Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 35 (2009) 967–973
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Synthesis and characterization of Si/SiC ceramics prepared using cotton fabric

G. Amirthan [a], A. Udayakumar [b], V.V. Bhanu Prasad [c], M. Balasubramanian [a,*]

[a] Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai 600 036, India
[b] National Aerospace Laboratories, Bangalore 560 017, India
[c] Defense Metallurgical Research Laboratory, Kanchanbagh PO, Hyderabad 500 058, India

Received 17 January 2008; received in revised form 2 February 2008; accepted 2 April 2008
Available online 10 July 2008

Abstract

A Si/SiC ceramic was prepared from cotton fabric by the reactive infiltration of liquid silicon into the carbon template. A large density difference between the samples has been observed. This may be due to the variation in the pore size and its distribution within the sample. Scanning electron microscopy with energy dispersive spectroscopy shows the presence of three distinct phases, i.e., SiC, free Si and free carbon. X-ray diffraction pattern also confirms the presence of SiC and Si phases. However, there is no peak corresponding to carbon. So, it is inferred that the carbon exists in amorphous form. Micro-hardness, fracture toughness and bending strength of the ceramics were also studied. The values are lower than commercially available SiC ceramics. This may be due to the highly porous nature of cotton fabric-based SiC, as compared to commercially available SiC.

Keywords: B. Porosity; C. Fracture; C. Mechanical properties; D. SiC; E. Thermal application

1. Introduction

Silicon carbide ceramics possess outstanding mechanical, thermal and electrical properties. Hence these are widely used in structural, nuclear and semiconductor applications. SiC has been fabricated by various methods since the invention of Acheson process. Most generic processes used for the fabrication of SiC in recent days are hot pressing/hot isostatic pressing, reaction bonding/reaction forming, polymer pyrolysis and chemical vapor deposition [1–5]. All the above methods have their own advantages and limitations. In the last two decades, a new approach has been developed that has received particular interest in scientific field, in which the ceramic is made from a biological structure, such as wood. The SiC ceramic developed from this route is called biomorphic silicon carbide. In recent years, properties of this ceramic have been studied extensively. The main advantages associated with this process are low cost, renewable raw material (i.e., wood), easy fabrication of complex shapes and retention of the complex hierarchical cellular structure in the final product [6–11]. The combination of the hardness of SiC with the low density and high flexibility of the biological structure makes biomorphic ceramics a unique material [12].

In the same way, silicon carbide ceramics can be produced from cotton fabric, since it is also a carbonaceous material. In this study, SiC has been produced using cotton fabric and the resulting product has been characterized for its physical and mechanical properties.

2. Experimental procedure

2.1. Fabrication

Phenolic resin (PR) powder was purchased from Chemisol Polymer India limited. Commercially available cotton fabric was used. In the initial step, 20% phenolic resin solution was made by dissolving in isopropyl alcohol. Cotton fabric was cut into the dimensions of 200 mm × 200 mm and treated with diluted sodium hydroxide solution to remove the starch coating on the cloth. Cotton fabric laminate was made by hand lay-up

* Corresponding author. Tel.: +91 44 2257 4767; fax: +91 44 2257 0039.
E-mail address: mbala@iitm.ac.in (M. Balasubramanian).

