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Development and characterization of SiC fiber reinforced B_4C composite

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Abstract

This study is conducted to investigate the effects of silicon carbide short fiber (SiC_f) reinforcement on processing and properties of boron carbide ceramic. Studies have been carried out on the hot pressing, mechanical property measurement, microstructure evolution and oxidation study of SiC_f reinforced B_4C composite. B_4C-SiC_f composites have been prepared by hot pressing at 1950°C with varying SiC_f content in the range of 10 vol% to 30 vol%. All the composites are densified to near theoretical density. It is noticed that hardness of composite is decreased and fracture toughness of composite is increased by addition of SiC fiber. Hardness of the composites are found in the range of 32 GPa to 38 GPa. Fracture toughness of the composites are obtained to be higher than that of the monolithic boron carbide. The values are measured in the range of 4.3 $MPa{\cdot}m^{-½}$ to 5.1 $MPa{\cdot}m^{-½}$. In microstructure evolution it is found that SiC fibers are uniformly distributed throughout the matrix. The developed B_4C-SiC_f composites have been found to have good resistance to oxidation at 800°C in air.

1. Introduction

Boron carbide (B_4C) is an attractive material owing to its outstanding properties such as high hardness, low specific weight, high melting point, excellent chemical stability, good wear resistance and high neutron absorption cross section [1-4]. These fascinating properties make it superior candidate material in versatile engineering applications such as lightweight body armor, wear resistant tools, sand blasting nozzles, grinding and lapping agent, neutron shield, high temperature thermocouple etc. [2-4]

However, the applications of B_4C are limited due to its poor fracture toughness and difficulties involved in obtaining dense shapes. Various reinforcements (CrB_2, HfB_2, WC, TiC, Al_2O_3, SiC) have been used to enhance its fracture toughness and strength [5-9]. He *et al.* [10] have used Titanium diboride (TiB_2) and SiC particles as additive to B_4C and observed that fracture toughness increases upto 8.21 $MPa{\cdot}m^{-½}$. Qu *et al.* [11] have reported that silicon carbide (SiC) addition resulted in improvement in high temperature flexural strength of B_4C composite. Solodkyi *et al.* [12] have prepared B_4C-SiC composite by Si infiltration into carbon fiber reinforced B_4C composite. It was reported that Si reacted with carbon fiber and formed composite core shell fiber with SiC shell and carbon core. The composite was found to have better strength than the monolithic B_4C. Moshtaghioun *et al.* [13] have used SiC, as reinforcement to B_4C and reported that it increases the fracture toughness of B_4C considerably.

Although there are some studies on the use of SiC as reinforcement for B_4C, there is limited study reported on the use of SiC in the fiber form [10-12]. In this study SiC fibers (SiC_f) are used as reinforcement to form B_4C-SiC_f composite. This paper presents the results of studies on processing, microstructure, mechanical properties and oxidation behavior of B_4C-SiC_f composite. SiC_f addition is expected to improve mechanical properties and oxidation resistance. The important properties of B_4C and SiC are summarized in the Table 1.

Table 1. Salient properties of B_4C and SiC_f [1].

Property	**B_4C**	**SiC_f (β phase)**
Crystal structure	Rhombohedral	Cubic
Density ($g{\cdot}cm^{-3}$)	2.52	3.14
Melting point (°C)	2450°C	2830°C
Thermal expansion coefficient ($^{o}C^{-1}$)	5×10^{-6}	4.5×10^{-6}
Thermal conductivity ($W{\cdot}m^{-1}K^{-1}$)	13-30	82-90
Hardness (GPa)	29	25
Elastic modulus (GPa)	448	406
Fracture toughness ($MPa{\cdot}m^{-½}$)	3.6	4.6

2. Experimental

2.1 Starting material characterization

The starting materials used in this study are B_4C powder (In-house synthesized, Median diameter: 2.1 µm, Oxygen: 0.2 wt%) and SiC short fibers (supplied by Global nanotech, Mumbai, India). Boron carbide powder was produced by reacting elemental boron and carbon at high temperature. More preparation details and characteristics of boron carbide powder is presented elsewhere [14]. X-ray diffraction (XRD) pattern of B_4C powder and SiC_f is shown in Figure 1. It corroborates that the SiC fibers are beta silicon carbide. Scanning electron microscope (SEM) microstructures of B_4C powder and SiC fibers are presented in Figure 2. It manifests that B_4C particles are equiaxed in shapes and their size is around 3 µm to 20 µm. SiC_f have been found to have length in the range of 20 µm to 80 µm and diameter around 7 µm.

