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Properties of Si/SiC ceramic composite subjected to chemical vapour infiltration

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Abstract

Si/SiC ceramic composite was prepared by infiltration of liquid silicon into carbon preforms that was made from cotton fabric and phenolic resin. This composite was subjected to the chemical vapour infiltration (CVI), using methyltrichlorosilane as a precursor gas. The effect of infiltration time on densification and mechanical properties was studied. Results show a significant improvement in density by pore closure. Flexural strength increases with increasing infiltration time. However, beyond 60 h of infiltration, the strength improvement was insignificant. The high temperature oxidation resistance of the above ceramics was also studied. The CVI treated samples show considerable resistance to oxidation compared to untreated samples. Thermogravimetric analysis also confirmed the better oxidation resistance of the CVI treated samples.

Keywords: SiC; Cotton fabric; Chemical vapour infiltration; Porous ceramic; Carbothermal reaction

1. Introduction

Silicon carbide has long been recognized as an ideal material for applications where superior hardness and stiffness, strength and oxidation resistance at elevated temperatures, high thermal conductivity, low coefficient of thermal expansion, and resistance to wear and abrasion are of primary importance [1–5]. Silicon carbide has been made using various methods such as hot pressing, reaction bonding, etc. In the last decade, making silicon carbide ceramics from natural materials has evoked particular interest [6–9]. In this approach, the carbon preform is prepared by pyrolysing the natural wood under N_2 atmosphere in a furnace. The resulting porous carbon preform is infiltrated with liquid silicon. The main advantages of this approach are cheap and renewable raw material and capability to create near net shape. The significance of wood based SiC is that the complex hierarchical cellular structure is preserved in the final product [10–13]. Similarly, one could produce silicon carbide ceramics from any carbon yielding materials. A few researchers attempted to make silicon carbide ceramics from cellulose fiber based on cotton [14,15]. The main drawback, however, is the inhomogeneous pore distribution and pore size. The strength of this ceramic is controlled by pores, free silicon and free carbon. The reported open porosity values vary from 2% to 20%.

Chemical vapour deposition remains an important technique to synthesize ceramics in structural and electronic industries [16–18]. A range of precursors have been used for the deposition process, under widely varying conditions of input gas composition, temperature and pressure [19]. In chemical vapour infiltration (CVI) processing, the substrate is heated up to the desired temperature in an inert atmosphere and then the reactant gases are introduced into the open channels. This is a promising method for obtaining highly dense silicon carbide ceramic components [20–22], but it is a time consuming and expensive process.

The present work was undertaken to combine the advantages of liquid silicon infiltration (LSI) and CVI to obtain better properties in the final ceramic product. Commercially available cotton fabric has been used to make a laminate with phenolic resin as a binder. This was pyrolysed to get a carbon preform, which was used for obtaining silicon carbide ceramics by

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silicon infiltration. A low density (2.05 g/cm^3) cotton fabric based silicon carbide ceramic produced from LSI was taken for further densification through chemical vapour infiltration. The physical and mechanical properties of the CVI treated and untreated ceramics were compared. Thermal stability of the above ceramics was also studied.

2. Experimental procedure

Phenolic resin 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 dilute sodium hydroxide solution to remove the starch coating on the cloth and then dried. Cotton fabric laminate was made by hand lay-up method using phenolic resin as the binder. Cotton fabric was positioned manually in an open mould, resin was poured, and brushed over the fabric. Entrapped air was removed manually with squeeze rollers. This process was repeated for several times until the desired thickness (7 mm) is reached. Subsequently the laminate was kept in an oven at 130 °C for curing. To avoid any delamination, the laminate was submerged again in phenolic resin solution and cured at 130 °C. Carbon preforms were prepared by pyrolysing the cured cotton fabric laminates under N_2 atmosphere in a 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 carbon to form SiC.

