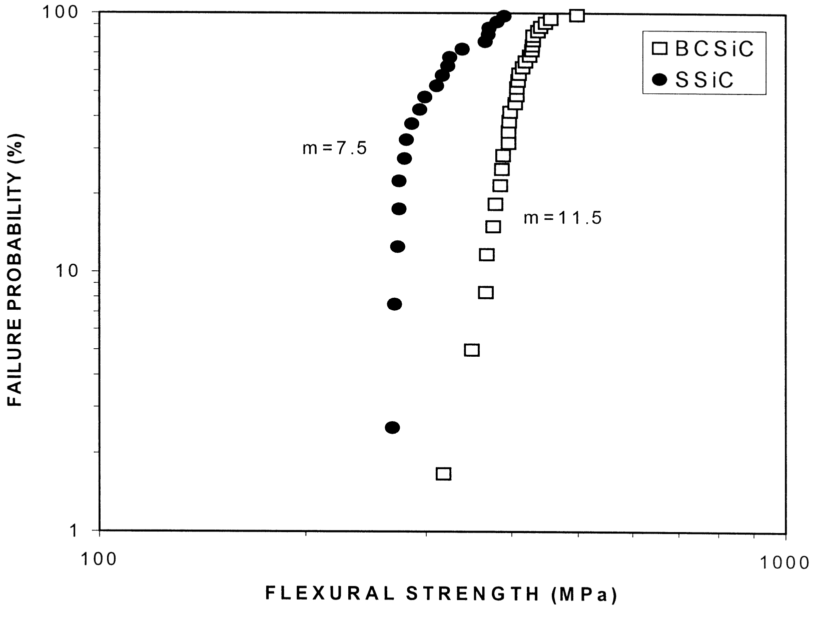

Fig. 6. Weibull diagram for BCSiC and SSiC materials.

Table 2
Fracture toughness and hardness of BCSiC composite and two different SSiC materials

Material	Fracture toughness (MPa m$^{0.5}$)	Hardness (GPa)
BCSiC	4.19±0.09	30.2±2.4
SSiC	4.25±0.10	27.5±1.3
HEXOLOY SA	4.31±0.03	28.6±1.3

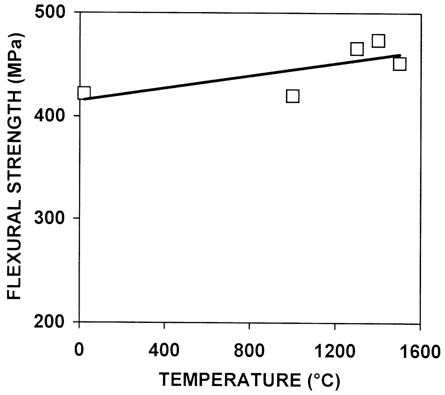

Fig. 7. BCSiC flexural strength variation with temperature.

tested at RT and experimental results were elaborated to determine Weibull modulus by means of maximum likelihood method as indicated in the standard EN 843-5. Results are reported in Fig. 6 together to the values obtained with SSiC material (20 samples). From this graph it was possible to determine σ_0 values (flexural strength at 50% of failure probability) for each material; they resulted 422 MPa for BCSiC material and 333 MPa for SSiC. This value makes SiC–B_4C composite a very interesting material from the structural application point of view if it is compared with different SSiC materials; for example SSiC commercial material (Hexoloy SA) tested in the same condition showed a σ_0 value of 378 MPa. For SiC-based material, it is possible to reach flexural strength value higher than BCSiC material using alumina–yttria system[10,11] as sintering aids or more expensive sintering process like hot pressing[16,17] which is not useful from industrial point of view. These methods permit to reduce sintering temperature and consequently grain growth. In BCSiC material, boron carbide seems to act as grain growth inhibitor and therefore flexural strength is increased in comparison to SSiC material. Furthermore, the strength-controlling flaws, such as porosity and graphite inclusions typical of SSiC material, were reduced in quantity and dimension in BCSiC composite contributing to the flexural strength increasing. In this way, reliability was also improved as indicated from Weibull modulus reported in Fig. 6.