2.2 Hot pressing

B_4C powder and SiC fibers were blended to get homogeneous mixture using a planetary ball mill for 5 h in alcohol medium. During mixing, tungsten carbide balls were employed as grinding media to facilitate grinding of the starting powder. The mixed powder was dried in a vacuum oven at 150°C to remove the alcohol. The dried powder is hot pressed at a temperature of 1950°C and a pressure of 35 MPa for 2 h using high density graphite die (18 mm cavity). The density of hot pressed sample was measured by Archimedes' principle.

2.3 Phase analysis and microstructural characterization

The hot-pressed samples were polished using diamond powder in an auto polisher (laboforce-3, Struers). X-ray diffractometer (Rigaku Miniflex II, Cu Kα, λ=1.5405 Å) was used for phase analysis of the densified sample. The microstructures analysis of composite samples was carried out by using scanning electron microscopy (Camscan MV2300CT/100) and energy dispersive spectroscopy (Oxford Instruments, X-max 80).

2.4 Mechanical property measurement

Microhardness tester was used to measure hardness of the B_4C-SiC_f sample at a load of 100 gf and dwell time of 10 s. Total 6 measurements was carried out and the average value obtained is reported. Fracture toughness of the composite samples were acquired by indentation method by the measurement of crack length of the crack pattern developed around Vicker's indent using the equation proposed by Anstis *et al*. [15]

$$K_{IC} = 0.016(E/H)^{1/2}P/c^{3/2} \tag{1}$$

Where, E is the Young's modulus, H the Vickers's hardness, P the applied indentation load, and c the half crack length. Total 6 measurements were carried out and the average value obtained is reported.

2.5 Oxidation study

For oxidation study, the samples were exposed to a temperature of 800°C, in air atmosphere for different time interval (2 h, 4 h, 8 h, 16 h, 32 h, and 64 h). After oxidation, the change in weight in the samples have been recorded. The surface of the sample after oxidation test was analysed by XRD and SEM.

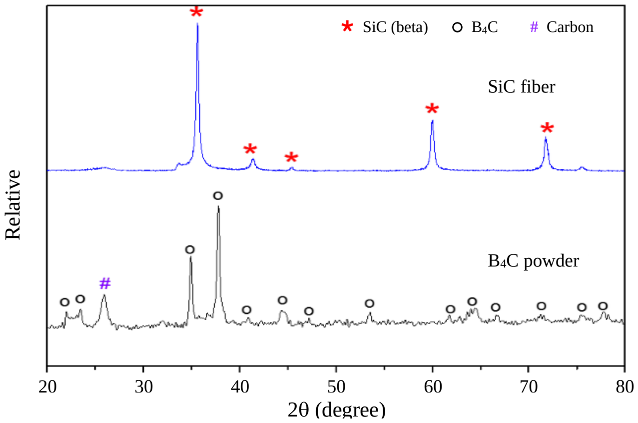

Figure 1. XRD pattern of starting Material.