The density of the Si/SiC ceramics varied from 2.05 to 2.58 g/cm^3. The low density (2.05 g/cm^3) ceramic was used for isothermal CVI treatment because of the ease of reactant gas infiltration. Four-point bend test specimens were prepared according to the ASTM C 1161 standard. These specimens were subjected to the CVI treatment for 40, 60 and 80 h. A minimum of three samples was used for every CVI treatment. The SiC ceramic samples were placed in an ICVI reactor (M/s Archer Technicoat Ltd., UK) chamber and SiC infiltration was carried out using the methyltrichlorosilane (MTS, 99%, M/s. Spectrochem, India) and H_2 (99.995%, M/s. Inox air products Ltd., India) precursor system with the fixed pressure of 1.65 mbar. In order to avoid the formation of excess free silicon and carbon, the MTS/H_2 molar flow rate ratio was maintained at 1:16 (MTS = 700 g/h, H_2 = 28 SLM). The reactor was evacuated and heated at slow rate (3– 4 °C/min) with Ar purging. Once the temperature reached the set value (950–1100 °C), it was stabilised for 10–20 min. MTS precursor gas was passed through a liquid mass flow meter (M/s. Bronkhorst, Netherlands), vapourised in the evaporator and mixed with H_2 in the mixing chamber. The MTS/H_2 mixture entered the reactor and formed SiC in and around the samples.

3. Characterisation

The X-ray diffraction (XRD) patterns of CVI treated and untreated SiC ceramics and heat treated samples were recorded using X-ray diffractometer (Bruker, Discover D8) with nickel filtered Cu Kα radiation. The microstructures were observed with scanning electron microscope (SEM) (FEI, QUANTA 200) operated at 30 kV and 20 mA and with an optical microscope. Density was determined by the Archimedes method. The thermal characteristics of CVI treated and untreated cotton fabric based SiC ceramics were studied by thermogravimetric analysis (TGA) at a heating rate of 10 °C/min from room temperature to 1200 °C under atmospheric conditions (Netzsch, STA 409C).

The flexural strength of infiltrated and non-infiltrated SiC ceramics was measured by four-point bend test according to ASTM C 1161 standard. Four-point bend testing was carried out using an Instron 4301 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 tester (Matsuzawa co. ltd, Japan, MMT-7). Vickers hardness of the CVI treated and untreated samples was determined according to the ASTM C 1327-03 standard.

To determine the thermal stability of the above CVI treated (80 h) and untreated ceramics, the flexural specimens (prepared according to the ASTM C 1161) were exposed to 600, 1200 and 1400 °C for 2 h under atmospheric condition. After thermal exposure, these samples were tested for flexural strength. A minimum of three samples has been treated at each temperature and then the flexural strength was determined.

4. Results and discussion

CVI treatment leads to significant improvement in density. Fig. 1 shows the variation of density with infiltration time. The density increases with increasing infiltration time. However there is very little improvement in density after 60 h. During CVI treatment, the deposition of SiC mainly depends on the diffusion of the gaseous reactant species into the pores. The diffusion rate is decreased when the pore size is reduced. As a result, it is very difficult to completely infiltrate the pores. For the large pores, the bottleneck effect hampers the densification. Therefore, beyond 60 h, the infiltration of reactant gases may

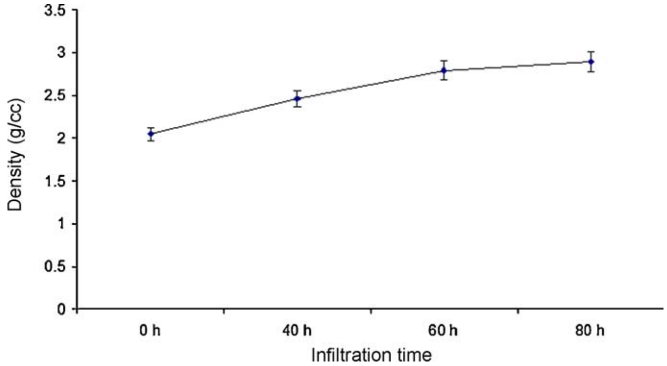

Fig. 1. Variation of density with infiltration time.

not be much effective and it may just coat the surface of the samples. Consequently, the samples end up having closed pores. Furthermore, the craters and surface connected pores observed in 40 h infiltrated samples are not observed in 60 h infiltrated samples (Fig. 2).

XRD patterns obtained from untreated and CVI treated samples are shown in Fig. 3. The peaks at 2θ values of 28.4°, 47.9° and 56.9° correspond to (1 1 1), (2 2 0) and (3 1 1) planes of cubic silicon (Fig. 3a). XRD peaks around 2θ values of 35.6°, 41.4°, 60.8° and 72.4° correspond to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of cubic silicon carbide (β-SiC), respectively.

