

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF CARBON/CARBON-SILICON CARBIDE COMPOSITES PREPARED BY SOL-GEL PROCESSING

MIKROSTRUKTURA IN MEHANSKE LASTNOSTI KOMPOZITOV OGLJIK/OGLJIK-SILICIJEV KARBID, PRIPRAVLJENIH PO SOL-GEL METODI

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In this work the preparation of a C/C composite with SiC precipitates in the matrix was studied. The formation of SiC particles in the matrix was achieved by substituting the phenolic resin used for the preparation of the composites with a phenolic resin-silica precursor prepared with the sol-gel method. The change of the matrix-phase composition resulted in improved mechanical properties of the composites which was attributed to the change in the interface between the matrix and the fibres. The silicon-carbide particles precipitating from the silicon containing a matrix are present directly at the interface increasing the bonding strength between the matrix and the fibres.

Keywords: ceramic-matrix composites, carbon fibres, silicon carbide, sol-gel methods, mechanical properties

V delu smo raziskovali pripravo C/C-kompozitov z izločki SiC v matrični fazi. SiC-delce smo pripravili z zamenjavo dela fenolne smole, ki se uporablja za pripravo kompozitov, s prekurzorjem fenolna smola-SiO₂, ki smo ga pripravili po sol-gel metodi. Zaradi spremembe matrične faze so se izboljšale mehanske lastnosti materiala, kar smo pripisali spremembi na fazni meji med vlaknom in matrično fazo. Delci silicijevega karbida so se namreč izločali na površini vlaken in s tem povečali trdnost spoja med matrico in vlaknom.

Ključne besede: kompoziti s keramično matrico, ogljikova vlakna, silicijev karbid, sol-gel, mehanske lastnosti

1 INTRODUCTION

Non-oxide composites with a ceramic matrix (C/C, C/SiC and SiC/SiC) have aroused great interest in the past years as a high-temperature structural material for use as a construction material in modern engines, braking systems, gas turbines and heat exchangers.^{1,2} On the one hand, we have C/C composites, which are, compared with the ceramic materials, relatively tough and elastic, but have low corrosion and wear resistance and lower thermal conductivity, and, on the other hand, there are C/SiC and SiC/SiC composites with good corrosion and wear resistance and higher thermal conductivity, but they are more rigid and brittle. Recently, new types of C/C-SiC composites were developed, which combine the good properties of all the above-mentioned systems.³ These materials preserve the structure of a C/C composite in the core, which gives the material the required toughness and elasticity; however, on the surface there is a layer of a C/SiC composite with good corrosion and wear resistance, which makes it ideal for use in the advanced braking systems. The weakness of these materials is a thermal-expansion mismatch between C/C in the core and C/SiC on the surface leading to an intensive cracking of the surface layer, which is amplified also

because of the low thermal conductivity of the C/C core perpendicular to the carbon fibres leading to high-temperature differences between the surface and the core.⁴

The aim of this work was to prepare a C/C composite with SiC precipitates in the matrix since such precipitates can improve the mechanical properties and possibly improve the thermal conductivity of the matrix phase. The formation of SiC particles in the matrix was studied by substituting the phenolic resin used for the preparation of the composites with a phenolic-resin-silica precursor (a ceramic-forming polymer) prepared by the sol-gel method.^{5,6} The microstructure and its influence on the mechanical properties of such composites were also investigated.

2 EXPERIMENTAL

The materials used in this study were as follows: for the preparation of all composites staple fibre fabrics (SGL Technik, Germany) were used. The samples of ceramic-matrix composites (CMCs) were prepared by impregnating the fabrics with a precursor produced via the sol-gel procedure from a phenolic resin (resolic type; Fenolit, Slovenia), TEOS (Acros Organic, USA), absolute ethanol (Carlo Erba Reagenti, Italy) and deionised