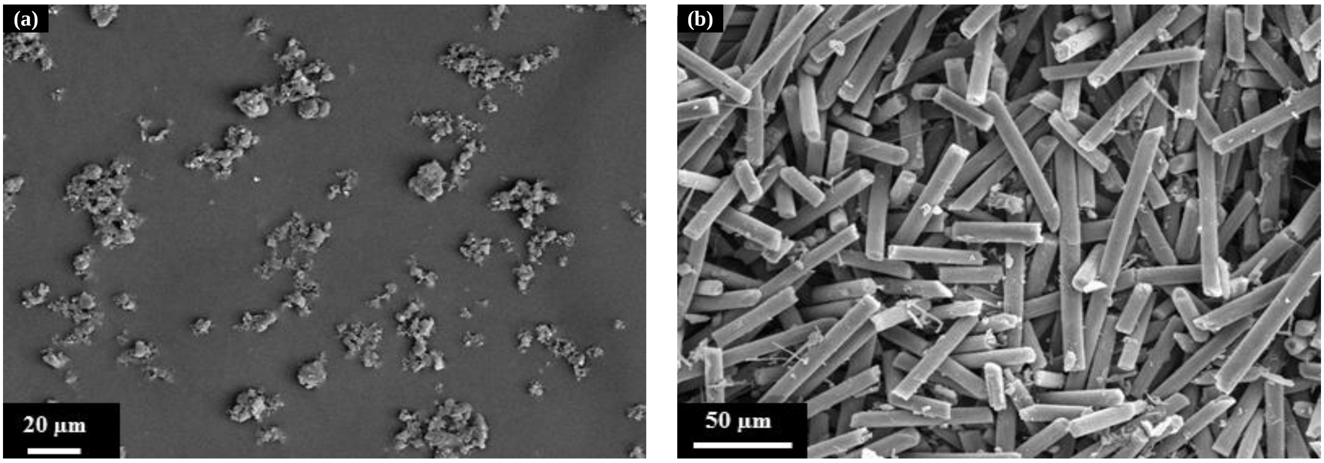

Figure 2. SEM images of starting material (a) B_4C and (b) SiC_f.

3. Results and discussions

3.1 Densification

Results of hot pressing experiments on the B_4C-SiC_f composites are presented in Table.2. B_4C-10% SiC composite was densified to a density of 98.5% of theoretical density at a temperature of 1950℃ under a pressure of 35 MPa. On increasing SiC_f content, the achieved density decreased slightly to ~96% of theoretical density under the identical processing parameters. It is hard to sinter both B_4C and SiC because of their covalent bonding and associated low self-diffusion. Generally, high temperature and external pressure is required for getting dense shapes of these materials.

Some researchers have tried to prepare B_4C-SiC composite using powder-pellet route. Sahin *et al.* [16] have studied the spark plasma sintering of B_4C-SiC composite and found that close to 98% of theoretical density is obtained at 1750℃. Moshtaghioun *et al.* [13] have densified B_4C-15% SiC to 99.4% density by spark plasma sintering at 1700℃. Zhang *et al* [17] have densified B_4C-50% SiC composite to 96% density by hot pressing at 1950℃ after mechanical alloying.

3.2 Microstructure evolution

Figure 3(a) presents microstructure of B_4C-SiC_f composite. It exhibits the presence of two phases. Figure 3(b) and 3(c) depicts the EDS spectra of both phases. The bright phase is indeed SiC fibers as it is analyzed to have silicon and carbon. The dark matrix phase is indeed B_4C as its EDS analysis confirmed the presence of boron and carbon. The microstructure displayed that SiC fibers are distributed uniformly in the B_4C matrix. In the composite, SiC fibers were found to have length around ~70 μm and dimeter around ~7 μm. It showed that the fibers preserved their initial dimensions. There is no damage of fibers during hot pressing operation. It also revealed that there is no fiber agglomeration. Figure 4(a)-(d) presents the elemental mapping of B, C and Si in the composite. Figure 4(a) presents the BSE image of composite. Figure 4(b)-(d) presents the distribution of silicon, boron and carbon in respectively. It was found that silicon is present only in the bright phase which is fiber. Boron was found only in matrix phase and carbon is found in both matrix and fiber.

Figure 5 presents the microstructures of fracture surfaces of B_4C-SiC_f composites. All the composites exhibited dense microstructures. There is no signature of fiber pullout. It is observed that the mode of fracture is transgranular, which confirms that there are no weak phases on the grain boundaries and the grains are bonded very strongly.