SEM micrographs show (Fig. 4) the surface morphology of CVI treated and untreated samples. The surface of CVI treated samples is uniformly covered by spherical particles of silicon carbide. The untreated sample clearly shows the presence of three distinct phases. Based on the EDAX analysis, the near white, light grey and dark grey regions are free silicon, silicon

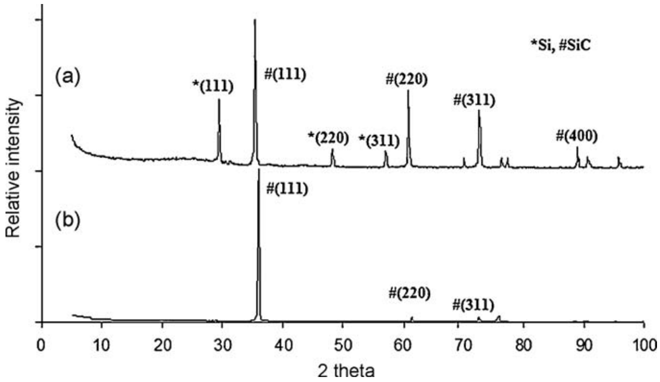

Fig. 3. XRD patterns of (a) cotton fabric based Si/SiC ceramic and (b) CVI treated Si/SiC ceramic.

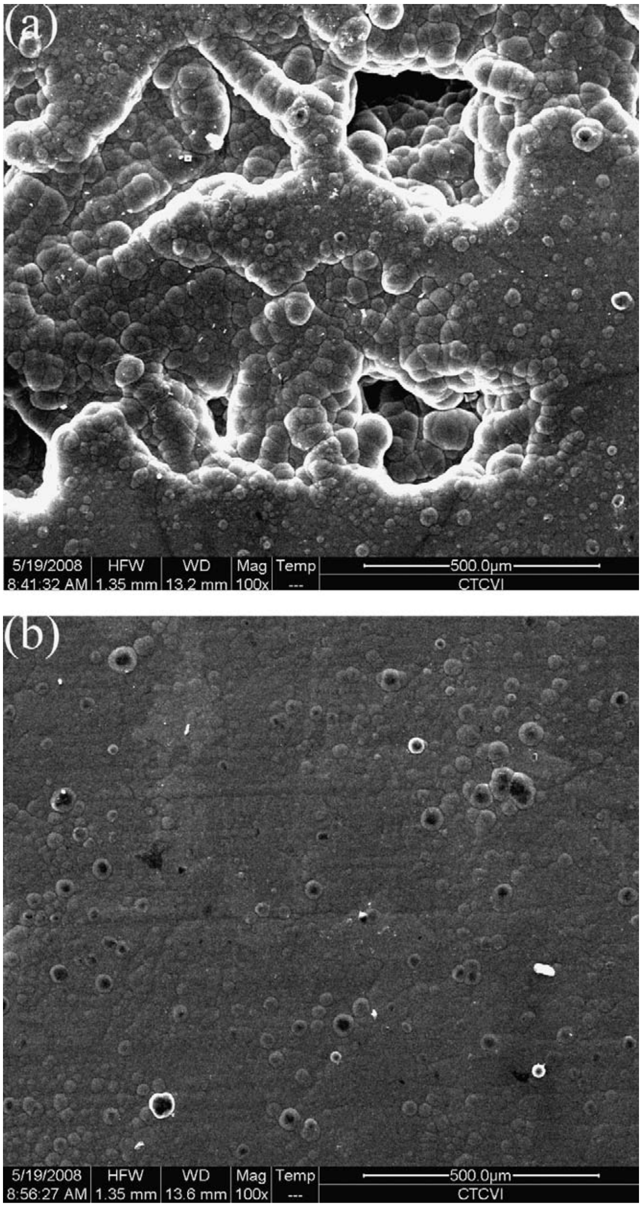

Fig. 2. SEM micrographs of CVI treated sample surface (a) 40 h and (b) 60 h.

