

Morphological Studies on CNT Reinforced SiC/SiOC Composites

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Abstract

Carbon nanotubes (CNTs) have been grown on commercially available silicon carbide (SiC) fabric by the catalytic chemical vapour deposition (CCVD) technique. These CNT coated SiC fabrics were used to develop Silicon Carbide–Carbon Nanotube–Silicon oxy Carbide matrix composites (SiC/CNTs/SiOC) by sol gel technique. Silicon oxy Carbide refers to carbon containing silicates wherein oxygen and carbon atoms share bonds with silicon in the amorphous network structure. In this approach, alkyl-substituted silicon alkoxides, which are molecular precursors containing oxygen and carbon functionalities on the silicon, are hydrolyzed and condensed in the presence of sucrose, which provides excess of carbon to bond into the silicon alkoxide network during hydrolysis. A low-temperature (1000°C) heat-treatment of the gel creates a glassy silicate material whose molecular structure consists of an oxygen/carbon anionic network. The microstructures of these hybrid materials and their composites have been studied using scanning electron microscope (SEM), transmission electron microscope (TEM) and Raman spectroscopy.

Introduction

Silicon oxycarbide denotes the chemical structure in which silicon is simultaneously bonded with carbon and oxygen. These tetrahedral network species can be generally described as $[C_xSiO_{4-x}]$ where $x=1, 2,$ or 3 . The incorporation of carbon in silicate glasses presents the possibility of replacing some oxygen, which is only two-coordinated, with carbon which can be four-coordinated. This increased bonding per anion is expected to strengthen the molecular structure of the glass network, and thereby, to improve the thermal and mechanical properties [1-3]. Carbon incorporation in silicates has been most successfully achieved by sol gel process.

The use of alkyl-substituted silicon-alkoxide as silica precursors and the use of sucrose as carbon precursor results in gels containing Si atoms bonded simultaneously to carbon and oxygen atoms, thus creating a silicon oxycarbide structure. These oxycarbide gels have applications by themselves, or they can be further processed to obtain dense glasses, porous glasses or composites. To synthesize silicon oxycarbide, pyrolysis at higher temperatures is required in order to dehydrogenate and cross-link the terminal organic groups. The resulting silicon oxycarbide are shiny, black, amorphous materials.

The black color is attributed to the presence of an elemental form of carbon [4].

Silicon carbide (SiC) is one of the most important ceramic reinforcing materials for composites for high-temperature structural applications because of its excellent high-temperature mechanical properties, potentiality of high thermal conductivity.

However, in order to increase their bonding with ceramic matrix systems as well as to make best use of their potential mechanical properties, SiC fibers are given a coating of carbon of varying crystallinity. Development of CNTs has opened new avenues as reinforcements for advanced composites. The exceptionally high mechanical properties of CNTs make them attractive candidate for reinforcements as such or in combination with other high performance reinforcements for fabrication of composites [5–9]. CNTs play an essential role in enhancing the mechanical properties of nanocomposites, influencing much more than the conventional fibrous reinforcements or bulk materials [10-14].

Experimental Details

Preparation of CNT coated SiC Hybrid Reinforcement

Carbon nanotubes were grown on commercially available Silicon Carbide (SiC) fabric by CCVD

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technique. SiC fabric of dimension 20 mm X 50 mm were pretreated at 550°C for the removal of the polymeric coating material on its surface. The surface cleaned SiC fabric was then placed in pyrolysis zone of the horizontal quartz reactor [15]. The temperature of the pyrolysis zone was monitored using programmable temperature controller. The reactor was connected to gas delivery system wherein inert gas/hydrocarbon vapours can be introduced at controlled rate. The furnace was heated with the ramp of 4°C/min up to growth temperature of CNTs. 2 wt% mixture of ferrocene in xylene was injected into the furnace by syringe pump. The growth temperature for CNTs was around 800°C. The growth and structure of CNTs were studied using SEM, TEM & Raman microscope. In present studies metallic system has been used as catalyst for the growth of aligned CNTs therefore, these need to be purified. Purification was carried out using acid cleaning method by treating SiC/CNTs sample with HCl (50%) for 24 hours followed by washing with distilled water [16-18]. Washed CNTs samples were

dried at 70°C for overnight to remove moisture. SiOC matrix was synthesized using the sol gel technique.

