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Ceramics International 36 (2010) 749–753

CERAMICS INTERNATIONAL

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A microstructural study of carbon–carbon composites impregnated with SiC filaments

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Received 22 July 2009; received in revised form 17 September 2009; accepted 4 October 2009

Abstract

Porous multidirectional carbon/carbon composite obtained by pulse chemical vapour infiltration (PCVI) was impregnated with silicon carbide (SiC) derived from pyrolysis of polymethylsiloxane resin (PMS). The impregnation process was made to improve oxidation resistance and mechanical properties of MD C/C composite. The resin was used as a source of silicon carbide component of the composite forming after heat treatment above 1000 °C. During this process SiC thin filaments were formed inside the porous carbon phase. The aim of this work was to investigate the structure and microstructure of the constituents of carbon composite obtained after pyrolysis of SiC PMS precursor. Microscopic observations revealed that during careful heat treatment of crosslinked polymethylsiloxane resin up to 1700 °C, the filaments (diameter 200–400 nm) crystallized within porous carbon phase. The filaments were randomly oriented on the composite surface and inside the pores. FTIR spectra and XRD analysis of the modified C/C composite showed that filaments had silicon carbide structure with the crystallite size of silicon carbide phase of about 45 nm. The Raman spectra revealed that the composite contains two carbon components distinctly differing in their structural order, and SiC filaments present nanocrystalline structure.

Keywords: A. Precursors: organic; B. Composites; B. Microstructure; D. SiC

1. Introduction

Recently, one-dimensional forms of SiC, such as nanorods, nanowires, whiskers and submicron filaments became more and more popular subject of investigations. Due to this specific fibrous form of very low volume and inhomogeneities, they are structurally more stable at elevated temperatures. Theoretical calculations indicate that elasticity and strength of such one-dimensional structures are much higher than that of bulk SiC. Due to significant enhancement of the properties of ceramic, metallic or polymer matrix composites this form of silicon carbide is already commercially applied in limited scale. Silicon carbide whiskers have been widely applied as fracture toughness improving component in the ceramic matrix composites, especially in alumina (Al_2O_3) matrix composites for cutting tools [1–3]. Nanosized form of SiC is also used as self-crack-healing agent for improvement of reliability of structural ceramics [4]; at high temperature and in an oxidative atmosphere nanosized silicon carbide located in the ceramics crack reacts with oxygen to form silicon dioxide welding the cracks [4]. The most effective crack-healing-ability for welding over the whole crack was observed while silicon carbide was well dispersed in a material. Dispersion of nanosized and submicron SiC forms in the composite matrix is the main problem in manufacturing of products with well defined microstructural properties. As such materials have the tendency to be agglomerated it is difficult to produce fully homogenous material, and, even if well dispersed, some orientation leads to undesirable anisotropic properties [5]. Whiskers, commercially obtained by either CVD process, pyrolysis of rice husks (ARCO process) or by vapour–liquid–solid process (VLS process) [6–9] are also much more expensive in comparison with additives in the form of particles or fibrous forms.

Carbon/carbon (C/C) composites have received considerable interest for various advanced applications due to their high heat of ablation, small thermal expansion, good strength retention at

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doi:10.1016/j.ceramint.2009.10.015

high temperature and high thermal shock resistance. Application of C/C composites at higher temperatures is limited because of potential oxidation damage and erosion in air above 500 °C. The oxidation of C/C composites and their protection methods against oxidation are well documented in several publications [10,11,12]. The most common way to prevent C/C oxidation is to prepare ceramic coatings on their surface. Brittleness, lack of thermomechanical compatibility of coating and its weak adhesion to the composite surface cause cracking and debonding of the coating resulting in composite oxidation.