3.3 Mechanical properties

Table 2 summarizes the vickers hardness and fracture toughness values measured for B_4C-SiC_f composites. Hardness of B_4C with 10% SiC_f samples was measured to be 38.4 GPa. Increase in SiC_f content to 20% was found to slightly decrease the hardness to 37.0 GPa.. Further increase of SiC_f to 30 vol% was found to decrease the hardness of the composite to 32.2 GPa. The hardness is decreased due to lower hardness of beta silicon carbide (25 GPa) [1] as compared to boron carbide phase. Moshtaghioun *et al.* [13] have reported the hardness of monolithic B_4C as 39.4 GPa. In the same study hardness of B_4C-15% SiC has been reported as 36.2 GPa. Sahin *et al.* [16] have reported the hardness of spark plasma sintered B_4C-10% SiC composite as 33.4 GPa. Du *et al.* [18] have reported the hardness of B_4C-22% SiC as 33.5 GPa. Zhang *et al.* [17] have reported the hardness of B_4C-50% SiC composite as 24 GPa.

Indentation fracture toughness of B_4C-10% SiC_f sample was measured to be 4.3 MPa·m$^{-\frac{1}{2}}$. With increase in SiC_f content to 20%, fracture toughness was enhanced by ~7% to 4.6 MPa·m$^{-\frac{1}{2}.}$ Further increase in SiC_f content to 30% has further enhanced fracture toughness by ~11% to 5.1 MPa·m$^{-\frac{1}{2}}$. In case of composite samples, higher fracture toughness values were obtained as compared to the values reported for monolithic B_4C in literature. Monolithic B_4C has been reported to have a fracture toughness value of 3.5 MPa·m$^{-\frac{1}{2}}$ [13]. Fracture toughness of B_4C-30% SiC composite obtained in the present study is 45.7% higher than the fracture toughness of monolithic B_4C reported in literature.

Moradkhami *et al.* [19] have reported the fracture toughness of B_4C-SiC composite in the range of 5 MPa·m$^{-\frac{1}{2}}$ to 6 MPa·m$^{-\frac{1}{2}}$. Moshtaghioun *et al.* [13] have reported the fracture toughness of B_4C-15% SiC as 5.7 MPa·m$^{-\frac{1}{2}}$. Du *et al.* [18] have measured the fracture toughness of B_4C-22% SiC to be 5.57 MPa·m$^{-\frac{1}{2}}$. Zhang *et al.* [17] have reported the fracture toughness of B_4C-50% SiC composite as 4.6 MPa·m$^{-\frac{1}{2}}$. Addition of SiC in fiber form is found comparable to these results.

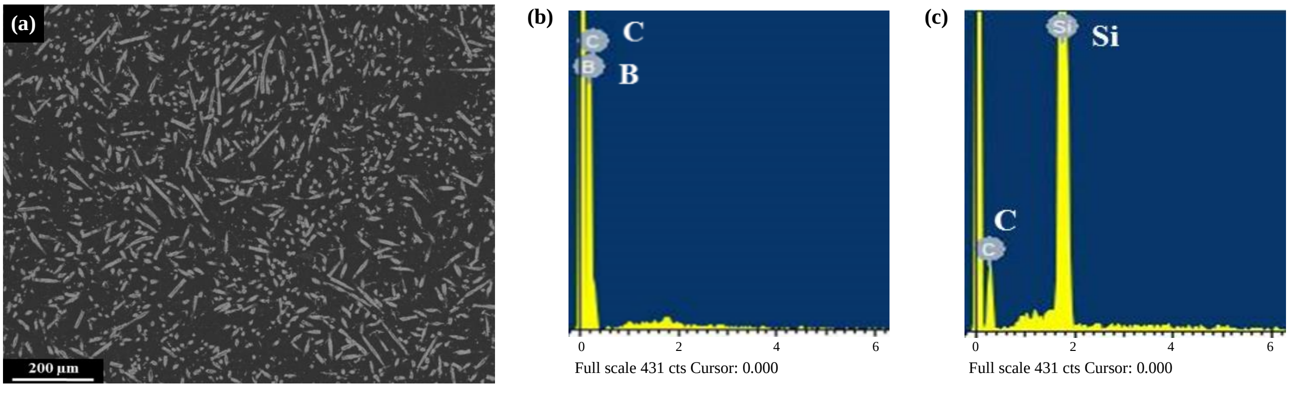

Figure 3. SEM-EDS analysis of B_4C+30% SiC (a) BSE image (b) EDS pattern of matrix phase (dark phase) (c) EDS spectra of fiber phase (brighter phase).