0272-8842/$34.00
doi:10.1016/j.ceramint.2008.04.014

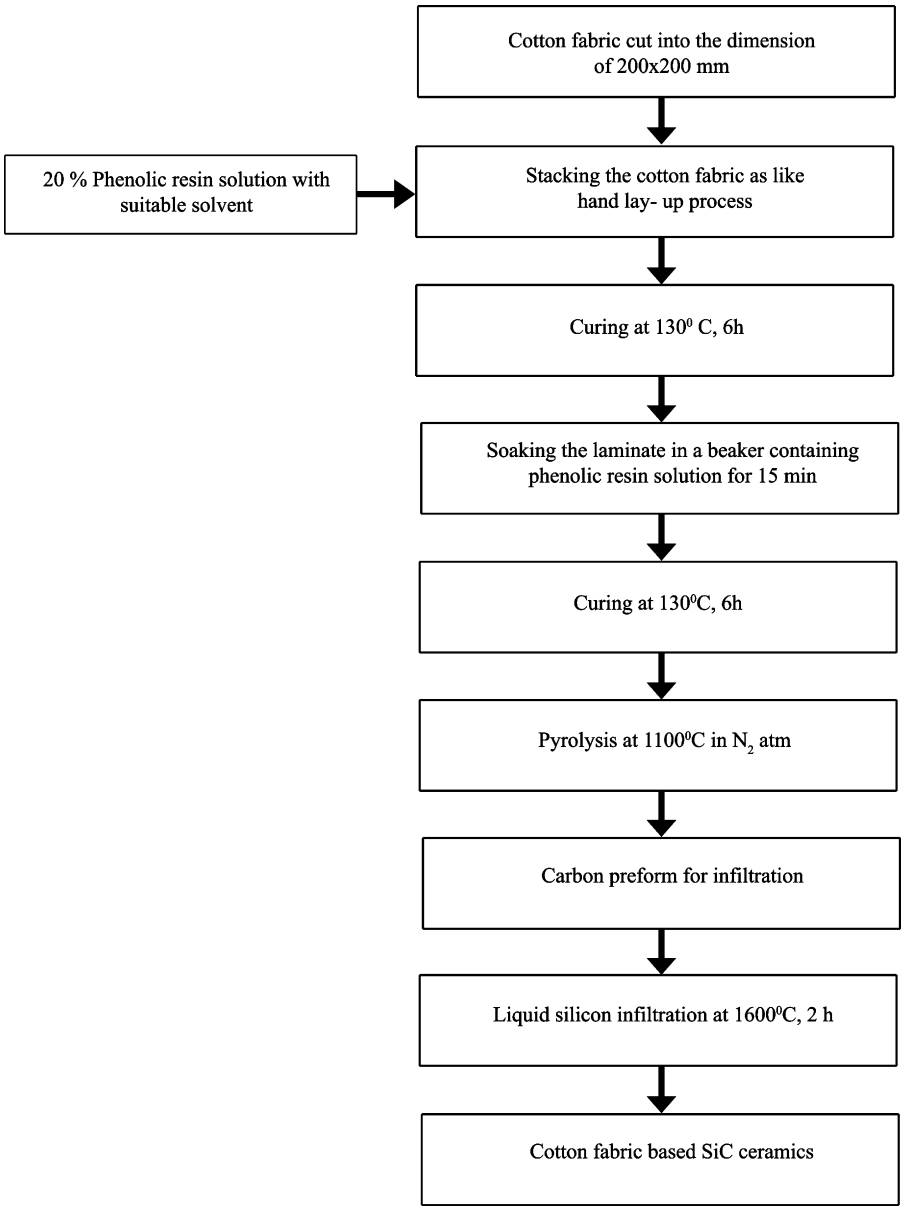

Fig. 1. Processing scheme of manufacturing of Si/SiC ceramics from cotton fabric.

method using phenolic resin as the matrix. Cotton fabric was positioned manually one over the other in an open mold, and resin was poured, brushed over and into the cotton cloth plies. Entrapped air was removed manually with squeeze rollers. This process was repeated for several times to get a desired thickness. Subsequently the laminate was kept in the oven at 130 °C for curing. To avoid any delamination, the laminate was submerged in a beaker containing phenolic resin solution for 15 min and then cured again at 130 °C. Carbon preforms were prepared by pyrolyzing the cured cotton fabric laminates under N_2 atmosphere in a tubular furnace. A heating rate of 2 °C/min was used up to 600 °C and a heating rate of 5 °C/min was used up to 1100 °C. The specimens were held at this temperature for 2 h. The resulting porous carbon preform was infiltrated with liquid silicon in a vacuum graphite furnace at 1600 °C under argon atmosphere. The specimens were kept at this temperature for 2 h to allow complete reaction of silicon with the carbon structure to form SiC. Fig. 1 summarizes the processing scheme. The samples made from cotton fabric are shown in Fig. 2.