Preparation of SiOC matrix

Preparation of the SiOC matrix is carried out by low temperature and low cost sol gel synthesis. The mixing conditions of the precursors of silicon dioxide (SiO₂) and carbon greatly influences the properties of the final product formed [19-21]. In sol gel processing mixing takes places in liquid phase, with tetraethoxyorthosilicate and sucrose solution prepared in water serving as the sources of SiO₂ and carbon, respectively. Hydrolysis and successive condensation of the silica precursor, TEOS was carried out in alcoholic medium in an acid catalysed reaction using hydrochloric acid. In a typical preparation, molar ratios of TEOS: Ethanol: Water was maintained at 1:2:4. The mixture was vigorously stirred till partial hydrolysis of the solution was obtained. To the solution, carbon precursor sucrose

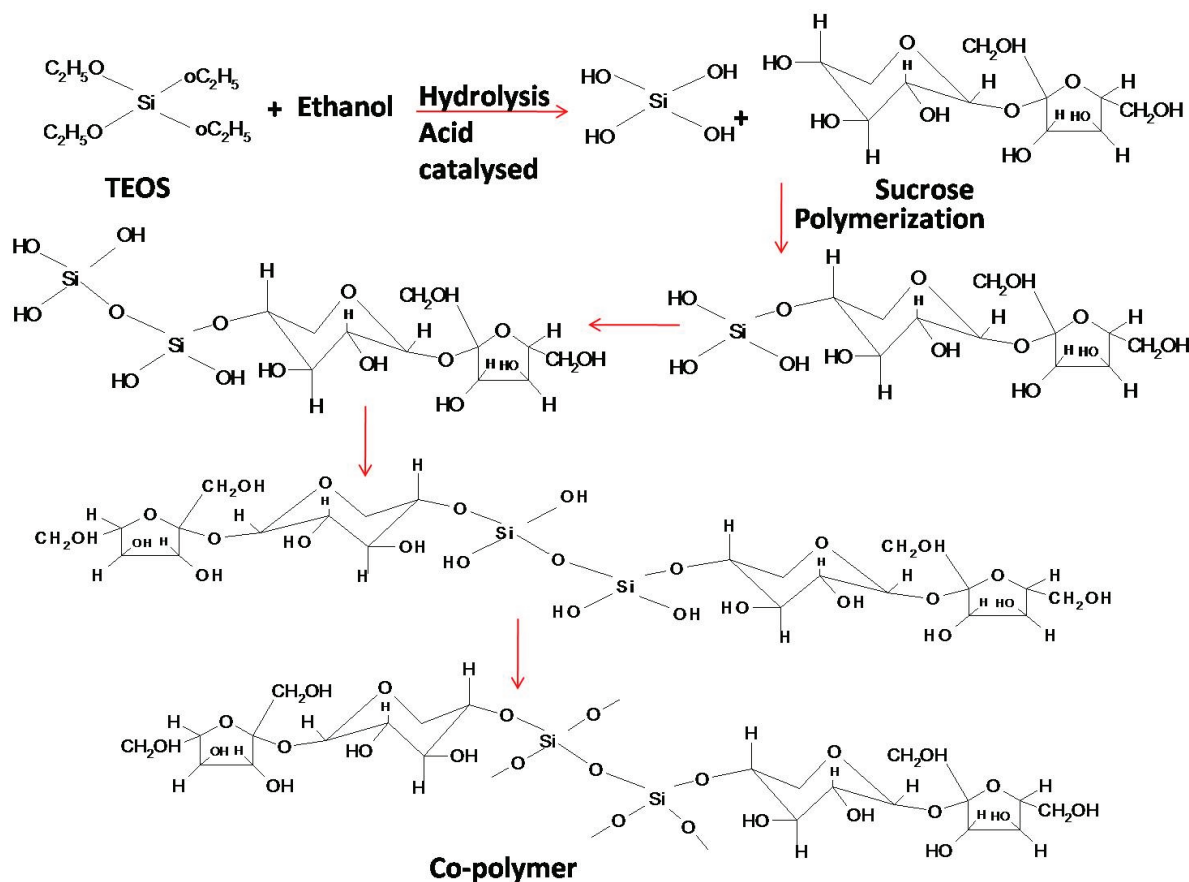


Fig. 1. Formation of Co-Polymer

was added and the reaction was continued to the point of complete hydrolysis.

A reaction for the formation of the co-polymer is shown above. First reaction which takes place between TEOS and ethanol is the hydrolysis step where the ethoxy groups are replaced by hydroxy groups forming hydrolysed silica ($\text{Si}(\text{OH})_4$) and the partially hydrolysed silica then further reacts with sucrose. The hydrolysed silica groups undergo condensation reaction with itself and with sucrose forming a co-polymeric chain as shown in Fig.1.