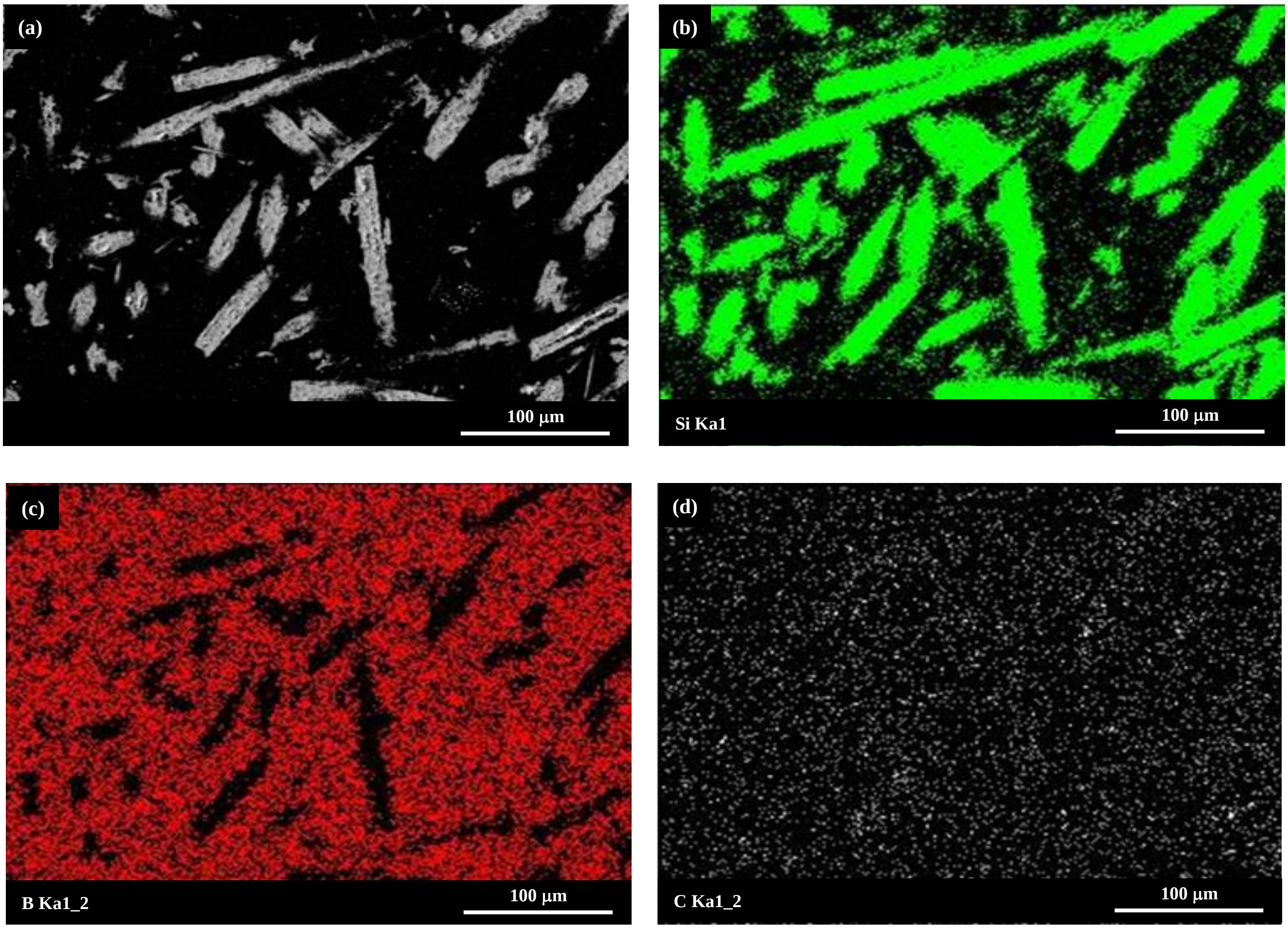

Figure 4. Elemental mapping of B_4C-20% SiC_f (a) back scattered electron image (b) distribution of silicon in the composite (c) distribution of boron (d) distribution of carbon.