2.2. Characterization

The decomposition behavior of phenolic resin and cotton fabric was studied by thermogravimetric analyzer (TGA) at a heating rate of 10 °C/min from room temperature to 1000 °C in inert atmospheric condition. TGA was performed in Netzsch (STA 409C) thermal analyzer with alumina powder as the reference sample. The X-ray diffraction (XRD) patterns of carbon template and porous microcellular SiC ceramics were recorded using X-ray diffractometer (Bruker, Discover D8) with nickel filtered Cu Kα radiation. The microstructures were

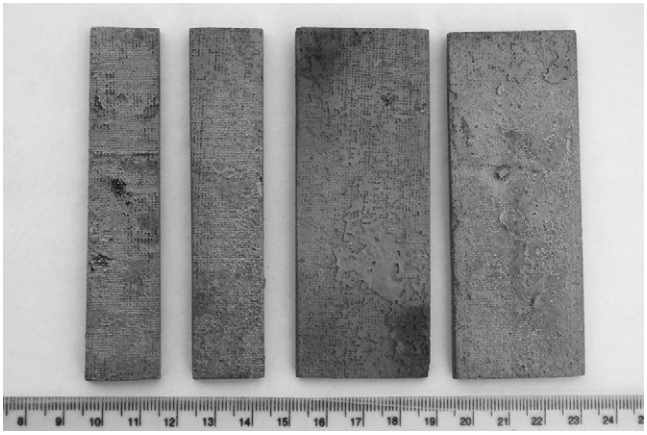

Fig. 2. Si/SiC ceramic product from cotton fabric.

observed with a scanning electron microscope (FEI, QUANTA 200) operated at 30 kV and 20 mA and with an optical microscope. Density was determined by the Archimedes method.

The flexural strength of the porous SiC ceramics was determined by four-point bend test using ASTM C 1161. Four-point bend strength testing was carried out using an Instron 3367 universal testing machine with a span of 50 mm and a crosshead speed of 0.5 mm min^{-1}. Hardness was measured with the help of Vickers hardness machine (Matsuzawa Co. Ltd, Japan, MMT-7). Vickers hardness of the Si/SiC ceramic was determined according to the ASTM C 1327-03.

In this work, fracture toughness of the Si/SiC ceramic was determined by indentation fracture toughness technique (IF). This technique is appropriate for highly brittle materials [13,14]. It is a simple technique and requires only a few specimens with small dimension; however, it results in high variation because of difficulties inherent with the accurate measurement of crack length and subcritical slow crack growth [15–17]. The indentation fracture toughness determined according to Anstis equation [18].

$$K_{IC} = 1.6 \times 10^{-2}(E/H)^{1/2}(P/C_0^{3/2})$$

$$H = 1.8544\ (P/a^2)$$

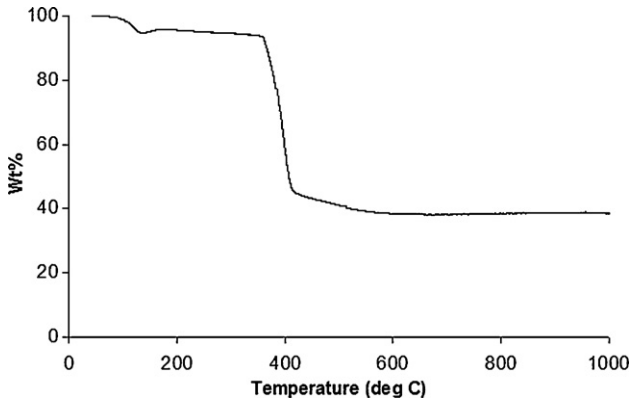

Fig. 3. TGA of cotton fabric.

where P is the load in Newtons, C_0 is the crack length from the center of the indent to the crack tip in (m), E is the Young's modulus in GPa and H is the Vickers hardness in GPa. Both a and C_0 in the above equation were measured using optical microscope.

3. Results and discussion

Thermal decomposition of cellulose produces solid residues, liquid materials and volatile gases when it is heated without oxygen. Combustion of cellulose is an oxidation process of the material under heat, which consumes flammable gases, liquids and solid residues produced in the pyrolysis of the materials, and results in excess amount of heat. The pyrolysis of cellulose is a very complex chemical process and is commonly believed to involve two different mechanisms. One of them is a process of dewatering and charring of cellulose, producing water, carbon dioxide and solid residues. According to the second mechanism, the cellulose produces nonvolatile liquid L-glucose by depolymerization, and L-glucose cleavage continues, producing low molecular weight products, which are more flammable. If there is oxygen existing, the decomposed products of L-glucose will be oxidized (fire), generating much more energy and heat to promote more cellulose cleavage. The competition between these two reactions exists throughout the thermal decomposition of cellulose [19–21].