water with an addition of the mass fraction of concentrated HCl (37 %; Merck, Germany) used as a catalyst. 35.5 % of water was mixed with 33 % of ethanol and 1.5 % of HCl. 30 % of TEOS was added and the solution was mixed for 5 min to obtain a stable sol which was mixed with the phenolic resin for another 10 min in various ratios. The name of the samples, e.g. 50/50, denotes the mass ratio between the phenolic resin and the silica gel used for the preparation of the creamer to be 50 % phenolic resin and 50 % silica gel. All the samples were prepared with a polymer infiltration and pyrolysis process (PIP) with 5 subsequent impregnations and pyrolysis cycles. The carbonisation conditions were as follows: 950 °C, 2 h, a heating rate of 2 °C/min in Ar gas. An additional heat treatment at 1600 °C for 2 h in the flowing argon with a heating rate of 20 °C/min was conducted to allow the matrix phase to crystallise. All the samples were characterised by XRD (D4 Endeavor, Bruker AXS, Germany), scanning (JSM-5800, JEOL, Japan) and a transmission electron microscope (JEM-2000 FX, JEOL, Japan). The flexural strength was measured with a 3-point bending test with a span length of 80 mm (1362, Instron, UK).

3 RESULTS AND DISCUSSION

Figure 1 shows the microstructures of the samples prepared from the precursor synthesised using the sol-gel procedure after the last cycle of the PIP process. In all

the figures the carbon fibres are surrounded by a brighter matrix phase that is rich in silicon. The presence of the silicon was confirmed using an EDXS analysis shown in **Figure 2**. In all the samples the presence of some porosity and inhomogeneity can be seen; there is almost no brighter, silicon-rich phase present in between the fibres in the fabric. The reason for this is a relatively high viscosity of the phenolic-resin-silica ceramer used for the impregnation of the fabrics and the spaces between the fibres, which are not well filled. They are only filled later, during the re-impregnation of the composite with a pure phenolic resin. The variation of the SiO₂-gel/phenolic-resin ratio does not have any influence on the microstructures of the composites after the PIP process.

The microstructures of the samples after the crystallisation heat treatment at 1600 °C are shown in **Figure 3**. At this temperature the precipitation of small nanometric particles can be observed in the matrix phase, preferentially around the carbon fibres. There is also a relatively large amount of free carbon present. After the thermal treatment the influence of the SiO₂-gel/phenolic-resin ratio can be observed, and with an increased amount of SiO₂ gel the number of SiC precipitates increases as well. The precipitates shown in **Figure 4** were analysed using transmission electron microscopy. The results are presented in **Figure 5**. Electron diffraction patterns of the nanocrystalline material, consisting of a few broadened rings and many scattered spots could not be easily analyzed, thus simulated electron-diffraction patterns of

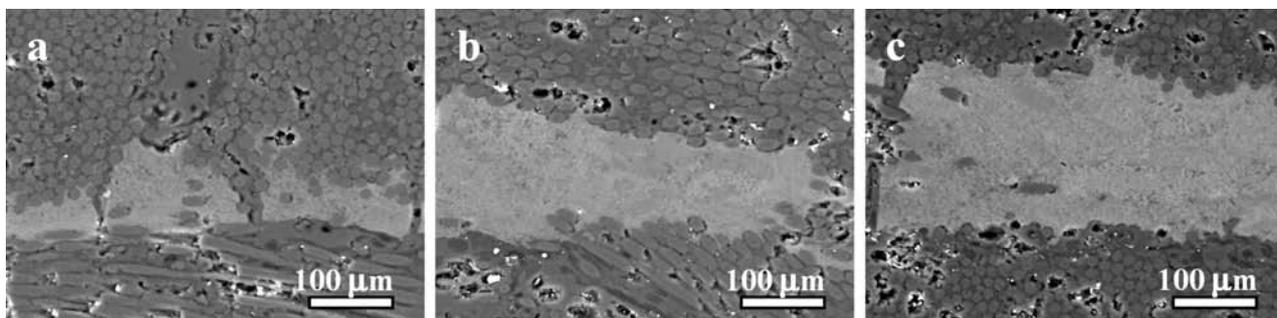


Figure 1: SEM microstructures of the samples prepared from a sol-gel precursor after PIP: a) sample CMC 70/30, b) sample CMC 60/40 and c) sample CMC 50/50

