

Barrier Coating of Carbon and Carbide Silicon Fibres for Composites with Ceramic Matrix

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Abstract

Hard melting carbide and oxide barrier coatings over carbon and carbide silicon continuous fibres were studied with respect to their morphology, microstructure, composition and resistance to oxidation, as far as these fibres are meant for the arming of composites with ceramic matrix for construction purposes. Coatings are proved to show a good adhesion towards the fibres, and are longwise and crosswise uniform. Coating methods do not permit fibres splicing with each other. Fibres strength after coating remains the same or insignificantly decreases. Composites with carbon silicon matrix, armed with carbide silicon fibres with the interface coatings are characterized by expanded destruction viscosity, provided by the weakening of the fibres–matrix bonding and fibres stretching. Therefore, they may be used as construction materials in various fields, including atomic energy production.

INTRODUCTION

In the 21st century energy production will essentially depend on the increasing necessity for inexpensive energy sources on one hand, and on severe demand towards environment protection and production safety on the other hand. Therefore, nowadays energy production strategy focuses on the development of highly efficient environmentally safe systems for energy conversion and their introduction into practice. With this regard there is necessity for the strong, corrosion resisting and reliable materials with a long service life. Ceramics and ceramic composites seem to become the key components of such systems [1]. Therefore, in material science for atomic energy production composites with ceramic matrix (CCM) armed by ceramic fibres, SiC/SiC composites in particular, attract a lot of engineering attention. They possess all above-mentioned properties, and also well resist neutron and gamma irradiation [1].

Composites with ceramic matrix, armed with continuous silicon carbide fibres, for example SiC/SiC composites, are enough rigid, strong

and heat resistant. However, ceramic matrix is fragile, and it is necessary to improve its impact viscosity in order to enhance its potential [2]. There are several well-known mechanisms of the CCM destruction energy dissipation. One of them is fibres exfoliation and their extraction from the matrix [3]. Fibres protection with a thin barrier coat is a very efficient way to weaken the fibre–matrix bonding and thus to improve the composite destruction viscosity [4, 5]. Various hard melting compounds are tried for the barrier coating [4–6] however this problem still remains unsolved.

In the present study we aim at the design of barrier materials based on the hard melting compounds meant for coating carbon and SiC fibres for CCM. Barrier coatings are investigated with regard to their morphology, microstructure, composition and resistance to oxidation.

EXPERIMENTAL

Carbon braids and ribbons “Kulon” and UKN-5000P as well as silicon carbide fibres and

cloths NicalonTM and TyrannoTM were used as starting materials. In order to form oxide coating we used the sols of alumina, titanium dioxide, zirconia, including the oxides of rare-earth elements (REE), and mixed oxides. Coating procedure included dipping, drying, and heating in vacuum or inert atmosphere [6]. Gas-transport reactions were used to coat with the carbides of hard melting metals of groups IV–VI [7].

Coated fibres were studied using X-ray phase analysis (diffractometer DRON-3, $\text{CuK}\alpha$ radiation), scanning electron microscopy (SEM LEO 1430VP, equipped with spectrometer for energy dispersion analysis), atomic force microscopy (SolverP47Bio, NT-MDT, Russia), micro-Raman spectroscopy (Triplemate, SPEX spectrometer, excitation wavelength 488 nm), and X-ray photoelectron spectroscopy. Resistance to oxidation was studied under steady state conditions in air at 1000 °C in muffle furnace KO-14.

RESULTS AND DISCUSSION

Electron microscopic image of carbon fibre coated with HfC is shown in Fig. 1. Obviously, coating is indeed uniform along and across the fibres, mimics the fibre relief and does not exfoliate from the surface. No fibres' binding happens, if coating is performed *via* the gas-transport reaction. Carbide coating thickness varies from 200 to 300 nm, and is well regulated. Energy dispersion analysis of the HfC coating shows some non-uniformity of the hafnium distribution over the same fibre surface, most likely provided by many surface defects (lengthwise grooves, incrustation) present on the starting carbon surface. Blown up photo, showing the coating structure and morphology peculiarities, reveals a well-distinguished boundary between the fibre and the coating, and no transition zone is observed within the resolution limits. Coating is composed by the nanosize particles gathered in aggregates of round shape.