TGA of cotton fiber (Fig. 3) reveals that the pyrolysis of cellulose fiber occurs in three stages: initial, main and char decomposition. In the initial stage, where the temperature range is below 300 °C, the most important changes of the fibers are some change in physical properties with little weight loss. Here, the damage of the cellulose occurs mostly in amorphous region of the polymers. The main pyrolysis stage occurs in the temperature range of 360–420 °C. In this stage, the weight loss is very fast and significant. Most of the pyrolysis products are produced in this stage. L-Glucose is one of the major products, together with all kinds of combustible gases. Generally speaking, the pyrolysis takes place in crystalline region of cellulose fibers in this stage [22].

The char pyrolysis occurs at the temperature above 430 °C. During this process, dewatering and charring reactions compete with the production of L-glucose. The mass decomposition continues to dewater and decarboxylization, releasing more water and carbon dioxide and producing double bond, carboxyl and carbonyl products. The carbon content in the decomposed products becomes higher and higher, and charred residues are formed. Although the exact temperature ranges of cellulose pyrolysis may vary depending on the cellulose source and experimental conditions, the three steps always exist in pyrolysis of cellulose. The pyrolysis will go from amorphous regions to crystalline regions in cellulose [23].

The TGA of phenolic resin is shown in Fig. 4. In the case of phenolic resin, the weight loss is taking place in three stages. The first weight loss occurs around 80–120 °C. Second stage of weight loss takes place from 150 to 280 °C. Weight losses attains maximum between 420 and 980 °C. The weight loss below 450 °C was caused by the dehydration reaction of

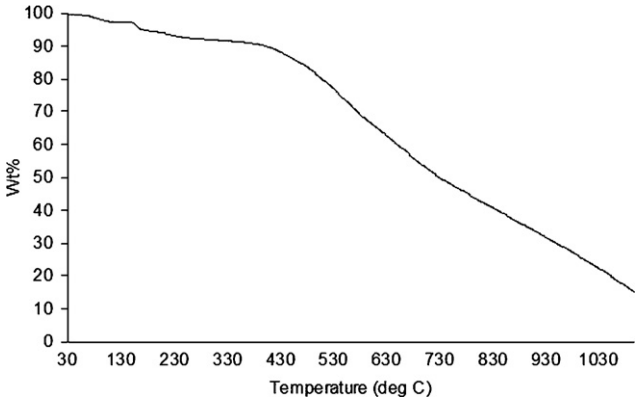

Fig. 4. TGA of phenolic resin.

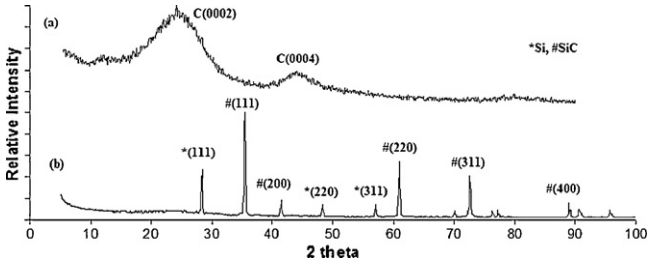

Fig. 5. XRD patterns of (a) carbon preform and (b) Si/SiC ceramics from cotton fabric.

phenolic resin, including thermocuring reaction between hydroxymethyl groups and hydrogen groups within aromatic rings and the condensation reaction between methylene and hydroxyl groups [24]. The condensation of aromatic polynuclear structure started to form above 450 °C and developed above 500 °C, releasing small molecular substances, such as CH_4, H_2, CO, CO_2, etc. Weight loss at ≈700 °C was attributed to further carbonization and dehydrogenation reactions in phenolic resin [25–27].

XRD patterns obtained from carbon preform and Si/SiC ceramic are shown in Fig. 5. The two broad peaks centered around 25° and 44° suggest that the carbon preform obtained from cotton fabric laminate is amorphous. The peaks at 2θ values of 28.4°, 47.9° and 56.9° belong to (1 1 1), (2 2 0) and (3 1 1) planes of cubic crystalline silicon. XRD peaks around 2θ values of 35.6°, 41.4°, 60.8° and 72.4° are from (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of cubic silicon carbide (β-SiC), respectively. The peaks of carbon are not present in XRD profile of the Si/SiC ceramics (Fig. 5b). α-SiC phase is not found in this XRD pattern. It can be inferred that the highly localized exothermic reaction between liquid Si and carbon does not lead to temperatures higher than 2000 °C, because the