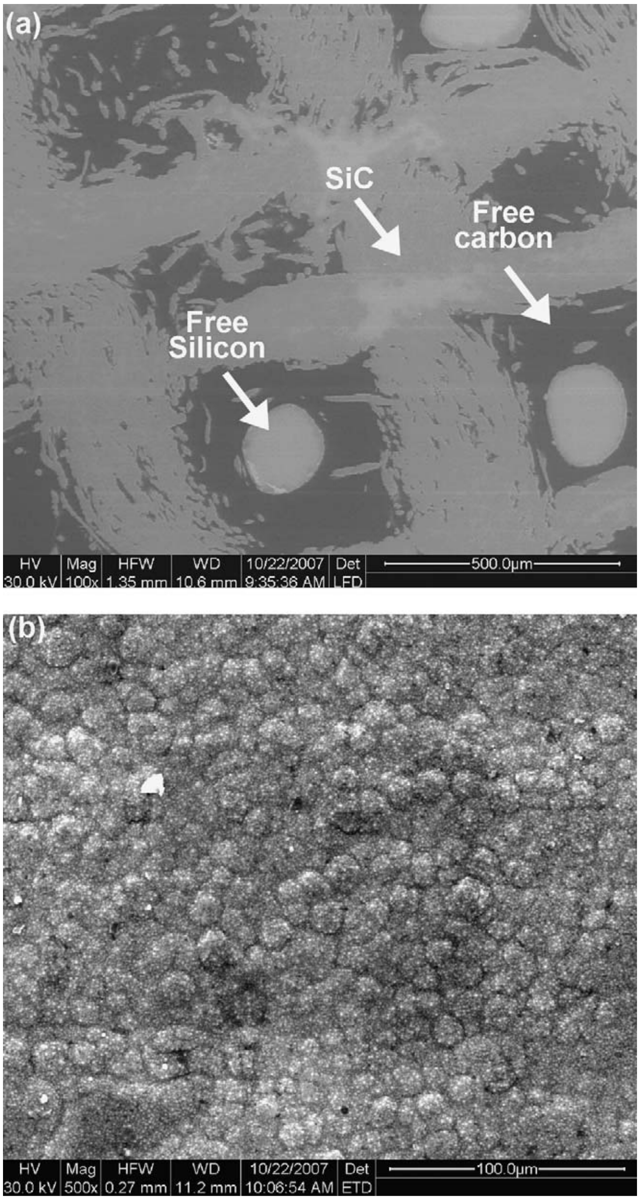

Fig. 4. SEM micrographs of (a) surface of Si/SiC ceramic and (b) surface of CVI treated sample (80 h).

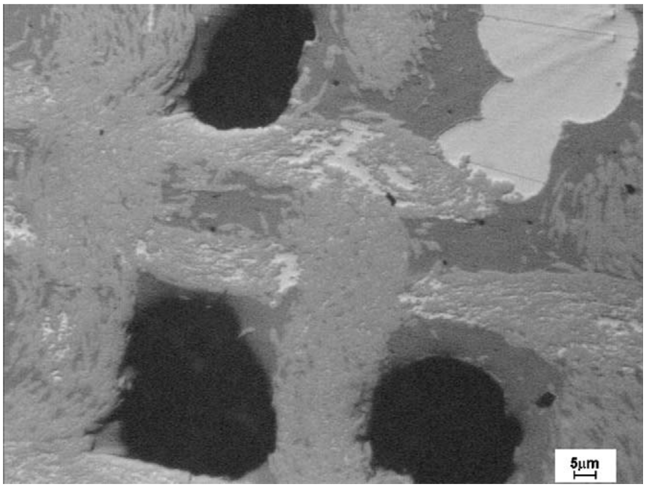

Fig. 5. Optical micrograph of a Si/SiC ceramic surface.

carbide and free carbon, respectively. The optical micrograph (Fig. 5) is an evidence for the porous nature of the untreated Si/SiC ceramics. The pore size varies from 20 to 40 μm.

The flexural strength values of CVI treated and untreated samples are shown in Fig. 6. The flexural strength values increase with increasing infiltration time. There is a significant improvement in strength after 60 h infiltration compared to 40 h infiltration. Besides density improvement, the samples subjected for 60 h of CVI treatment are free from surface defects, such as craters and surface connected pores. This may be one of the reasons for improved strength, since the three- or four-point flexural tests are more sensitive to the surface imperfections [23–25]. Beyond 60 h of CVI treatment, there is very little improvement in strength because the pore size reduction during CVI treatment inhibits the further reactant gas penetration. It is difficult to obtain a fully dense material even after prolonged exposure to CVI (80 h), since some residual closed pores are always retained. Porosity in these materials is believed to act as the origin of failure. In addition to the porosity, large pockets of silicon are likely to be detrimental to the material in several ways [1]. The properties of the SiC ceramic produced from the various routes are given in the Table 1 [26]. As compared with the commercially available silicon carbide, the cotton fabric based SiC ceramic has very low strength. It may be due to the presence of pores and low strength phases. In this present study, the CVI treatment has been carried out without removal of the free carbon in the samples. It is possible to improve the flexural strength by removing the free carbon from the samples by oxidation before the CVI treatment, since it would give additional pores for efficient gaseous reactant infiltration.