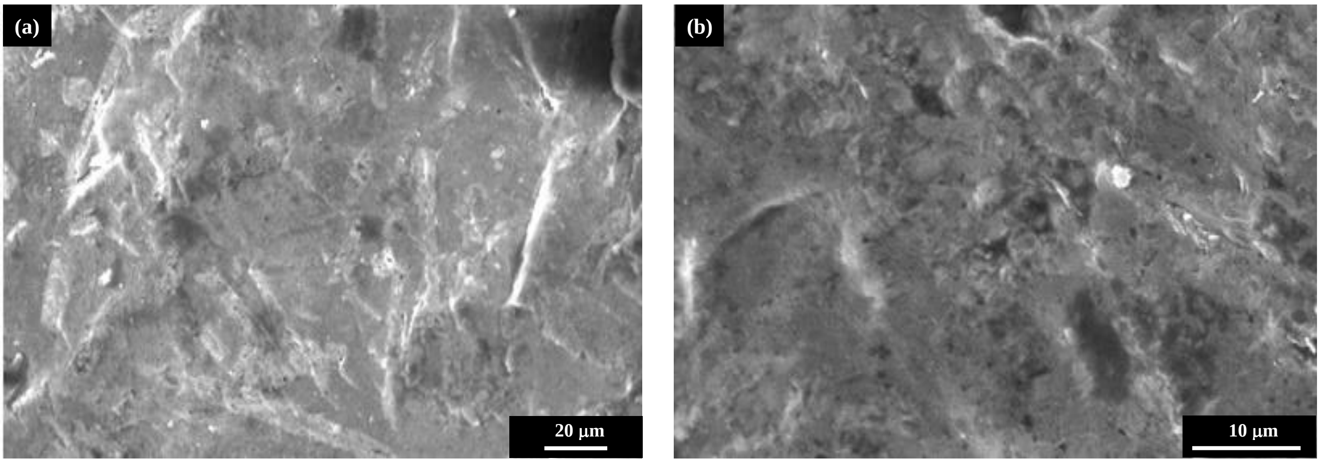

Figure 5. Fracture surface of B_4C-SiC_f composite (a) B_4C-20% SiC (b) B_4C-30% SiC.

Table 2. Density and mechanical properties of hot pressed B_4C-SiC_f composites.

Sample	Bulk density ($g \cdot cm^{-3}$)	Theoretical density ($g \cdot cm^{-3}$)	Relative density (%)	Hardness (GPa)	Fracture toughness ($MPa \cdot m^{-½}$)
B_4C + 10% SiC_f	2.55	2.59	98.5%	38.4±1	4.3±0.1
B_4C + 20% SiC_f	2.55	2.66	95.8%	37.0±1	4.6±0.1
B_4C + 30% SiC_f	2.64	2.73	96.6%	32.2±1	5.1±0.1

*Hot pressing temperature: 1950°C, Pressure: 35 MPa

3.4 Oxidation study

Isothermal oxidation studies of B_4C-SiC_f samples were carried out at 800°C to assess the possibility of using the developed composite in oxidizing atmosphere at 800°C. The specific weight gain with time during oxidation test is plotted in Figure 6. Continuous weight gain with time was recorded in all the three samples. However, the rate of oxidation was found to decrease with time. This decrease in oxidation rate indicates the formation of protective layer.