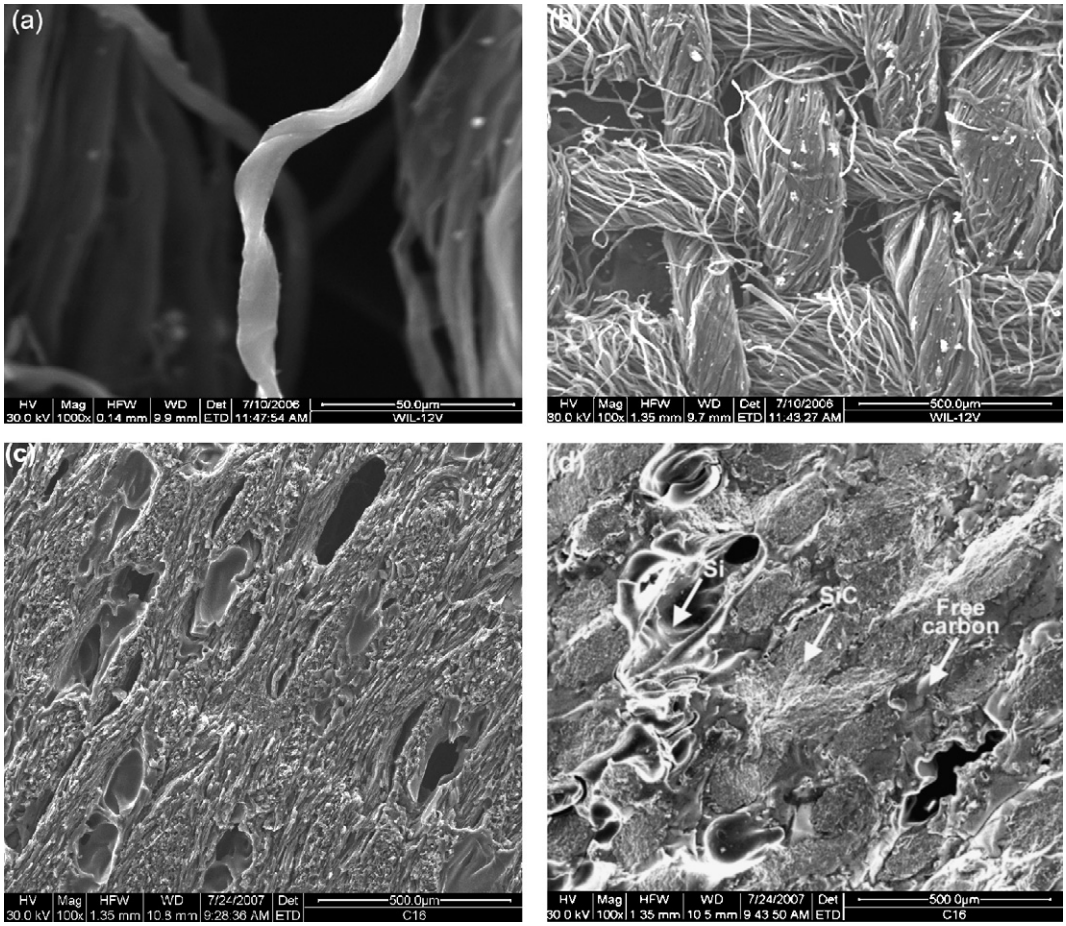

Fig. 6. SEM micrographs of (a) carbon single filament from cotton fiber; (b) carbon fiber bundle from cotton fabric; (c) cross-section of carbon preform from cotton fabric laminate; (d) fracture surface of Si/SiC ceramic from cotton fabric.

