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Organometallic polymer-derived interfacial coatings on carbon and SiC fibers

Natalya Baklanova[a,*], Larisa Zhilitskaya[b], Anatoly Titov[c]

[a] Institute of Solid State Chemistry and Mechanochemistry SB RAS, Kutateladze Street 18, Novosibirsk 630128, Russian Federation
[b] Favorsky Institute of Chemistry SB RAS, Favorsky Street 1, Irkutsk, Russian Federation
[c] General Institute of Geology, Geophysics and Mineralogy SB RAS, Novosibirsk 630090, Russian Federation

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ABSTRACT

Organosilicon and organogermanium polymers containing unsaturated carbon–carbon bonds were used as precursors for the SiC-based interfacial coatings on commercially available carbon and silicon carbide fibers and fabrics. The approach based on usage of the organometallic polymer solutions allowed to obtain uniform, adherent, crack-free and non-bridging SiC-based interfacial coatings on carbon and SiC fibers. The coated fibers retain their tensile strength. The morphology, composition, structure of coated fibers were evaluated by various analytical techniques. The drop-like germanium-containing phase was detected in the organogermanium polymer-derived coating on carbon and SiC fibers.

1. Introduction

Fiber reinforced matrix composites are advanced structural materials for application in civil aviation, power generation gas-turbine engines, and brake disks [1]. There are three critical components to composites reinforced by fibers, namely, matrix, reinforcement, and interface coating. Matrix makes up the majority of the volume of composite and it is what provides the load transfer to fibers and thermophysical properties of the composites. The reinforcement provides the strength and structural foundation or shape for composite and it is typically carbon or SiC-based fibers. The interface coating is a thin coating (usually not more than 200–300 nm) on each fiber.

Two main functions of interphase are to maintain a good load transfer between fibers and matrix and to act as a "mechanical fuse", i.e. to deflect the matrix microcracks [2]. The last is especially important for brittle ceramic and glass–ceramic matrix composites. In addition, in very reactive systems such as metal, glass-ceramic or reaction-bonded SiC matrix composites reinforced by carbon fibers an interphase must act as a diffusion barrier to protect fibers from melted metals, glasses or silicon during the composite fabrication stage. Finally, most composite materials reinforced by carbon or SiC fibers operate at high temperatures and in oxidizing atmospheres. Therefore, interphase must be also oxidation resistant one.

There are several positive examples of the development of oxidative and corrosive resistance interfacial coatings for carbon and SiC fibers. As candidates for carbon and SiC fibers, refractory carbides, nitrides, and oxides were proposed [3–11]. In general, the results showed that an application of ceramic coatings is successful approach to improve the oxidation or corrosion resistance of fibers. Among listed above candidates, SiC itself and in combination with other compounds is widely used as interfacial coating for both carbon and SiC fibers [6–12]. This is because of excellent oxidation resistance SiC.

The most common techniques for depositing SiC coatings are chemical vapor deposition (CVD), physical vapor deposition (PVD), sputtering, molecular beam epitaxy. However, these methods are not always practical and cost efficient. Therefore, there is an interest in the development of alternative techniques of SiC deposition. One such approach involves an organometallic polymer precursors that can be deposited through a liquid route and then pyrolyzed to form a ceramic phase. With this process, it is possible to coat large surfaces, objects with irregular geometry and textile fibers [12–16].

It was stated that the processing of polymer-derived ceramics occurs in three stages, namely, (i) cross-linking of polymer resulting in the formation of rigid three-dimensional network; (ii) transformation of the organic network into inorganic amorphous covalent ceramics by thermolysis; (iii) high-temperature evolution of products derived from amorphous ceramics, and their crystallization [17–19]. Cross-linking occurs at relatively low temperatures in air or in the presence of a catalyst and curing agent. This is determining stage in obtaining a good ceramic yield. Polymers with a high ceramic yield are preferred. Organosilicon precursors to SiC ceramics including those containing germanium atoms in the main chain and triple carbon–carbon bonds are promising in terms of high ceramic yields (66–82%) [20–22]. The cross-linking of these

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[*] Corresponding author. Tel.: +7 383 3363839; fax: +7 383 3322847.
E-mail address: baklanova@solid.nsc.ru (N. Baklanova).

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polymer molecules occurs through the formation of the conjugated bonds and $-CH_2-$ bridges that prevents fragmentation reactions and as a consequence leads to high chemical residue.

The aim of the present work is (i) to study the peculiarities of the formation of the coating on carbon and SiC fibers from organosilicon and organogermanium polymer solution-based precursors and (ii) to characterize these coatings.

2. Experimental

2.1. Initial substances

Syntheses of polysilethyne $(-SiMe_2C{\equiv}C-)_n$ and polygermasilethyne $\{(-SiMe_2C{\equiv}C-)_5GeMe_2C{\equiv}C-\}_n$ have been described earlier [22,23].The elemental composition of initial PSE (wt.%) is 7.34H; 57.84C; 32.48Si; 2.34O and stoichiometry is $SiC_{4.15}H_{6.32}O_{0.12}$. The elemental composition of initial PGSE (wt.%) is 6.68H; 52.93C; 12.63Ge; 25.09Si; 2.67O and stoichiometry is $GeSi_{5.15}C_{25.36}H_{38.40}O_{0.95}$. PSE and PGSE are terra cotta amorphous powders soluble in chloroform to form dark-yellow solutions.