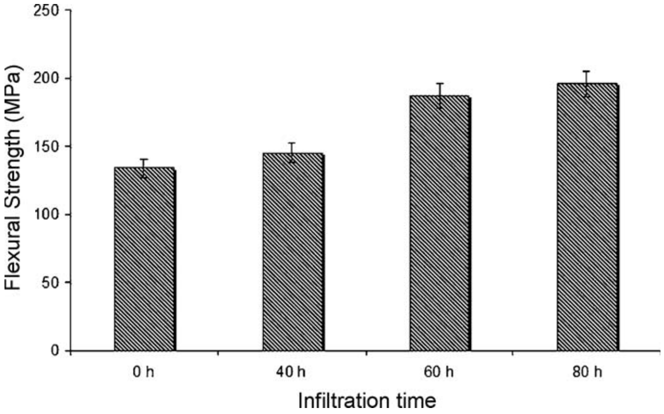

Fig. 6. Variation of flexural strength with infiltration time.

Vickers hardness was measured at the surface of the coated samples. There is vast variation in hardness values. The values vary from 2220 to 3565 H_V. This vast variation in values may occur from the presence of low hardness materials such as free silicon and free carbon beneath the coated surface. In the case of uncoated samples, the average Vickers hardness values of silicon carbide, free silicon and free carbon are 1845 ± 55, 1045 ± 59 and 364 ± 43, respectively.

The thermal stability of the above ceramics was studied by exposing the flexural test samples at various temperatures i.e. 600, 1200 and 1400 °C for 2 h in atmospheric condition. Fig. 7 shows the variation of flexural strength of the samples with the treatment temperatures. The flexural strength data show that there is relatively little strength loss for the CVI treated materials at temperature up to 1200 °C. However, the strength dropped significantly when the samples were exposed to

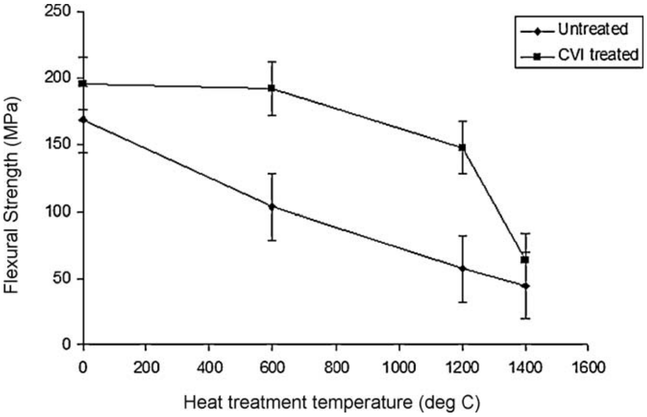

Fig. 7. Flexural strength after exposing the samples at various temperatures.

Table 1
Properties of SiC ceramic.

Properties	Cotton fabric based SiC	CVI treated cotton fabric based SiC	Sintered SiC	HIP SiC	Hot pressed SiC
Density (g/cc)	2.56	2.9	3.15	3.21	3.20
Porosity (%)	<19	<10	<2	0	0
Fracture toughness (MPa $m^{1/2}$)	0.9–1.6	–	2.5-6.5	–	3.0–4.0
Flexural strength (MPa)	169	196	430	640	640