Figure 7 exhibits SEM microstructures of the oxidized surface of B_4C-SiC_f composite. It depicts that a protective layer is present on the oxidized surface. EDS analysis of oxide layer is presented in Figure 8. It illustrates that boron, silicon and oxygen are present throughout the oxide layer. Figure 9 displays the XRD pattern of B_4C-30% SiC_f after oxidation at 800°C. It revealed that B_4C and SiC is present along with B_2O_3 on the surface of sample after oxidation. This indicated that oxide layer formed on the surface is very thin and very less oxidation has taken place. Following chemical reactions are probable during the oxidation test. These reactions have resulted in increase in weight due to formation of B_2O_3 and SiO_2.

$$B_4C + 7/2O_2 \rightarrow 2B_2O_3 + CO \quad (1)$$

$$SiC + 3/2O_2 \rightarrow SiO_2 + CO \quad (2)$$

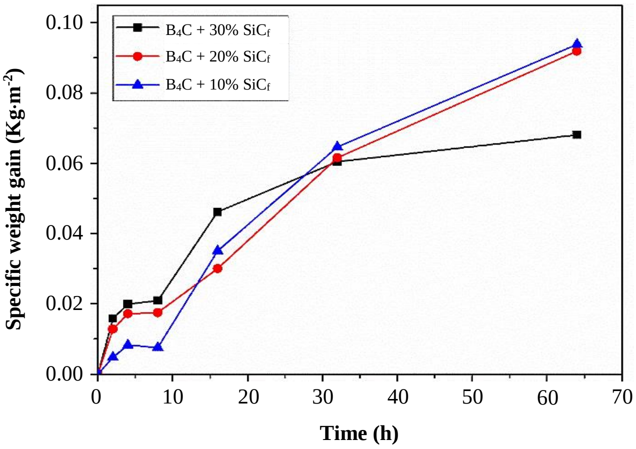

Figure 6. Specific weight gain with time during oxidation of B_4C-SiC_f composite at 900°C.

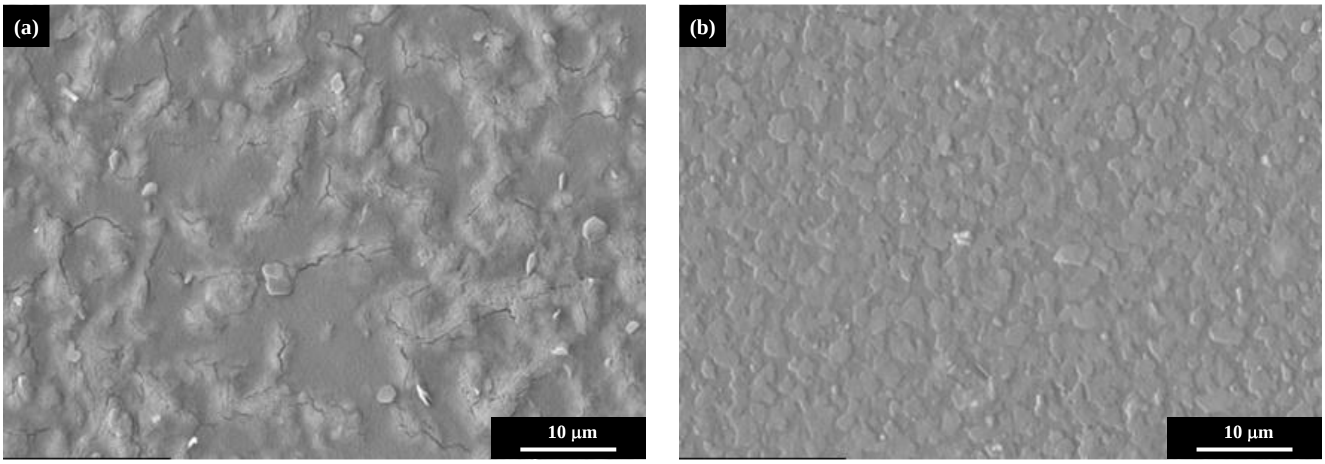

Figure 7. SEM Microstructure of B_4C- SiC_f composites after oxidation at 800°C for 64 h (a) B_4C-20% SiC_f (b) B_4C-30% SiC_f.