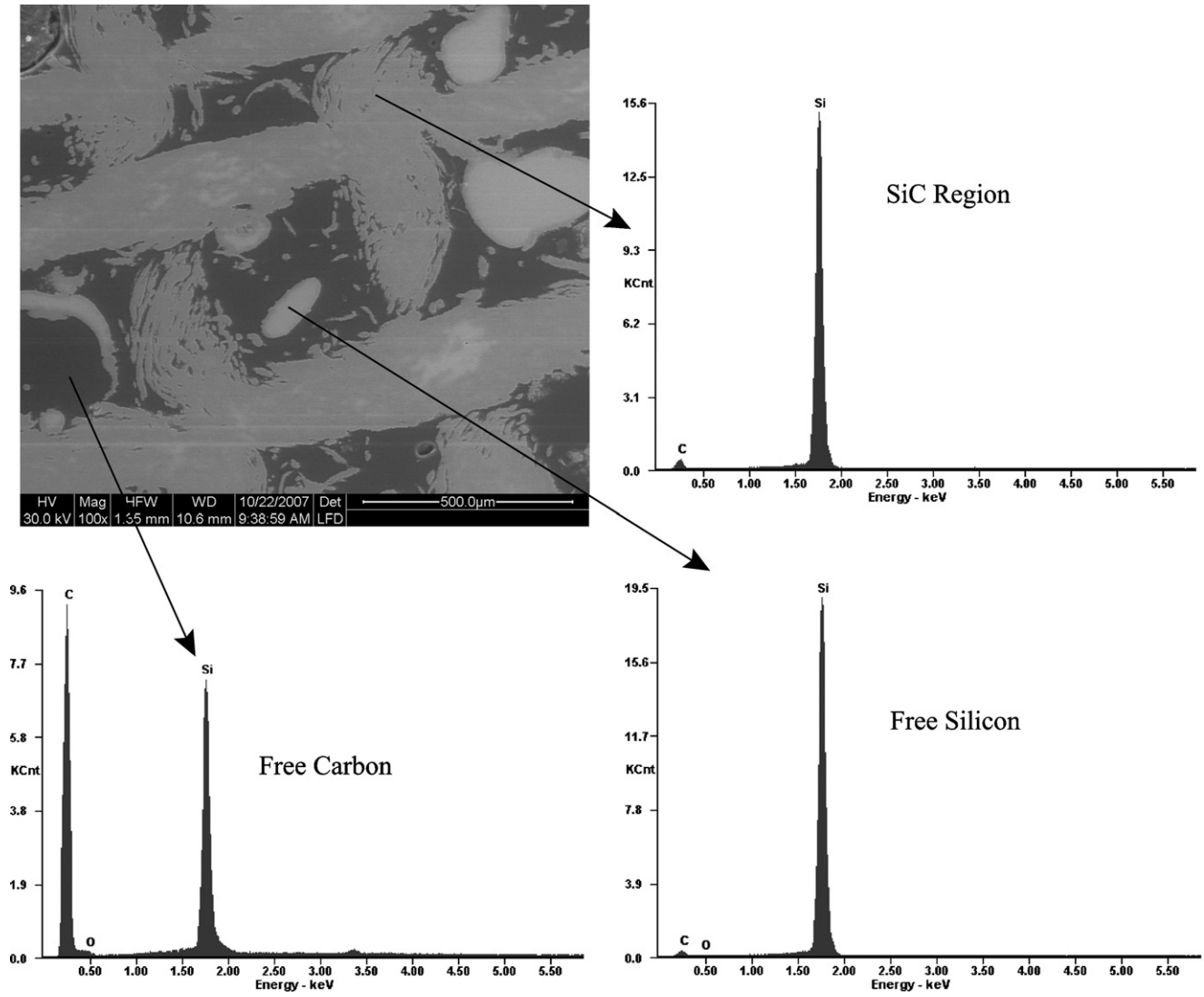

Fig. 7. EDAX analysis of Si/SiC ceramic.

β → α transformation does not take place. The results show that the resulting porous products are essentially constituted of SiC of cubic type (β-SiC) [28].

Fig. 6a shows the SEM micrograph of single carbon filament derived from cotton fiber. Its diameter varies from 13 to 15 μm and its surface is more irregular as compared to the commercially available carbon fiber. The carbon fiber bundle obtained from the cotton fabric is shown in Fig. 6b. The cross-section of the pyrolysed cotton fabric laminate is shown in Fig. 6c. Pores in the laminate are multimodal pores and some of the pores are elliptical in shape. Its length is around 200 μm. The microstructure of Si/SiC ceramic derived from the above laminate is shown in Fig. 6d. It clearly shows that the large pores are still open and the fiber bundles are surrounded by free silicon and free carbon.

Fig. 7 clearly shows the presence of three distinct phases in the ceramics. The near white, light grey and dark grey regions are free silicon, silicon carbide and free carbon, respectively. Those regions are subjected to EDAX analysis (shown in Fig. 7). It shows that the free silicon regions (near white) are enriched with 70 wt% of silicon and trace quantity of carbon. Similarly the carbon and silicon wt% in the SiC regions (light grey) are 47 and 52%, respectively. In the free carbon region (dark grey), the carbon wt% is around 90. It is inferred that the carbon which formed from cotton fiber is completely transformed into SiC. On the other hand, the carbon which formed from phenolic resin remains unreacted.