Another new and promising way is to use organosilicone precursors to produce SiC in one-dimensional form. Those polymers are valuable precursors of ceramic materials, as their controlled thermal conversion may lead to formation of various ceramic phases [13–17]. Pyrolysis of crosslinked organic polymers from 400 to 1000 °C in an inert atmosphere leads to formation of silicon oxycarbide glass-like material (containing various ratio of Si:C:O) and, at higher temperatures, nanosized ceramic material appeared [13–16]. Moreover, various additives (reactive or inert) may also influence final products of pyrolysis process [13,15,16,18,19]. The structure and microstructure of such materials may vary depending on the type of organic precursor, type of substrate and preparation conditions. The structure and microstructure of fibrous form of SiC was the subject of many works using a variety of methods, such as XRD, Raman spectroscopy, micro-Raman scattering measurement, TEM, Auger electron spectroscopy and IR [20–22].

The aim of this work was to investigate the structural properties of porous carbon composite containing SiC phase. The ceramic phase was obtained by impregnation of carbon specimens with polymethylsiloxane resin (PMS) resin followed by heat treatment to 1700 °C. Such modification of C/C composite allows for further impregnation of porous matrix phase with a ceramic phase in order to obtain non-brittle SiC thin filaments reinforced C/C composites. The microstructure and phase composition of composite consisting of carbon and ceramic phases were investigated.

2. Materials and methods

Carbon/carbon composites (MD C/C composite) were prepared from unwoven carbon fabrics obtained from PAN precursor, with an average diameter of carbon filament 12.3 μm. The carbon fabrics were cut (50 mm × 50 mm × 3 mm) and stacked into the form of blocks. Ten plies of fabrics were then mounted and pressed between two graphite blocks in order to minimize the open porosity of fibrous carbon sample. Such sample was placed into the reactor for densification under pressure by means of pulse chemical vapour infiltration (PCVI). The PCVI process was realized under the following conditions:

- source of carbon–propane,
- time of reactor gas filling—5 s,
- time of reactor gas removing—10 s,
- temperature of pyrolysis—930 °C,
- total time of impregnation—120 h,
- lower pressure – 0.2 kPa, upper pressure – 1 kPa.

The mean thickness of pyrolytic carbon layer deposited on carbon fibres was about 10 μm. The open porosity of such obtained C/C composite sample was 44% by volume, and its apparent density was 0.89 g/cm^3.

C/C composite modified with SiC component (C/C/SiC composite) was obtained by liquid impregnation of carbon preforms (C/C composite) with silicon-containing resin solution. M 130 Lukosil polymethylsiloxane resin produced by Lucebni zavody, Kolin (Czech Republic), that is described in details in [17,19], was used. After impregnation, the samples were air dried to remove the solvent, cured and subjected to heat treatment in argon atmosphere to 1700 °C (heating rate—4 °C/min; total time of heating—7 h). The study was focused on the microstructure and structure of the composite manufactured after one-step impregnation followed by heat treatment to 1700 °C. The final temperature was chosen on the basis of our preliminary experiments in order to determine the temperature of transformation of oxycarbide compound into pure silicon carbide [19].

The microstructure of such obtained samples was characterized by means of scanning electron microscope JEOL 5400. Fourier transformation Raman spectra were collected on Bio Rad, FT Raman accessory spectrophotometer (based on FTS 6000) with Ge liquid nitrogen cooled detector with 4 cm^{-1} resolution. The sample was excited with 1064 nm line of diode pumped, Nd-YAG Spectra Physics laser. Fourier Transformation Infrared Spectroscopy (FTIR) in the range from 600 to 1400 cm^{-1} was applied. The experiments were made on a FTS—60 V Bio Rad spectrometer. The phase composition of composite samples was investigated by XRD diffractometer (Cu K_α radiation, Ni-filtered). The average grain sizes were calculated using the Scherrer equation.

In order to determine and to distinguish various structural and microstructural parameters of carbon constituents in the composite (carbon fibres, pyrolytic phase), the samples of pure pyrolytic carbon (without carbon fibres) were also obtained separately by CVD method with the use of propane as a source of carbon. These samples were obtained at 930 °C and additionally heated to 1700 °C.

3. Results

Fig. 1 shows SEM microphotographs of C/C composite sample after PCVI infiltration with pyrolytic carbon. The sample has highly porous microstructure created by carbon fibres in the form of fabric covered with concentric layers of pyrolytic carbon. Before infiltration the mean diameter of carbon fibres in the fabric was about 10 μm. Pulse chemical vapour infiltration leads to an increase of fibres diameter up to about 40–50 μm (Fig. 1a and b). Such a composite was then impregnated with resin solution, cured at 140 °C and heat treated to 1700 °C.

