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Effects of B_4C addition on the microstructural and thermal properties of hot pressed SiC ceramic matrix composites

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Properties

ABSTRACT

Purpose: The purpose of paper is to evaluate effects of B_4C addition on the microstructural and thermal properties of hot pressed SiC ceramic matrix composites.

Design/methodology/approach: The effect of B_4C addition on microstructural and thermal properties of the SiC-B_4C powder composites were investigated after high energy milling and hot pressing. SiC powders containing 5wt%, 10wt%, 15wt% B_4C were mechanically alloyed in a high energy ball mill for 8 h.

Findings: Microstructural characterisation investigations (SEM, XRD) were carried out on mechanically alloyed SiC powder composites containing 5 wt %, 10 wt %, 15 wt % B_4C powders and on these powder composites sintered in vacuum at 50 MPa at 2100ºC. The thermal properties were characterised using DTA, TGA and dilatometer. The results were evaluated.

Research limitations/implications: In this study, the effect of B_4C addition on microstructural and mechanical properties of the SiC-B_4C powder composites was investigated after high energy milling and hot pressing.

Originality/value: Ceramic matrix composite (CMC) material systems are stimulating a lot of interest to be used and provide unique properties for aircraft and land-based turbine engines, defence applications, rocket motors, aerospace hot structures and industrial applications. Boron carbide (B_4C)-silicon carbide (SiC) ceramic composites are very promising armour materials because they are intrinsically very hard. Advanced SiC-based armour is desired so that the projectile is completely defeated without penetrating the ceramic armour.

Keywords: Ceramic matrix composites; Hot press; SiC; B_4C

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1. Introduction

Ceramic matrix composites (CMC's) were developed to overcome intrinsic brittleness and lack of reliability of monolithic ceramics, with a view to introduce ceramics in structural parts used in severe environments, such as rocket and jet engines, gas turbines for power plants, heat shields for space vehicles, fusion reactor first wall, aircraft brakes, heat treatment furnaces, etc [3,7]. It is generally admitted that the use of CMC's in advanced engines will allow for an increase of temperature at which engine can be operated and eventually the elimination of the cooling fluids, both resulting in an increase of yield [13] There is a wide spectrum of CMC's depending on the chemical composition of the matrix and reinforcement [16]. Non-oxide CMC's are by far those which have been the most studied [15].

Among the various non-oxide ceramics that found commercial applications, silicon carbide (SiC) is the leader. Attractive properties, such as good specific strength and Young's modulus as a function of temperature, the specific stiffness, corrosion and erosion resistance made SiC an attractive alternative to the hard metal compositions [6]. SiC has turned a special attention as advanced ceramic material recently since it offers superior properties such as high hardness, low bulk density, high oxidation resistance, thermal conductivity and thermal shock resistance [8]. Furthermore, it is an important ceramic used in structural applications, such as automotive engines, cutting tools, heat exchange and mechanical seals [2, 11]. Additionally, it is used in bulk form as refractory products, as electric heating elements and resistors, as igniters for gas appliances, as ceramic burners, as mechanical seal faces, as radiation sensors, as low-weight high-strength mirrors, as high power and high temperature semiconductor devices, as radiation resistant semiconductors and as light-weight armours [2,17].

Sintering of SiC was first performed by Prochazka [8] using boron (B) and carbon (C) as sintering aids. These additives permitted to reach high density at temperature over 2000°C by means of superficial energy of grains (B) and reaction with residual silica (C) presented on the SiC particle surface [4, 19]. It is difficult to achieve high densities. Normally, it is very difficult to achieve high densities at these temperatures as a result of transformation of β-SiC to α-SiC between 1900 and 2000°C which causes porosity entrapping between grains due to different morphology of β and α grains [5]. In order to control phase transformation, grain growth and enhancing mechanical properties, boron carbide (B_4C) is used with SiC in many applications [9, 11].

B_4C is one of the hardest materials known, ranking third behind diamond and cubic boron nitride (c-BN) [10, 12]. It is the hardest material produced in tonnage quantities. Due to its high hardness, B_4C powder is used as an abrasive in polishing and lapping [1, 18].

In this investigation, three different SiC-B_4C composite materials, viz. 100 vol% SiC and SiC containing 5 vol%, 10 vol% and 15 vol% B_4C, were developed using planetary ball milling and sintering at 2100°C.