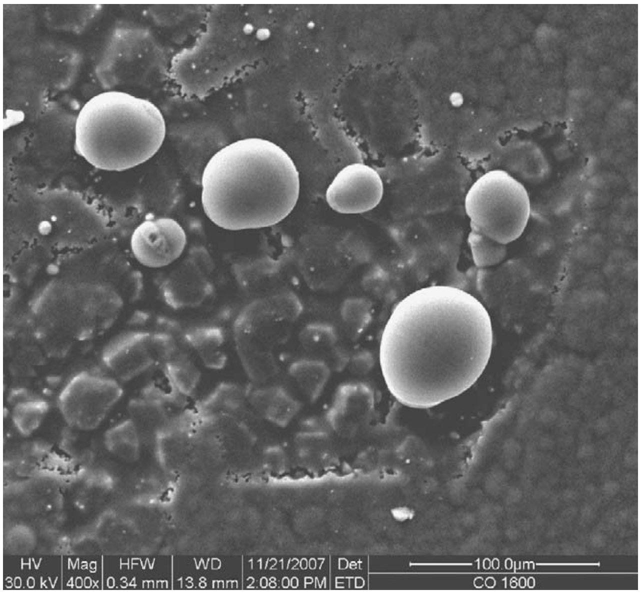

Fig. 8. SEM micrograph of CVI treated sample after heating to 1400 °C (white spheres are SiO_2).

1400 °C. The SiC surface layer gives some protection to the inner carbon and silicon from oxidation. However, at 1400 °C, free silicon in the samples melts and squeezed out. Later it reacts with the oxygen to form SiO_2 spheres. SEM micrograph (Fig. 8) clearly shows the formation of SiO_2 spheres on the surface of the samples. Due to the above reason, the samples exposed at 1400 °C are left with silicon carbide network and voids and show low flexural strength. On the other hand, the strength of the untreated samples is drastically reduced due to severe oxidation of free carbon and free silicon present in these samples. Fig. 9 shows the surface of untreated sample after thermal exposure at 600 °C. It shows that free carbon is oxidised completely and leaves empty space between the warp and weft regions on the surface. So, the SiC network is not strong enough to bear the high load. The above facts have been confirmed by the TGA. The untreated samples show more weight loss as compared to CVI treated samples (Fig. 10). The residue content of the CVI treated and untreated samples after 1200 °C are 92% and 86%, respectively. The weight loss starts at 490 °C in both the cases. But, the weight loss is more in untreated samples as compared with CVI treated samples. This may be due to good contact of free carbon with atmospheric oxygen. The weight loss may be described by the following reactions [27–29]:

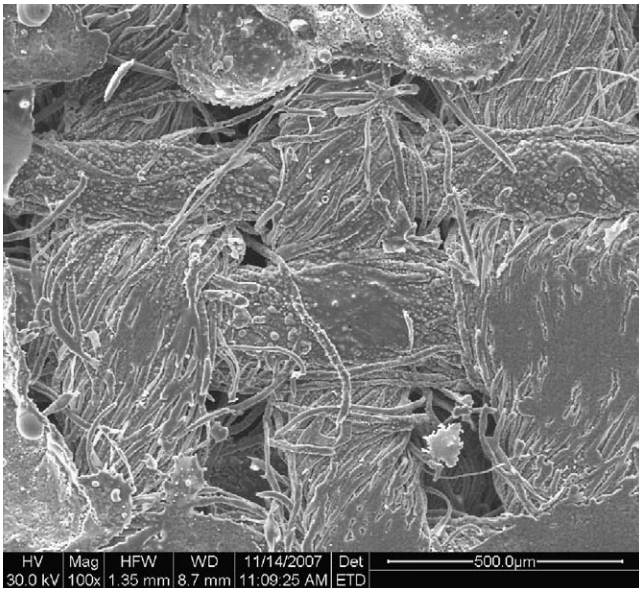

Fig. 9. SEM micrograph of untreated sample after heating to 600 °C.

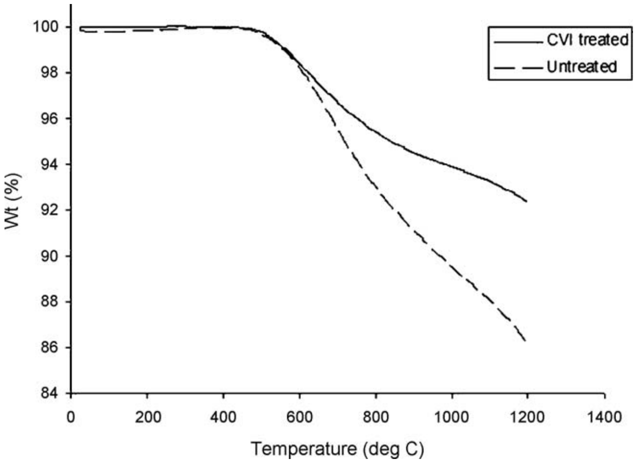

Fig. 10. TGA of CVI treated and untreated Si/SiC ceramics.