The carbon preform has multimodal pore size distribution. Some of the regions in the samples are packed with large size pores. In those regions, capillary action failed to fill the pores with free silicon. On the other hand, area with small pores of size less than 90 μm is completely filled with free silicon. Hence the density of the individual bars varies from 2.15 to 2.58 g/cm^3 with an average of about 2.36 g/cm^3. Similarly the porosity of the individual bars is varying from 7 to 18%.

The hardness values from the indentation test are given in Table 1. The areas of SiC are large enough to make an indentation easily. The average Vickers hardness value of all SiC areas is 1811, which is significantly lower than the

Table 1
Average vickers hardness values at the three regions

SiC region	1811 ± 55
Si region	899 ± 57
Free carbon region	365 ± 45

expected value, probably due to the difference in densities of the infiltrated sample. The areas with excess Si were also subjected to hardness measurement. The average hardness value for Si region is 899, which is closer to the reported hardness values of 950–1150. Free carbon present in the samples is amorphous and it has the hardness value of 345.

To measure the fracture toughness of the Si/SiC ceramic, five indentations in the SiC regions have been made. The measured toughness values varied from 0.97 to 1.57 $MPa\sqrt{m}$ which is much lower than the reported sintered SiC fracture toughness values. This may be due to the density difference between the Si/SiC and sintered SiC ceramics.

The flexural strength of the samples is varying from 135 to 169 MPa. This inconsistency is due to the inhomogeneous porosity distribution within the samples. The final materials are not completely dense and the porosity within the samples is believed to act as the failure origin. SEM fractograph (Fig. 6d) clearly shows that the failure origin is the pores within the samples. In addition to the porosity, large pockets of silicon are likely to be detrimental to the materials in several ways. Because, the fracture toughness of silicon is 1 $MPa\sqrt{m}$ and any small flaw in silicon packets may drastically reduce the flexural strength of the ceramic [1].

4. Conclusion

Si/SiC ceramic was prepared from cotton fabric by the reactive infiltration of liquid silicon into the carbon template. The final SiC ceramic composed of three major phases such as crystalline β-SiC, free silicon and free carbon. The resulting ceramic possessed lower flexural strength compared to conventionally produced silicon carbide. The unfilled multimodal pores may act as failure origin and thus lead to lower flexural strength. Careful control on pore size and its distribution within the samples while making laminate may be helpful to increase the strength. This process is fairly cheap because of inexpensive starting materials and a renewable resource. The ceramic produced by this method is suitable for non-load bearing applications.

Acknowledgment

The authors wish to thank Mr. Rajendra Ganesh for his help during the hand lay-up process.