Following the pyrolysis of the cured resin to 1700 °C, the filaments within the porous space of carbon composite and on its surface were grown, with diameters between 200 and 400 nm and up to 20 μm in length. The filaments were isotropically oriented between the carbon fibrous skeletons of the composite (Fig. 2a–c). The filamentous forms crystallized above 1350 °C by decomposition of oxycarbide phase. This

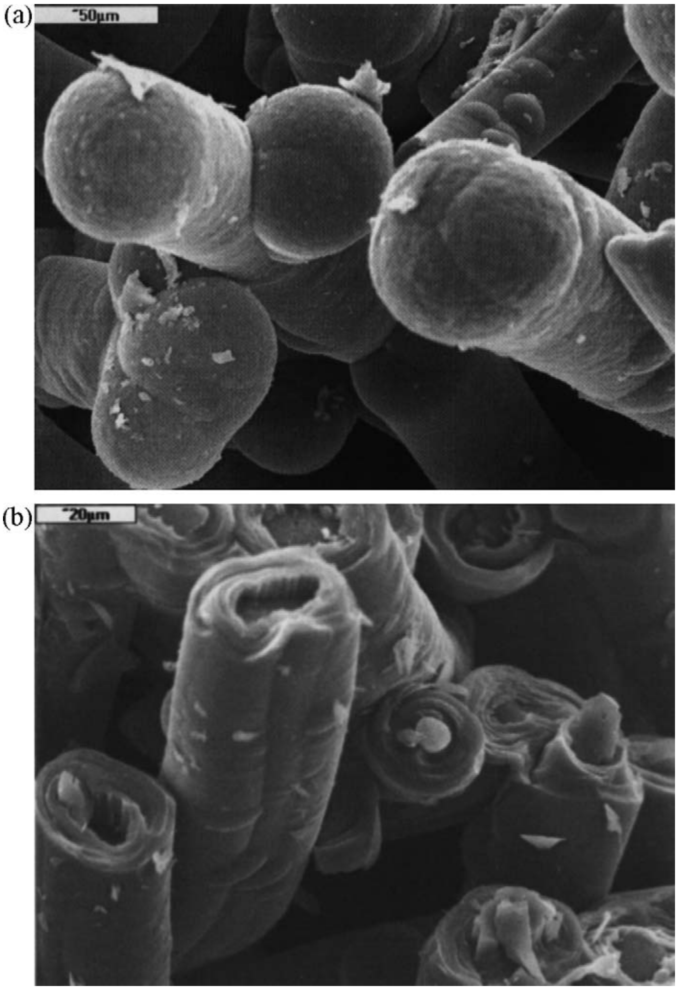

Fig. 1. (a) PCVI carbon/carbon composite and (b) cross-section of PCVI carbon/carbon composite.

compound constitutes an intermediate phase which was formed during pyrolysis of PMS precursor. The probably growth process of the filaments is by VS mechanism (without metallic particles) as the temperature of crystallization process is higher than 1350 °C. The SiO molecules releasing from decomposition reaction of oxycarbide diffuse to the surface of pyrolytic carbon and are condensed to form SiO_2. Following carboreduction reaction silicon carbide filaments are synthesized [8]. EDX analysis of filamentous forms shows the presence of silicon in their structure (Fig. 2d).

Table 1 gathers the values of the crystallites sizes and $d_{0\,0\,2}$ interplanar distance for pure C/C composites obtained at 930 and 1700 °C. The composite consists of two carbon components, namely carbon fibres and pyrolytic carbon phase. The results presented in the table indicate that both carbon phases significantly differ in the crystallite ordering degree. After subsequent heat treatment to 1700 °C the crystallite sizes of both components of carbon sample increases; from 1.0 to 1.2 nm for carbon fibres and from 2.9 to 5.1 nm for pyrolytic carbon phase.