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad (1)$$

$$CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)} \quad (2)$$

$$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)} \quad (3)$$

Eq. (2) is called Boudouard reaction; any CO_2 produced by the Eq. (1) will be consumed immediately by Boudouard reaction to form CO.

Based on the mass loss on the samples while heating, the percentage of free carbon in the untreated and CVI treated samples are 14% and 7%, respectively. The expected weight gain beyond 1000 °C due to passive oxidation of silicon carbide is not observed in TGA. The weight gain due to passive oxidation of silicon carbide might have been compensated by excess weight loss of carbon present in the samples or insufficient time for formation of sufficient SiO_2 phase because the degree of oxidation strongly depends on the applied environmental condition in combination with the time of exposure [30,31].

The phases formed during heat treatment in air were identified by XRD analysis. Fig. 11 shows the XRD patterns of CVI treated and untreated samples exposed to 600, 1200 and 1400 °C. At 600 °C, both CVI treated and untreated samples have only Si and SiC phases. Cristobalite is observed to be formed after heating the samples at 1200 °C. This cristobalite may be formed from oxidation of silicon carbide and oxidation of free silicon present in the material according to the following

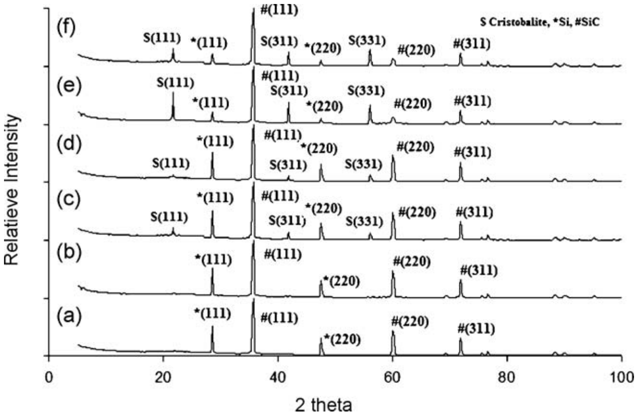

Fig. 11. XRD patterns of samples heat treated at (a) 600 °C, Si/SiC, (b) 600 °C, CVI treated Si/SiC, (c) 1200 °C, Si/SiC, (d) 1200 °C, CVI treated Si/SiC, (e) 1400 °C, Si/SiC and (f) 1400 °C, CVI treated Si/SiC.

reactions [32].

$$\mathrm{SiC_{(s)}} + 3/2\,\mathrm{O_{2(g)}} \rightarrow \mathrm{SiO_{2(s)}} + \mathrm{CO_{(g)}} \tag{4}$$

$$\mathrm{Si_{(s)}} + \mathrm{O_{2(g)}} \rightarrow \mathrm{SiO_{2(s)}} \tag{5}$$

But in the case of CVI treated samples, the characteristic peak of cristobalite ($2\theta = 21.58^\circ$) is not well developed. It has been proved earlier that the SiC produced from CVI has excellent oxidation resistance even above 1200 °C due to its high purity [33,34]. So, at 1200 °C, the CVI treated samples may be coated with a very thin layer of amorphous or partially crystalline SiO_2 phase, therefore the peak is not well developed. At 1400 °C, the SiO_2 peak intensity is increased in both the cases because of the increase in crystallinity of the SiO_2 phase. However, in CVI treated samples, the major portion of the cristobalite may be formed according to the Eq. (5) (Fig. 8). The peak intensity of free silicon is considerably reduced at this temperature, possibly because of its fine dispersion or decreased concentration within the SiO_2 phase [34].

5. Conclusions

Significant improvement in density has been observed after CVI treatment of porous Si/SiC ceramics. However, beyond 60 h, the infiltration rate is slow because of pore size reduction. Good improvement in flexural strength is observed after CVI treatment for 60 h.

The CVI treated samples also show good oxidation resistance up to 1200 °C. But, there is a loss in strength when the sample is subjected to 1400 °C due to the melting of free silicon. Thermal stability of the Si/SiC ceramic composite can be significantly improved by secondary CVI treatment.

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