References

[1] M. Singh, J.A. Salem, Mechanical properties and microstructure of biomorphic silicon carbide ceramics fabricated from wood precursors, J. Eur. Ceram. Soc. 22 (2002) 2709–2717.
[2] J.E. Mark, P.D. Calvert, Biomimetic hybrid and in-situ composites, Mater. Sci. Eng. C 1 (1994) 159–173.
[3] P. Griel, Biomorphic ceramics from lignocellulosics, J. Eur. Ceram. Soc. 21 (2001) 105–118.
[4] T. Ota, M. Takahashi, T. Hibi, M. Ozawa, H. Suzuki, Biomimetic process for producing SiC wood, J. Am. Ceram. Soc. 78 (1995) 3409–3411.
[5] P. Greil, T. Lifka, A. Kaindl, Biomorphic silicon carbide ceramics from wood: I and II, J. Eur. Ceram. Soc. 18 (1998) 1961–1983.
[6] E. Vogli, H. Sieber, P. Greil, Biomorphic SiC-ceramic prepared by Si-vapor phase infiltration of wood, J. Eur. Ceram. Soc. 22 (2002) 2663–2668.
[7] U. Vogt, A. Herzog, T. Graule, R. Klingner, T. Zimmermann, Porous ceramics derived from wood, Key Eng. Mater. 206–213 (2001) 1941–1944.
[8] C. Zollfrank, R. Kladny, H. Sieber, P. Greil, G. Motz, Manufacturing of anisotropic ceramics from preceramic polymer infiltrated wood, Ceram. Trans. 129 (2002) 43–50.
[9] J.M. Fernandez, M. Singh, F.M. Valera-Feria, High temperature compressive mechanical behavior of biomorphic silicon carbide ceramics, Scripta Mater. 43 (2000) 813–818.
[10] C.E. Byrne, D.C. Nagle, Carbonization of wood for advanced materials applications, Carbon 35 (1997) 259–266.
[11] D.W. Shin, S.S. Park, Silicon/silicon carbide composites fabricated by infiltration of a silicon melt into charcoal, J. Am. Ceram. Soc. 82 (1999) 3251–3253.
[12] H. Sieber, C. Hoffmann, A. Kaindl, P. Greil, Biomorphic cellular ceramics, Adv. Eng. Mater. 2 (2000) 105–109.
[13] M. Guazzato, M. Albakry, L. Quach, M.V. Swain, Influence of surface and heat treatments on the flexural strength of a glass-infiltrated alumina/zirconia-reinforced dental ceramic, Dent. Mater. 21 (2005) 454–463.
[14] M. Guazzato, M. Albakry, S.P. Ringer, M.V. Swain, Strength, fracture toughness and microstructure of a selection of all-ceramic materials. Part II. Zirconia-based dental ceramics, Dent. Mater. 20 (2004) 449–456.
[15] T. Ohji, Y.K. Jeong, Y.H. Choa, K. Niihara, Strengthening and toughening mechanisms of ceramic nanocomposites, J. Am. Ceram. Soc. 81 (6) (1998) 1453–1460.
[16] A.S. Rizkalla, D.W. Jones, Mechanical properties of commercial high strength ceramic core materials, Dent. Mater. 20 (2004) 207–212.
[17] J. Chevalier, C. Olagnon, G. Fantozzi, Subcritical crack propagation in 3Y-TZP ceramics: static and cyclic fatigue, J. Am. Ceram. Soc. 82 (1999) 3129–3138.
[18] G.R. Anstis, P. Chantikul, B.R. Lawn, D.B. Marshall, A critical evaluation of indentation techniques for measuring fracture toughness. 1. Direct crack measurements, J. Am. Ceram. Soc. 64 (1981) 533–538.
[19] P. Zhua, S. Sui, B. Wang, K. Sunb, G. Sunc, A study of pyrolysis and pyrolysis products of flame-retardant cotton fabrics by DSC, TGA, and PY-GC-MS, J. Anal. Appl. Pyrolysis 71 (2004) 645–655.
[20] D. Price, A.R. Horrocks, M. Akalin, A.A. Faroq, Influence of flame retardants on the mechanism of pyrolysis of cotton (cellulose) fabrics in air, J. Anal. Appl. Pyrolysis 40–41 (1997) 511–524.
[21] A. Richard Horrocks, D. Price, M. Akalin, FTIR analysis of gases evolved from cotton and flame retarded cotton fabrics pyrolysed in air, Polym. Degrad. Stab. 52 (1996) 205–213.
[22] A.A. Faroq, D. Price, G.J. Milnes, A.R. Horrocks, Thermogravimetric analysis study of the mechanism of pyrolysis of untreated and flame retardant treated cotton fabrics under a continuous flow of nitrogen, Polym. Degrad. Stab. 44 (1994) 323–333.
[23] J. Molto, R. Font, J.A. Conesa, I. Martin-Gullon, Thermogravimetric analysis during the decomposition of cotton fabrics in an inert and air environment, J. Anal. Appl. Pyrolysis 76 (2006) 124–131.
[24] Y. Yamashita, A study of carbonization of phenol-formaldehyde resin labelled with deuterium and ^{13}C, Carbon 19 (1981) 89–94.
[25] J.M. Kenny, G. Pisaniello, F. Farina, S. Puzziello, Calorimetric analysis of the polymerization reaction of a phenolic resin, Thermochimica. Acta 269/270 (1995) 201–211.

[26] K. Miura, J. Hayashi, K. Kashimoto, Production of molecular sieving carbons through co-carbonization of phenol-formaldehyde resin and other organic substances, Carbon 30 (1992) 946–947.
[27] T. Horikawa, K. Ogawa, K. Mizuno, J. Hayashi, K. Muroyama, Preparation and characterization of the carbonized material of phenol-formaldehyde resin with addition of various organic substances, Carbon 41 (2003) 465–472.
[28] J.M. Qian, J.P. Wang, Z.H. Jin, Preparation and properties of porous microcellular SiC ceramics by reactive infiltration of Si vapor into carbonized basswood, Mater. Chem. Phys. 82 (2003) 648–653.