2. Experimental procedure

The development of composite materials is based on formulations in the binary SiC-B_4C system with small amount of sintering aids. As a major raw material, black and green high purity SiC powders of different grades (SiC content larger than 98%) commercially produced by Herman Starck™ Inc. are used. B_4C powders used in this investigation are supplied by Boron Technologies Inc. - BMBT™ (Kayseri, Turkey) which has a B_4C content greater than 98 %wt. Four different powder batches having different nominal compositions were prepared as follows: A (100 wt% SiC), B (95 wt% SiC – 5 wt% B_4C), C (90 wt% SiC – 10 wt% B_4C) and D (85 wt % SiC – 15 wt% B_4C).

Powder particle size measurements were carried out in a Malvern™ Mastersizer operated between the size range of 0.02 - 3000 µm. Multiple recursive trials were made with each batch to account for the statistical size discrepancies of irregularly shaped particles and the last trial was accepted as the final data. To avoid possible agglomeration, powders were suspended in an ethylene alcohol solution which was stirred constantly during measurements. As seen in Figure 1, the SiC powders have a Gaussian particle size distribution and they have an average particle size of 0.107 µm and an estimated specific surface area of 59.6 m^2/g. As seen in Figure 2, average median particle size of the B_4C powders is 2.54 µm and their specific surface area is 9.06 m^2/g.

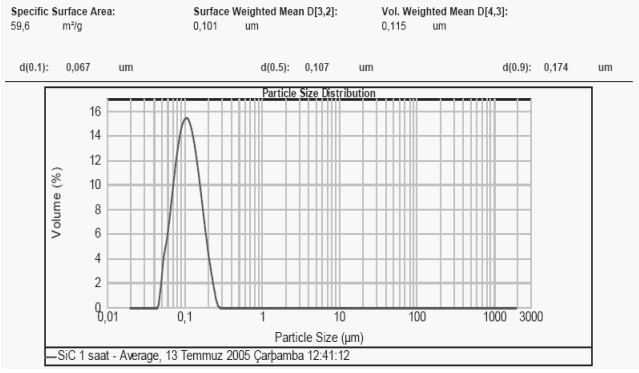

Fig. 1. Particle size distribution of SiC powder

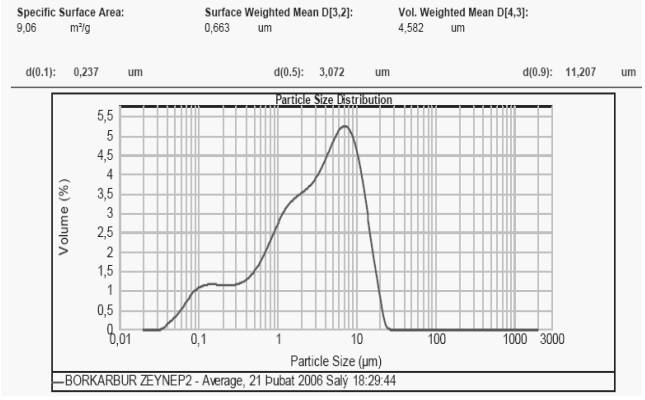

Fig. 2. Particle size distribution of B_4C powder

The powder batches A, B, C and D were milled in a Fritsch™ Pulverisette planetary ball mill for 8 hours. A ball-to-powder weight ratio of 10:1 and a 330 rpm speed were employed during milling. Scanning electron microscopy (SEM) investigations were carried out in a JEOL™ Model JSM 5410 SEM operated at 15 kV and linked with a Noran™ 2100 Freedom Energy dispersive spectrometer (EDS) attachment. X-ray diffraction investigations (XRD) were carried out in a Rigaku™ Model X-Ray Diffractometer.

Hot pressing of powder batches A, B, C and D were carried out in a Centorr Vacuum Industries™ Hot Press in a square die of 5 cm x 5 cm dimension under 50 MPa for 30 min. at 2100°C. The densities of the bulk sintered samples were measured by the Archimedes water immersion method while their Vickers microhardness was obtained under a 1000 g load for 15 seconds by using a Shimadzu™ microhardness tester. Three point bending tests were carried out in an Autograph™ Model instrument. Impact strength experiments were performed by means of a Mohr&Federhaff AG.™ Charpy Izod impact tester.