Preparation of SiC/CNT/SiOC Composites

Preform

SiC/CNTs/SiOC preforms were prepared by the application of aforementioned SiOC sol on the CNT coated SiC cloth by hand layup process. Five such plies of 50 mm length and 20 mm breadth were stacked one upon another to form a preform.

Densification

The density of the preform is usually very low on account of the large number of pores present. Thus, to obtain the desired properties in the final product, densification of the composite is necessary and was carried out by vacuum infiltration technique. Sample is placed inside the vacuum chamber and vacuum is generated within the system. The process removes air from the pores and creates a low pressure within. On account of low pressure the SiOC solution are forced to fill the pores thus densifying the preform. Extent of densification was studied from the

change in weight & density. Apparent density of the composites was determined through physical dimension and weight of the composites.

Characterization

The samples were viewed under SEM Hitachi S-3000N operated at 30 kV to study the growth and morphology of CNTs, SiOC matrix and the infiltration of the matrix. TEM Philips, Tecnai-20 operated at 200 kV was used to examine the tubular nature of CNTs as well as impurities present if any in the CNTs produced by CCVD method. For TEM, the SiC/CNTs samples were ultrasonicated in appropriate medium and then dispersed on copper mesh. Raman spectra were taken with Renishaw inVia Raman microscope using argon ion laser at 514 nm excitation. Using a 50 \times objective the laser beam was focused on an area of $\sim 1\mu\text{m}$.

Result and Discussion

TEM Analysis of CNT

Fig.2 shows the TEM micrographs of the CNTs grown on SiC cloth. These CNTs were separated from the SiC fabric by sonication. The small amount of catalyst particles embedded within the CNTs are removed by acid cleaning as described in Section 2.1, the metallic particles get removed, this is evident from Figure. The dimensions of the nanotubes were in the range of 22 nm to 28 nm.

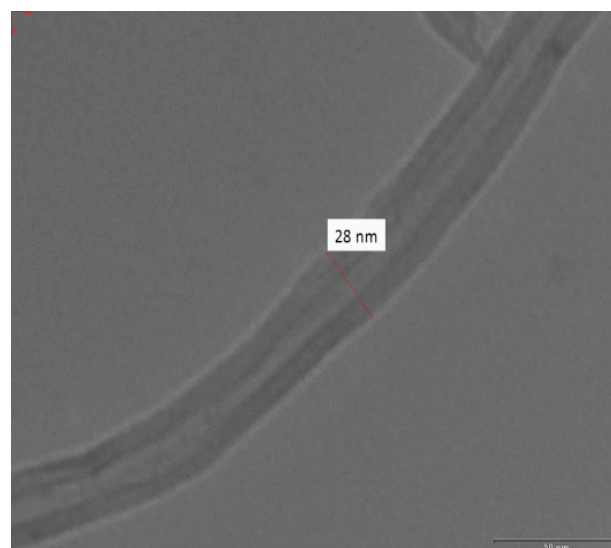
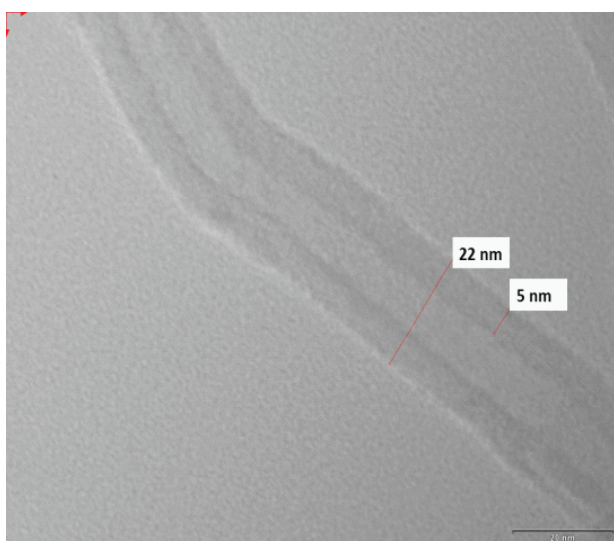