Figure 2 presents electron microscopic image of SiC/SiC composite with barrier coating TaC on fibre NicalonTM. If one carefully examines the zone of matrix–coating–fibre in the composite, one may notice that this coating is

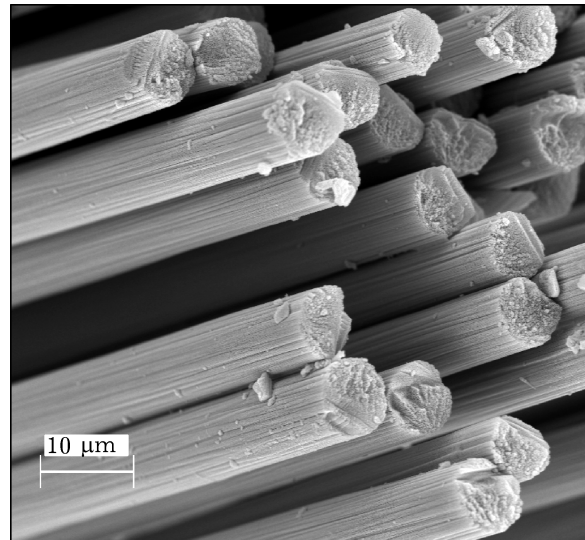


Fig. 1. Electron microscopic image of the HfC coated carbon fibre.

able to deflect the matrix crack. Under composite loading matrix exfoliates from the fibres, and the latter are pulled out of the matrix (see Fig. 2). Composite SiC/TaC/SiC demonstrates viscous destruction, and retains this property after a 24 h exposure in the oxidative atmosphere at 1000 °C.

In the view of resistance to oxidation hard melting oxides such as Al_2O_3 , ZrO_2 , TiO_2 and their mixtures are optimal as the interface coatings on the SiC fibres. Sol-gel method application gives coatings, which are uniform along and across the fibre, have no cracks, and show a good adhesion to the fibre. Investigation

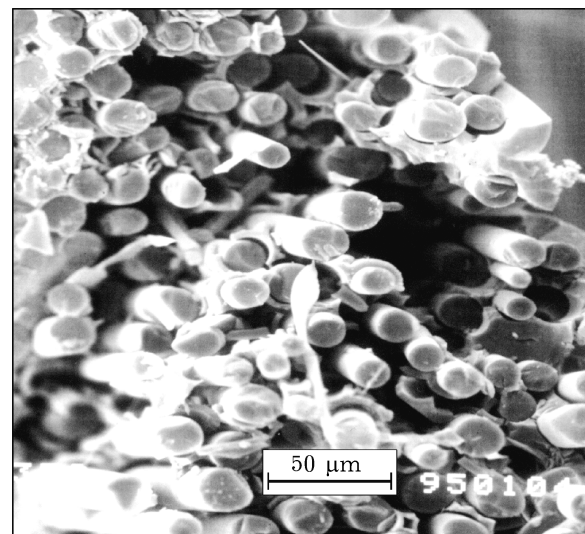


Fig. 2. Electron microscopic image of the SiC/TaC/SiC composite.

of the coatings morphology shows that non-stabilized zirconia and alumina have columnar structure, providing the low energy way for the cracks spread.

Cross sections of initial and $\text{Al}_2\text{O}_3/\text{TiO}_2$ coated NicalonTM fibres are demonstrated in Fig. 3. Apparently, crack spread over the coated fibres is of a zigzag character. "Mirror" radius is smaller in comparison to that of initial fibre, and is less than 1 μm . Experimental data prove that with $\text{Al}_2\text{O}_3/\text{TiO}_2$ coating cracking decelerates, and fibre strength against rupture increases [8].

Zirconium oxide is of particular interest as an interface coating. Owing to the martensite transition of tetragonal modification to the monocline one delamination inside the interface coating becomes possible, providing the viscous character of the CCM destruction. Figure 4 shows the EM images of Hi-NicalonTM fibre coated with ZrO_2 stabilized by the oxides of

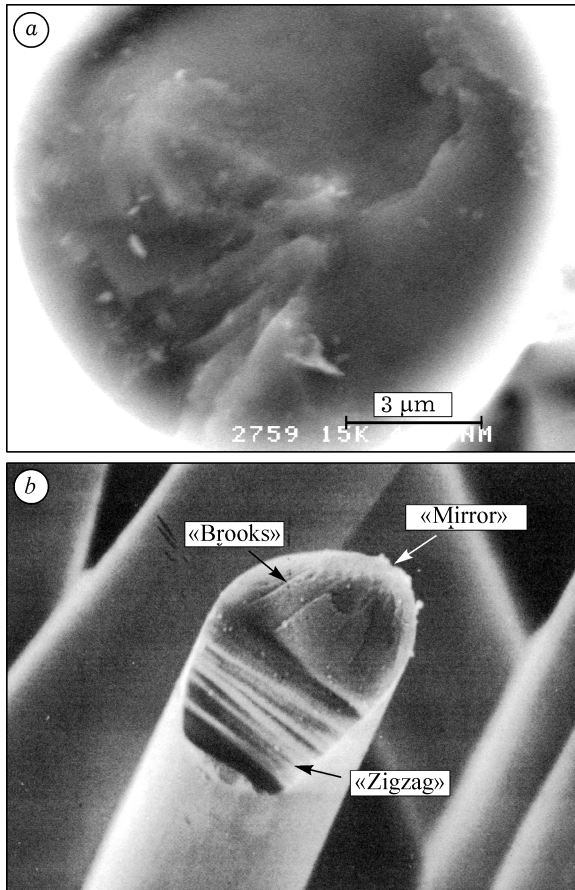


Fig. 3. Electron microscopic images of the silicon carbide fibre cross-sections: *a* – initial fibre, *b* – $\text{Al}_2\text{O}_3/\text{TiO}_2$ coated fibre.