3. Results and discussion

Using a glass pycnometer, density of SiC powders were measured to vary between 2.90 to 3.01 g/cc and those for the B_4C powders were around 2.4 g/cc. As shown in Figures 3, 4 and 5, the average particle sizes of the as-milled B, C and D are 0.767 μm, 0.834 μm and 0.844 μm, respectively.

The densities of hot pressed SiC-B_4C composites were measured using water immersion method based on the Archimedes Principle. Using Archimedes' method, the densities of A, B, C and D composites were measured as 2.38 g/cc, 2.36 g/cc, 2.39 g/cc and 2.40 g/cc, respectively corresponding to relative density values of %77 for A, %77 for B, %79 for C and %80 for D, respectively. In case of sintered samples, it is clear that the density is increased with sintering temperature and B_4C amount because the diffusivity of atoms, which is the key factor for sintering, is enhanced with increasing temperature.

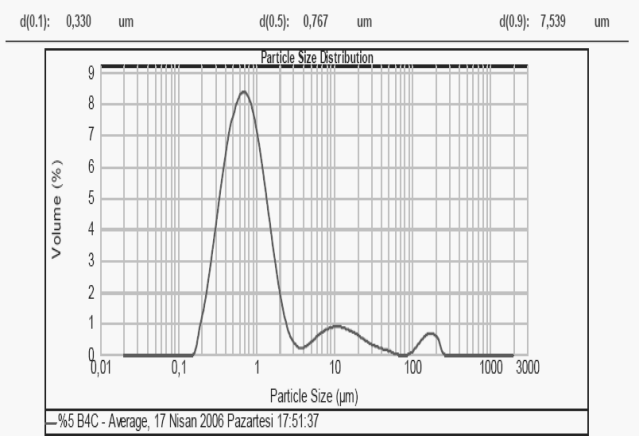

Fig. 3. Particle size distribution of the as-milled B composition

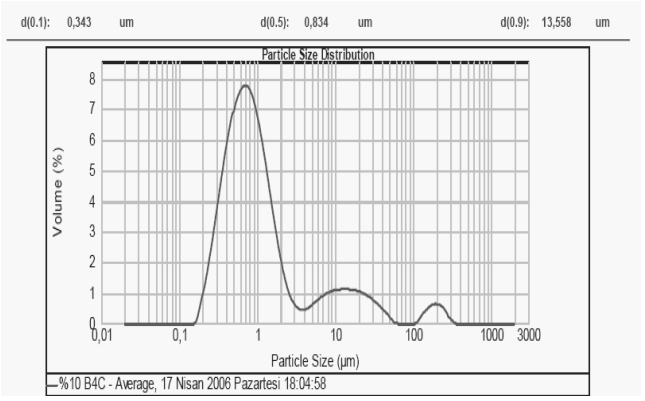

Fig. 4. Particle size distribution of the as-milled C composition

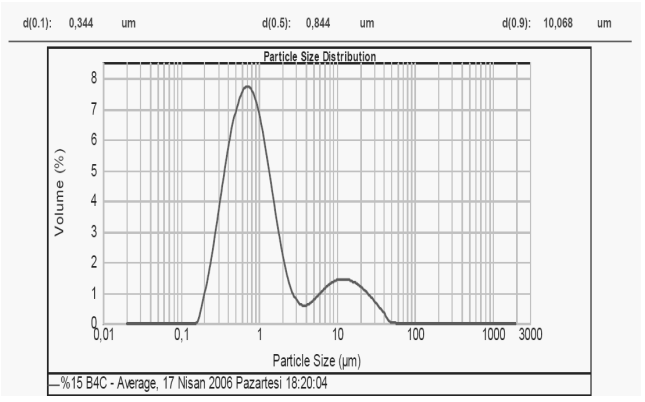

Fig. 5. Particle size distribution of the as-milled D composition

XRD diffraction patterns of sintered samples given in Figure 6 show that as a result of high energy milling, peaks are broadened and heights of peaks are decreased because of the decrease in the crystalline size and increase in the lattice strain. This is believed to be because of the recrystallization triggered by severe plastic deformation due to mechanical alloying. New grains might have pumped the excess Si and C in silicates and carbides out. In addition, the intensity of B_4C diffraction patterns increases as the amount of B_4C increases in the system.