Fig. 2. TEM micrographs of Carbon Nanotubes grown on SiC Fabric

Micro-Raman Spectroscopy

Micro-Raman Spectroscopy is a very useful technique to study the graphitic structure of carbon. The Raman spectra of carbon based materials mainly exhibits two main first order peaks. Fig. 3 shows a D-band at $\sim 1350\text{ cm}^{-1}$ which is due to scattering from a defect which breaks the symmetry of the graphene sheet, whereas the G-band occurring at $\sim 1580\text{ cm}^{-1}$ is basically due to the vibrational mode corresponding to the movement in the opposite directions of the two neighboring carbon atoms in a graphite sheet. The G-band is closely related to vibration in all sp^2 carbon materials. The Raman spectra of SiC fabric indicates the presence of D and G bands of carbon only which is attributed to the disordered carbon coating on the SiC fabric. Since Raman spectroscopy is a surface analysis system the true spectra for SiC fabric was not observed. CNT coated SiC fabric show higher level of ordered structure. The ratio of the intensities of the D-band and G-band are used to determine the amount of disorderedness within the carbonaceous material. The second order Raman spectra, also consists of a dominant D^* line, seen at around 2700 cm^{-1} , which is the second order of the D line 1350 cm^{-1} . The D^*

peak is unique for multiwalled carbon nanotubes. Except the strong D^* band, an additional weak band is observed at 2900 cm^{-1} which is thought to arise from a combination of the Raman modes at 1350 cm^{-1} and 1580 cm^{-1} [21-27].

The spectra for SiOC also show peaks of D band and G band indicating the presence of disordered free carbon present. The ID/IG ratio of the SiC/CNT/SiOC composite is slightly lower than that of pure SiOC. The ID/IG ratio for each spectra is tabulated in Tab 1.

Table 1.

ID/IG ratio derived from Raman spectra

Constituent	ID/IG
SiC Fabric	1.16
CNT coated SiC Fabric	0.81
SiOC Matrix	0.91
SiC/CNT/SiOC composite	0.83

SEM Analysis

SEM Micrographs are indicative of the morphology of the pyrolysed composites. The layer