Table 1
Structural and microstructural parameters of carbon components of C/C composites obtained at 930 °C and 1700 °C (crystallite size and $d_{0\,0\,2}$ parameter of single composite phases—chopped fibres and pyrolytic carbon).

Sample	930 °C		1700 °C	
	$d_{0\,0\,2}$ [nm]	L_c [nm]	$d_{0\,0\,2}$ [nm]	L_c [nm]
Chopped fibres	0.355	1.0	0.352	1.2
Pyrolytic carbon	0.345	2.9	0.341	5.1

Fig. 3 presents the XRD patterns of pure C/C composite and the corresponding heat-treated products of C/C composite impregnated with silicon-containing resin. Both types of composites were obtained at 1700 °C. X-ray diffraction pattern of composite containing ceramic residue shows the peaks corresponding to SiC phase and to the presence of pure carbon phase. Analysis of the structure parameters indicates that heat treatment of C/C composite impregnated with PMS leads to formation of 3C and 6H types of silicon carbide (C/C/SiC composite). The calculated SiC crystallites size in this composite is about 45 nm, and is typical for nanocrystalline material. Carbon phase contains the crystallites of 5 nm size, what is in good agreement with the crystallite size determined for pure pyrolytic carbon obtained at 1700 °C (see Table 1). However, carbon material in the composite consists of two components, distinctly differing in the structure ordering. Carbon fibres were obtained from polyacrylonitrile precursor and are characterized by turbostratic structure with disordered carbon arrangement. As it indicates from Table 1, after heating them to 1700 °C, their interplanar distance $d_{0\,0\,2}$ remains relatively high (0.352 nm). Broad asymmetric band of the diffractogram between (2θ) 42.5° and 45° reveals complex nature of the carbon phase structure consisting of turbostratic component of carbon fibre covered with well-ordered carbon layer related to the pyrolytic carbon.

The Raman spectrum (Fig. 4) shows three strong bands at around 1606 and 1284 cm^{-1}, and weak single band at 834 cm^{-1}. This spectrum may be considered as a superposition of three individual spectra consisting of two structurally different carbon phases (carbon fibres and pyrolytic carbon) and ceramic residue from PMS pyrolysis. The bands at 1606 and 1284 cm^{-1} are brought about C–C vibrations of polycrystalline graphite structure. Band at 1606 cm^{-1} is associated with C–C stretching vibrations, typical for well-ordered carbon structure (G band), whereas the 1284 cm^{-1} band (D band) can be attributed to the disordered carbon structure, not appearing in monocrystalline graphite [23,24]. It is evident that carbon composite contains well-ordered graphitic structure related to pyrolytic carbon (G band). The 1284 cm^{-1} band being broader has complex shape and results from the existence of turbostratic fibre and more disordered carbon phase on the boundaries of polycrystalline pyrolytic carbon. Hence, the interpretation of the Raman spectrum relating to carbon constituents is consistent with XRD data. The other bands found in Raman spectrum are associated with silicon carbide phase. The bands in the range of 975–750 cm^{-1} are different from typical spectrum of highly crystallized β-SiC [24–31]. The spectrum of crystalline β-SiC has two strong bands: 972 and 798 cm^{-1} corresponding to the TO phonon