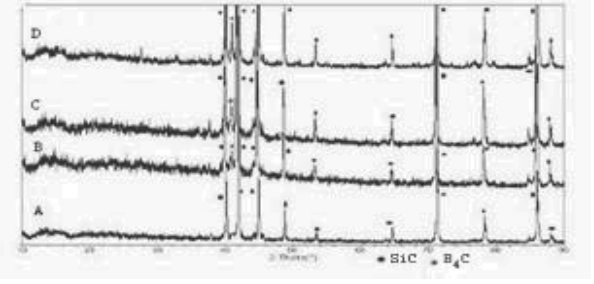

Fig. 6. XRD diffraction patterns of sintered samples

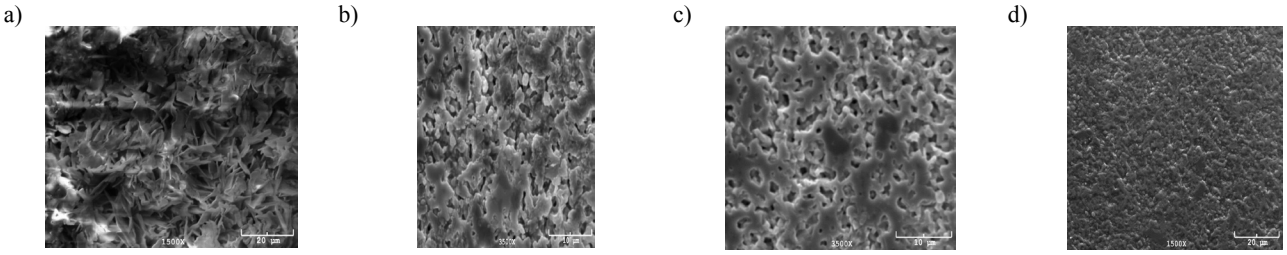

Fig. 7. SEM photographs of different compositions, a) A (100wt% SiC), b) B (95wt% SiC - 5wt% B_4C), c) C (90wt% SiC - 10wt% B_4C), d) D (85wt% SiC - 15wt% B_4C)

Figures 7a, 7b, 7c and 7d are a series of SEM micrographs taken from sintered A, B, C and D composites, respectively. As seen in Figure 7, all sintered composites have heterogeneous microstructure having large dark regions which are porosities. Based on the EDS analyses, SiC particles with sub-micrometer in particle size are mainly located at grain boundaries, while finer ones were within matrix grains, inferring that larger SiC particles suppress grain boundary movement of matrix. SEM pictures show that there is a good densification in the composites. As the particle size increase, sintering results become better and compact structures are occurred. A high level of the bonding between grains and a matrix is achieved due to a reaction bonding mechanism. This reaction bonding occurs due to mechanical alloying and sintering processes.

Bending strength was measured by the three point bending test (span 30 mm, crosshead speed: 0.5 mm/min). Dense composites demonstrated high mechanical strength (Figure 8).

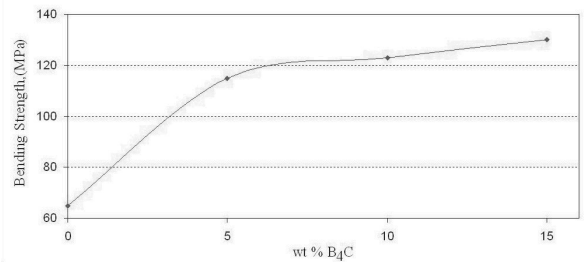

Fig. 8. Relationship between bending strength and % wt B_4C amount

Considering different compositions, bending strength is higher for composites having finer microstructure and less coarse SiC grains. As the B_4C amount in composites increase, bending strength results increase too (Table 1).

Table 1.
Bending strength results of the sintered samples with standard deviations

Sample name	Bending strength (MPa)	Standard deviation
A	64.8	±7.97
B	115.0	±14.13
C	123.0	±17.66
D	130.0	±39.61

Vickers hardness test, traditionally used for evaluation of dense ceramics was used for the sintered composites of the present investigation. Vickers hardness of dense carbide-based ceramics was tested in accordance with ASTM C1327 at indentation loads of 0.1-1000 g. 1000 g load was applied 15 seconds on the samples. As seen in Figure 9, compared with monolithic SiC, B_4C reinforced composites have higher hardness values because of higher hardness value of B_4C compared to SiC. In some samples, there are very high standard deviations and the reason is that the pores are non-uniform. Therefore, different hardness values obtained from a region with pores and from a region without any pores and cracks increase the value of standard deviation (Table 2).