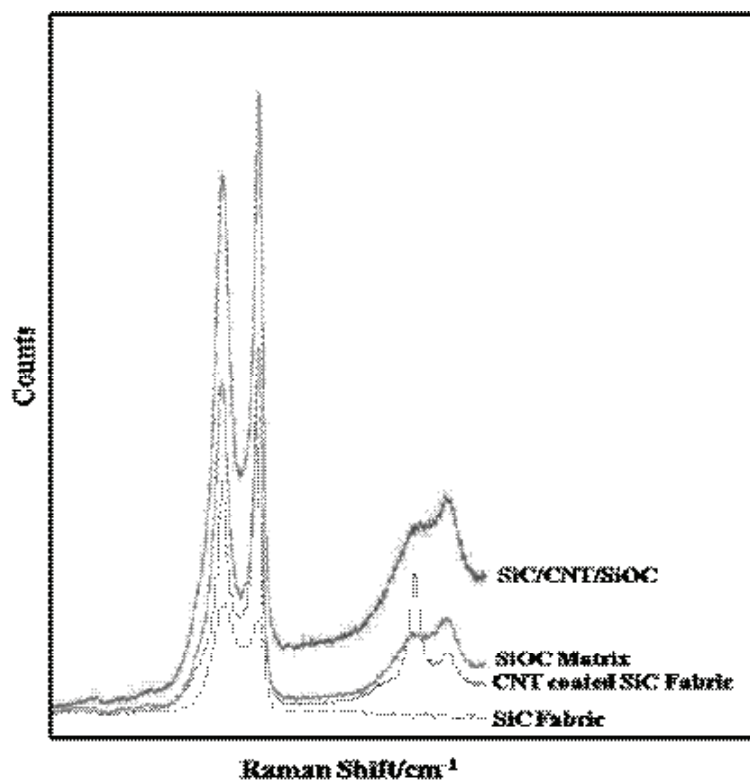


Fig. 3. Raman Spectra of the Various Components in the Composite

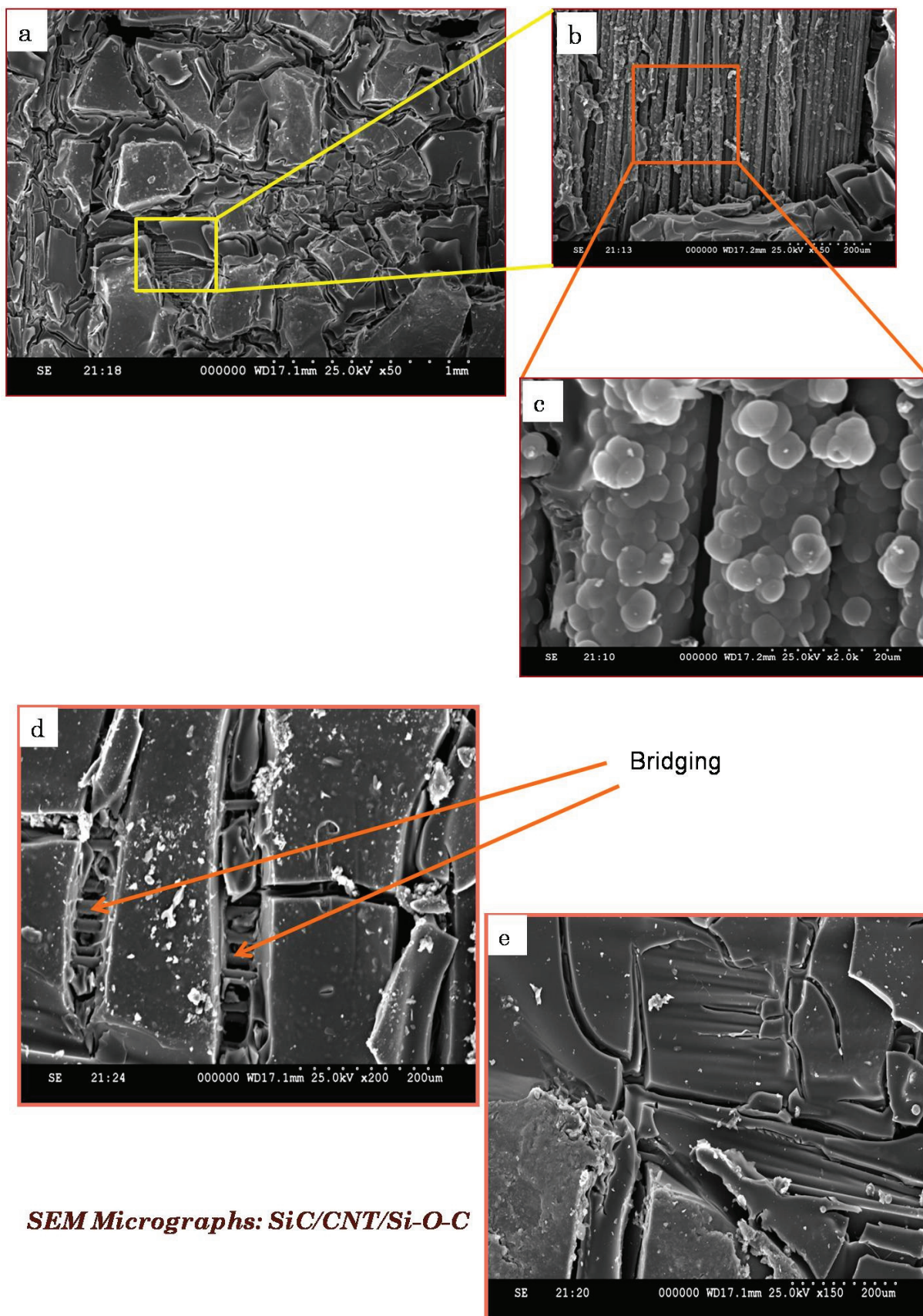


Fig. 4. SEM micrographs of heat treated SiC/CNT/SiOC composites

formation on account of each infiltration is clearly evident from Fig. 4 (a), the presence of a “patchy” matrix is due to solvent evaporation during pyrolysis. A more dense and uniform matrix can be achieved by higher number of infiltrations. Also suggestive from the SEM image is the different morphology of SiOC matrix obtained in each layer formation. Globular structures being formed during one of infiltrations. Bonding of the ceramic matrix to the SiC fabric is enhanced due to the presence of CNT. The SiC fabric acts as bridges between the matrix as shown in Fig.4 (d). The fibres also act as crack deviating points Fig.4. (e).

Conclusion

Carbon nanotube and SiC fabric reinforced SiOC matrix composites were fabricated by the combination of chemical vapour deposition and vacuum infiltration technique. SiOC was successfully prepared by sol gel synthesis. The Raman spectroscopic studies confirm the formation of black glass (SiOC) after heat treatment at 1000°C. The composites however possess low density. Heat treating these composites to a temperature of 1500°C may lead to the formation of SiC, hence these composites may also be used for the synthesis of SiC/CNT/SiC composites as well.

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