The coating solutions were prepared by dilution of the individual precursors in chloroform solvent. The concentration of solution was varied from 1.5 to 5 wt.%.

Ex-PAN continuous carbon fiber tow type “UKN-5000P” (Russia) and continuous SiC fiber tow and fabrics type Hi-Nicalon^{TM} (Nippon Carbon Co. Ltd., Tokyo, Japan) were used as substrate materials. Prior to coating, fiber tows were desized. They were immersed for 24 h in 50:50 acetone/ethanol mixture for removing a sizing agent, after that they were dried at ambient temperature. Then they were thermally treated in vacuum at 700 °C.

2.2. The coating procedure

The coating procedure involves a dipping of carbon or SiC fibers into 2–5 wt.% preceramic polymer solution and drying. The coated fibers and corresponding organometallic polymers were placed into a quartz reactor connected to a vacuum line. Before each heat treatment, quartz reactor was flushed three times with ultrahigh-purity argon. The samples were heated in argon atmosphere under controlled conditions in the 293–1273 K temperature range. To increase the thickness of coating on fibers a dipping-drying-pyrolysis procedure was repeated.

2.3. Coating characterization

The phases in the coatings were characterized by X-ray diffraction analysis (XRD) using monochromatic Cu-K$_\alpha$ radiation with DRON-3 diffractometer (Russia). Scanning electron microscope SEM LEO 1430VP, supplied by energy dispersive X-ray spectrometer EDX (Oxford) was used for studying of morphology and elemental composition of coated fibers.

2.4. Fiber tensile strength tests

Mechanical tensile tests of the desized initial and coated fibers were conducted at room temperature using FM-4 (Hungary) testing machine. Single fibers extracted from a tow were fixed on paper frame using a hard resin. The gauge of 10 mm in length was used. The diameter of each filament was measured in the middle of length by laser interferometry and used for calculation of mechanical properties. Next, the lateral sides of support frame were cut by a heated wire and the load was applied at constant crosshead speed of 1.3 mm/min. About 50 filaments for each type of fibers were tested. The average diameters for the desized carbon and Hi-Nicalon^{TM} fibers were determined to be equal to $7.49 \pm 0.06\,\mu m$ and $13.11 \pm 0.16\,\mu m$, respectively.

3. Results and discussion

3.1. Polysilethyne derived coating on carbon fiber

Scanning electron micrographs of polysilethyne (PSE) derived coating on *ex*-PAN carbon fibers are represented in Fig. 1a–c. The coating was obtained using PSE with concentration in chloroform of 1.5%, dipping time of 20 s and heating rate not more than $5\,^\circ C\,min^{-1}$. One can note several peculiarities of these coatings. First, the observation of a great number of carbon filaments showed that they are not bridged by coating (Fig. 1a). Second, the coating is rather uniform along length and diameter of filaments and repeats the tortuous relief of the initial carbon fiber. No spalling of coating was observed. One of the reasons could be the fact that chloroform has relatively high boiling point (61.2 °C). As a consequence, solvent evaporation occurs with low evaporation rates. It results in better film coalescence and does not create a high surface tension between the coating and the fibers and within coating itself.

The thickness of coating (one dipping-annealing cycle) was determined to be equal ~150–200 nm (Fig. 1b). The thickness of coatings can be controlled by adjusting either the concentration of polymeric precursor solution, the dipping time or the number of dipping-annealing cycles. Thicker coatings (more than 500 nm) were obtained when the concentration of solution was higher than 5 wt.% or the number of dipping-annealing cycles exceeds two. It was found that thicker coatings, in general, were prone to cracking and debonding. One can see from Fig. 1c, that the coating is formed by the radial oriented nanocrystallites, with crystals having a high aspect ratio. They are aligned in rows along the fiber axe.

According to XRD data, the coating derived from PSE is amorphous one (Fig. 2). Earlier it was shown that the thermolysis of PSE in the 293–1273 K temperature range resulted in the formation of amorphous residue. The formation of greatly disordered silicon carbide together with carbon phase was confirmed by solid ^{29}Si and ^{13}C MAS NMR spectra and XRD analysis [23]. Hence, it could be discreetly proposed that the composition of PSE derived coating is also represented by these inorganic phases. The data reported by

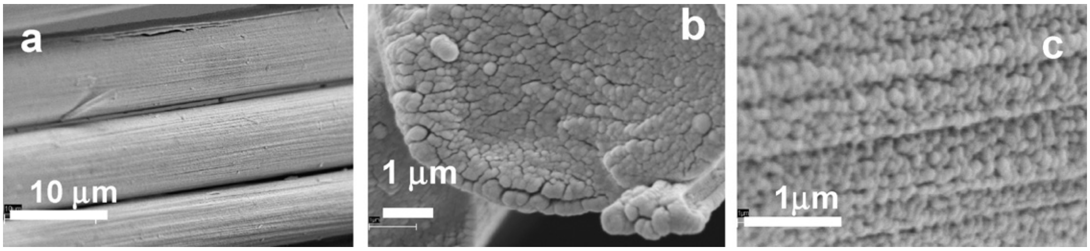

Fig. 1. (a–c) SEM images of PSE derived coating on *ex*-PAN carbon fibers.