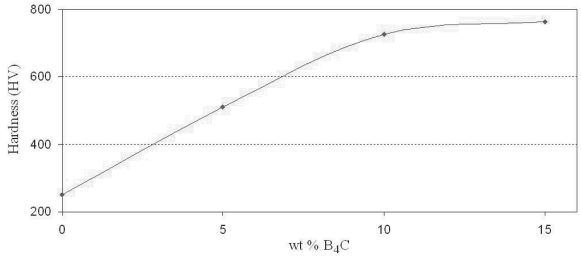

Fig. 9. Vickers hardness versus % wt B_4C content for different sintered compositions of the present investigation

Table 2.
Microhardness results of the sintered samples with standard deviations

Sample name	Hardness (HV)	Standard deviation
A	252	±12
B	511	±70
C	726	±154
D	764	±166

Impact testing was determined by measuring impact energy using a Charpy Impact Testing method with a swinging pendulum for rectangular bars. For this test, samples were prepared in 1 cm x 1cm x 5 cm dimensions. The specific energy (kJ/m^2) was calculated based on the measured impact energy and the sample cross-section dimensions. As seen in Figure 10, the impact strength is maximal for the sintered sample having 5 wt% B_4C (B) and it declines with increasing B_4C content. We believe that 5 wt% B_4C sets a threshold for the impact strength of the sintered

SiC-B_4C composites and above 5 wt% B_4C, the impact energy is being affected negatively because of brittle SiC- B_4C combination. There is not a linear relationship between impact strength and the amount of B_4C.

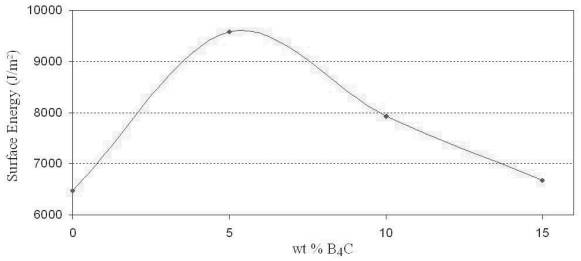

Fig. 10. Impact strength via % wt B_4C amount for different sintered compositions of the present investigation

The crack distribution in studied composites are rather complex. In general, the energy dissipation through mirocracking consists of a formation of numerous microcracks, characterised by the appearance of numerous stress-micro concentrators. It would appear the energy from ballistic impacts is spent on the formation of numerous surfaces. If the micro cracking occurs faster than general microcrack propagation, the energy dissipation is relatively more effective. Due to the presence of hard silicon carbide particles with different sizes and shapes, the direction in crack propagation is re-oriented that could be considered as a positive factor in impact energy dissipation and the ballistic performance. Also, the bridging of microcracks, which appears on the coarse SiC particles, may also promote the energy dissipation and decrease further crack propagation.

Due to the presence of brittle SiC and B_4C grains in these ceramic compositions, the compaction of the comminuted fragments and formed powder as a result of the projectile movement through this "coarse" ceramics appears to be less than for microcrystalline homogenous ceramics. This compaction effect may also promote the achievement of high ballistic performance.

4. Conclusions

In this study, the effect of B_4C addition on microstructural and mechanical properties of the SiC-B_4C powder composites was investigated after high energy milling and hot pressing. In case of sintered samples, it is clear that the density is increased with sintering temperature and B_4C amount because the diffusivity of atoms, which is the key factor for sintering, is enhanced with increasing temperature. XRD diffraction patterns of sintered samples show that with high energy alloying, peaks are broadened and heights of peaks are decreased because of the decrease in the crystalline size and increase in the lattice strain. As the B_4C amount in composites increase, bending strength and hardness values also increase. In some samples, there are very high standard deviations and the reason is that the pore distribution is not uniform, resulting in different hardness values obtained from a region with pores and from a region without any pores. Impact strength is maximal for the sintered composite containing 5 wt% B_4C.

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Additional information

The paper was published also in the Archives of Materials Science.

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