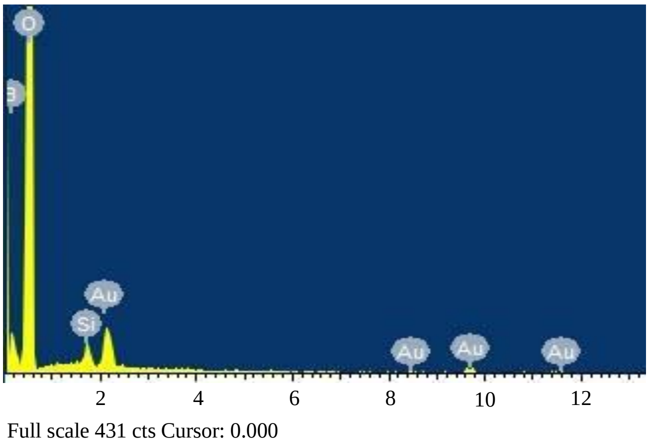

Figure 8. Typical EDS pattern of Oxide layer present on B_4C-SiC_f composite after oxidation at 800°C for 64 h.

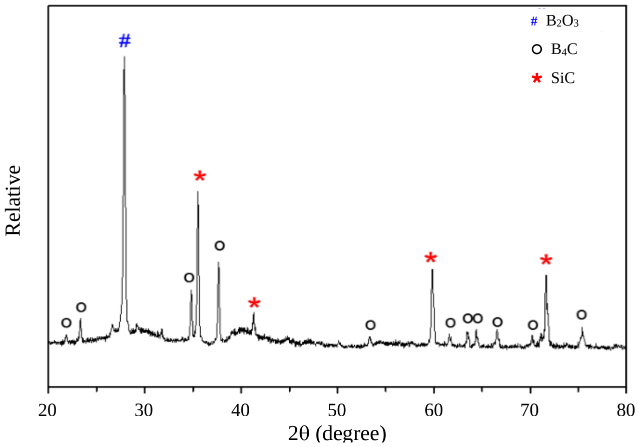

Figure 9. XRD Pattern of B_4C-30% SiC_f composite oxidized at 900°C for 64 h.

Litz *et al.* [20] have carried out study on oxidation of monolithic boron carbide and found that oxidation of B_4C starts at 450°C in dry air. Lavrenko *et al.* [21] studied oxidation behavior of B_4C in oxygen and reported that compacted B_4C started oxidizing at 600°C but remained sufficiently resistant to oxidation up to a temperature of about 1200°C. The oxidation of B_4C was parabolic initially but (upto 1 h) later it became linear. Narushima *et al.* [22] have reported the formation of liquid borosilicate on oxidation of B_4C-SiC composite at 1000°C. The increase in SiC content to B_4C was found to increase the oxidation resistance due to increase in silica content in the borosilicate glass. Hu *et al.* [23] have done oxidation study of B_4C-(ZrB_2-SiC) composite and reported that it has good oxidation resistance at 1600°C due to formation of ZrO_2 and SiO_2 layer. In this study B_4C-SiC composite was found to have good oxidation resistance at 800°C in air.

4. Conclusions

B_4C-SiC_f composite with varying SiC_f content (10 vol% to 30 vol%) was developed by powder pellet route. All the three composite samples were densified to near theoretical density by hot pressing technique at 1950°C and 35 MPa. B_4C-SiC_f composite was characterized to have high hardness in the range of 32 GPa to 38 GPa. However, increase in SiC_f content in the composite was found to decrease the hardness slightly. SiC_f addition to B_4C was resulted in the formation of a composite with higher fracture toughness as compared to monolithic B_4C. Fracture toughness of B_4C-SiC_f composite was found in the range of 4.3 $MPa\cdot m^{-½}$ to 5.1 $MPa\cdot m^{-½}$, which is much higher than that of monolithic B_4C. Oxidation study of the developed composite at 800°C in air atmosphere revealed that it has good oxidation resistance up to 800°C. The protective layer was formed which was analyzed to be composed of mainly B_2O_3.

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