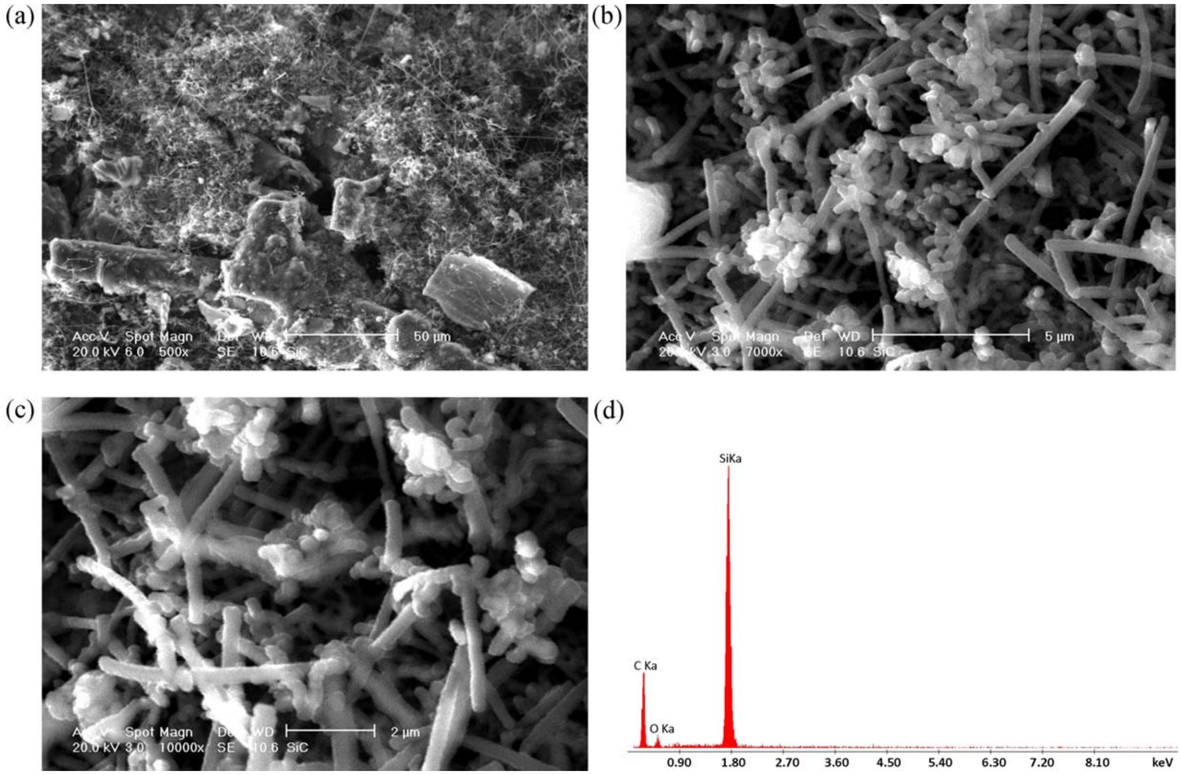

Fig. 2. Carbon/carbon composite with thin filaments (a) magnification 500×, (b) magnification 7000×, (c) magnification 10 000×, and (d) EDX analysis of the filaments.

mode and LO phonon mode, respectively. We found band with highest intensity at 919 cm^{-1}, that is associated with one-dimensional type phase or nanophase or nonstoichiometric phase of SiC [14]. Next band located at 789 cm^{-1} can be assigned to TO phonon mode of 3C–SiC. The band 834 cm^{-1} belongs to another polytype of SiC [33,34]. Those three bands form a complex envelope. In the Raman spectrum of this SiC, as compared to spectrum of bulk crystalline SiC, bands broadening is observed. The broadening is attributed to size confinement effects. Well defined repetitive structures (e.g. crystalline domains) typically give rise to Raman spectra with sharp, well-resolved bands [33]. The bands in the Raman spectrum in the range of (600–400 cm^{-1}) belong to silicon [14].

The presence of silicon carbide can also be detected from reflection and transmission FTIR spectra. Fig. 5 shows the spectra of two broad bands at 810 and 870 cm^{-1} characteristic for nanocrystalline SiC phase [8,25,32].

Spectroscopic investigations of carbon composite impregnated with silicon-containing polymer show silicon carbide structure of the filamentous phase.