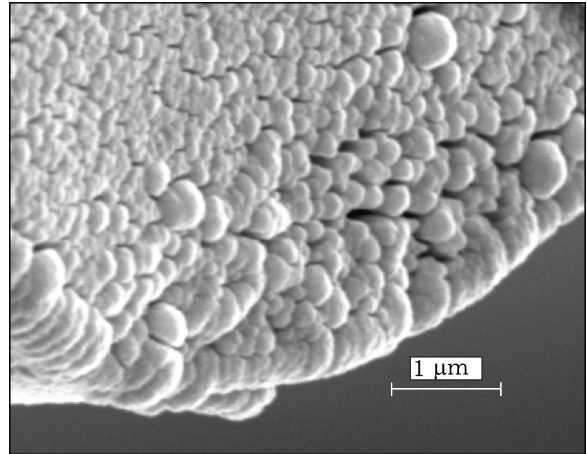


Fig. 4. Electron microscopic image of the SiC fibre with stabilized ZrO_2 coating.

the rare-earth elements. According to the XPS data [9] not only Zr-O-Zr and Zr-O-Re bonds are present in the coating, but also the Zr-O-Si ones. Most likely the latter are responsible for the strong coating adhesion to the fibre. Raman spectra (Fig. 5) confirm that martensite transition of phase ZrO_2 occurs, and is accompanied by delamination inside the coating. Moreover, atomic force microscopy directly demonstrates the martensite relief. Rupture strength normal value for the ZrO_2 coated SiC fibres tested at the ambient temperature is (2.17 ± 0.16) GPa, which is $\sim 13\%$ lower than that for the non-coated fibre.

Oxidative resistance data for the oxide barrier coated NicalonTM fibers evidence that oxidation rate is limited by the oxygen diffusion through the oxide layer [10]. Fibres, coated with non diluted sols *via* several impregnation-

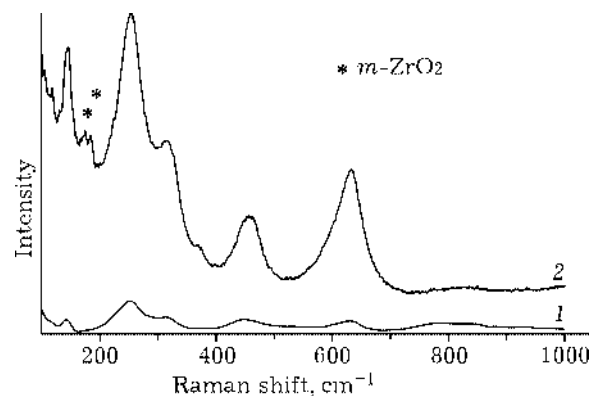


Fig. 5. Micro-Raman spectra of stabilized ZrO_2 coating on the SiC fibre before (1) and after oxidation in air at 1000 °C (2).

drying–heating cycles (4–6), demonstrate the best resistance towards oxidation. Relative mass increase ($\Delta m^2/m_0$) is 0.1–0.2 % at a 30 h exposure of oxide coated (1 cycle) fibres in air at 1000 °C. According to the electron microscopic data, after oxidation no coating exfoliation occurs, and barriers remain intact. Though coated fibres are mostly used as the CCM components and it is unlikely that these will be applied without matrix, our results may help, when composite behaviour in oxidative medium is estimated especially in the case when this composite has open cracks.

CONCLUSION

Therefore, sol-gel and gas-transport methods may be successfully used for coating carbon and ceramic fibres of construction purpose. These coatings have good adhesion to the fibres, are enough uniform along and across the fibre. Both methods allow one to avoid the splicing of fibres with each other. Fibres strength after coating remains the same or insignificantly decreases. Let us note that composites with the silicon carbide matrix armed with silicon carbide fibres with interface coating are characterized by the higher destruction viscosity owing to the weakening of the fibre–matrix bonding and fibres pull out. Therefore, they may be used as construction materials in various fields including atomic energy systems. However, it is necessary

to optimise the properties and composition of the barrier coatings to achieve reliable CCM functioning under sever conditions.

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