For application where high temperature resistance is requested, e.g. ceramic heat exchanger, it was already demonstrated that SiC specimens sintered via liquid phase mechanism showed a flexural strength decreasing at high temperature (>1200°C) due to the reaction between secondary phase YAG with silica (formed from SiC oxidation).[11] Instead SSiC material showed a flexural strength increasing at high temperature due to formation of silica superficial layer which protects specimen against oxidation up to 1400–1500°C.[17] BCSiC composite exhibited same behaviour up to 1500°C as reported in Fig. 7. Analysing specimen tested at 1500°C by means of XRD and SEM, we were able to identify superficial oxidation products. XRD spectrum reported in Fig. 8 (together to as-sintered spectrum) showed clearly that only SiO_2 (α-cristobalite) was formed at this temperature. In these spectra boron carbide was not detected due to its different reference to intensity ratio (RIR) compared to silicon carbide. This

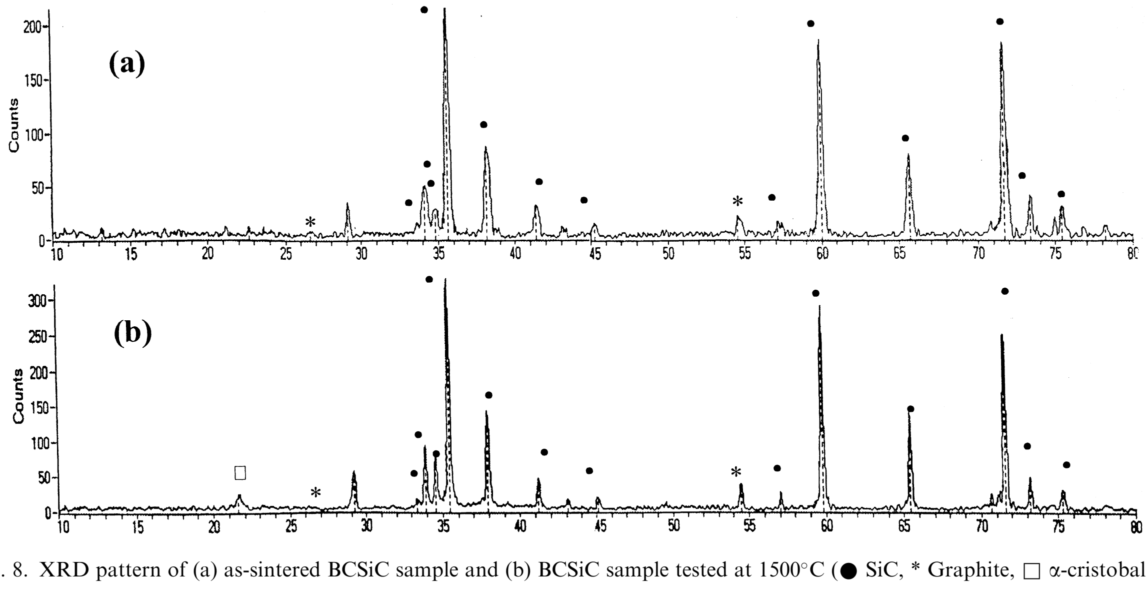

Fig. 8. XRD pattern of (a) as-sintered BCSiC sample and (b) BCSiC sample tested at 1500°C (● SiC, * Graphite, □ α-cristobalite).

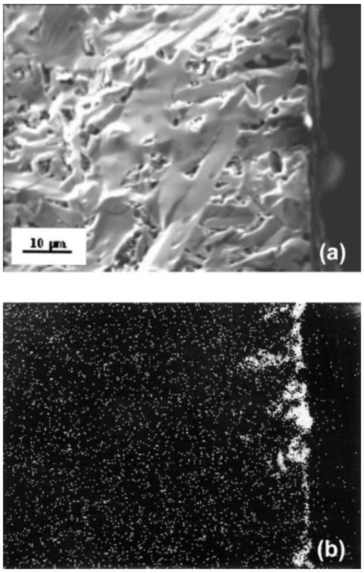

Fig. 9. (a) SEM micrograph of fracture surface of specimen tested at 1500°C and (b) EDS X-ray map of oxygen.

difference was evaluated by means of performing XRD analysis on boron carbide-rich mixture (up to 50% vol); in this manner it was possible to determine that the minimum quantity of boron carbide which it could be revealed by XRD analysis was 10% vol, more than boron carbide content in BCSiC.

Observing SEM micrograph and oxygen X-ray map reported in Figs. 9a and b it was clear that silica was mainly distributed on the surface forming a layer with thickness 1–2 µm. Silica was also detected inside the sample up to a depth of 10 µm due to superficial porosity which permitted oxygen diffusion into the sample. Nevertheless this fact did not cause formation of defects like voids or bubbles due to reaction of silicon carbide with oxygen[18] and thus flexural strength was not decreased. Finally boron carbide oxidation products were not identified; this confirmed that boron carbide oxidation resistance can be improved with addition of Si-based material.[19]

4. Conclusion

Pressureless sintering process of SiC-based material containing boron carbide as secondary phase (5% vol) was defined. Boron carbide addition permitted to increase sintering rate of SiC powder and to reach higher density than SSiC material at 2150°C. Furthermore BCSiC material showed a reduced grain growth respect to SSiC and consequently flexural strength was increased up to 1500°C. This fact together properties like fracture toughness and hardness makes BCSiC a material potentially promising for a wide range of application where wear and high temperature resistance are requested.

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