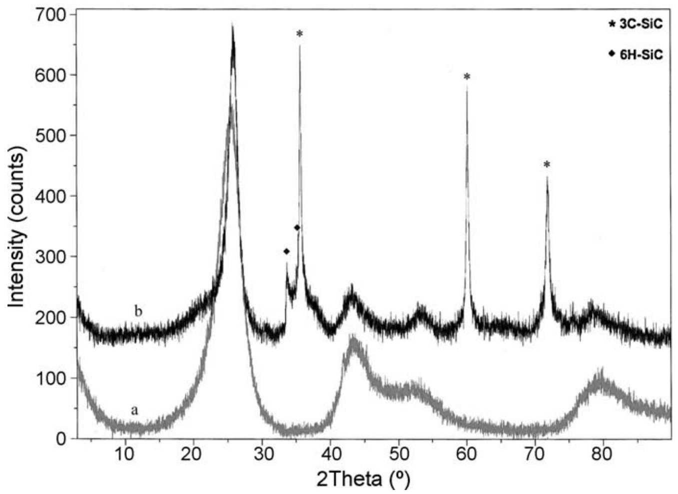

Fig. 3. XRD patterns of pure carbon/carbon composite (a) and carbon/carbon/silicon carbide composite with filaments (b).

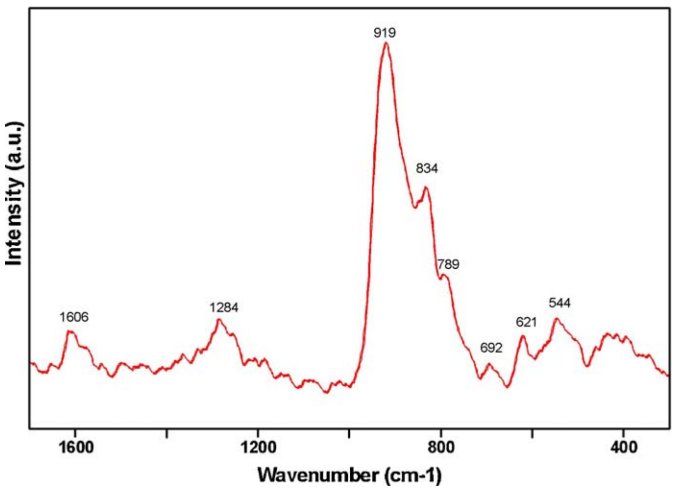

Fig. 4. Raman spectrum of carbon/carbon composite containing SiC filaments.

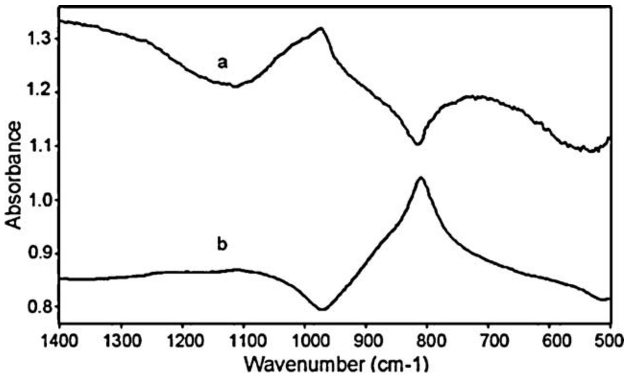

Fig. 5. FTIR spectra of carbon/carbon composite containing SiC filaments (a) reflection spectrum and (b) transmission spectrum.

4. Conclusions

Impregnation of porous carbon composite with polymethylsiloxane resin followed by heat treatment to 1700 °C allows for crystallization of filamentous form of silicon carbide within the carbon matrix. As a result of such a process C/C/SiC composite is formed. Study of the structure of the composite samples with XRD, FTIR and Raman spectroscopy showed that porous carbon substrate consists of well-ordered graphitic and turbostratic structures corresponding to pyrolytic carbon and carbon fibres, respectively. Thin filaments grown from polymer precursor demonstrated polycrystalline SiC with nanocrystallites.

The presented method of manufacturing of SiC filaments may be considered as the first step to obtain non-porous multiphase C/C composite containing thin ceramic filaments. An advantage of this method is homogenous arrangement of SiC filaments on the composite surface and within the pores. The process does not require any complex and hazardous handling associated with SiC filaments. Such a modified C/C composite surface can be filled with ceramic component in order to obtain non-brittle and non-porous SiC filaments reinforced ceramic coating.

Acknowledgements

This work was supported in part by the Polish State Committee for Scientific Research, grant PBZ/KBN/T08/99.

Teresa Gumula is beneficiary of the Foundation for Polish Science (FNP) in 2006 in Domestic Grants for Young Scientists Program.

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