Slika 1: Mikrostruktura vzorca, pripravljenega iz sol-gel prekurzorja po PIP: a) vzorec CMC 70/30, b) vzorec CMC 60/40 in c) vzorec CMC 50/50

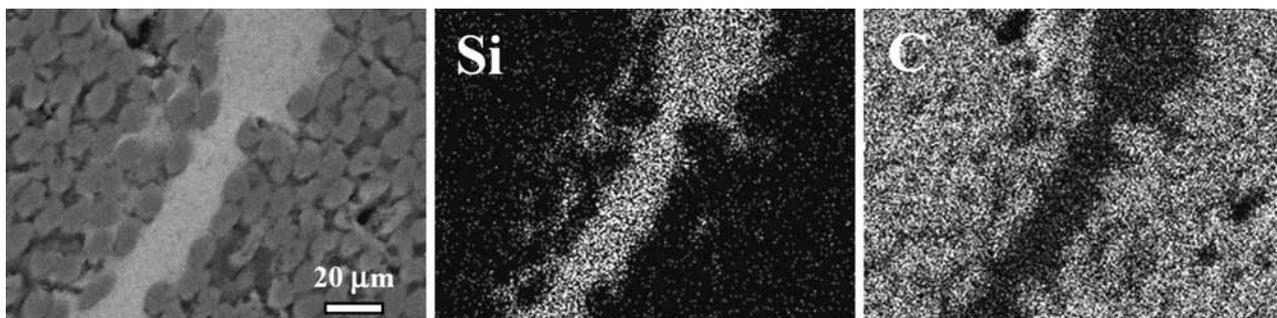


Figure 2: SEM microstructures and an EDX analysis of the CMC 50/50 sample after PIP

Slika 2: Mikrostruktura in EDX-analiza vzorca CMC 50/50 po PIP

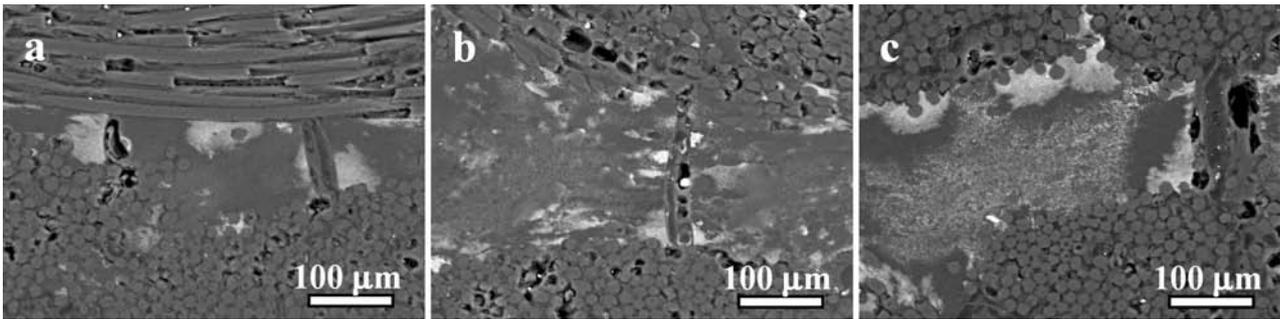


Figure 3: SEM microstructures of the samples prepared from a sol-gel precursor after crystallisation thermal treatment: a) sample CMC 70/30, b) sample CMC 60/40 and c) sample CMC 50/50

Slika 3: SEM-posnetek vzorcev, pripravljenih s sol-gel prekurzorjem po termični obdelavi: a) vzorec CMC 70/30, b) vzorec CMC 60/40 in c) vzorec CMC 50/50

possible candidates were calculated and compared to the experimental diffraction patterns. Based on these calculations it was concluded that nanocrystals have a structure of hexagonal (6H) silicon carbide that are embedded in an amorphous carbon matrix. The comparison of the experimental results with the calculated data for the nanocrystalline material is presented in **Figure 2b**.

In our first attempts the flexural strength of the samples prepared by using the phenolic-resin-silica ceramer was approximately the same as the flexural strength of C/C composites prepared by using only phenolic resin and the values were around 60 MPa.⁴ However, the microstructure analysis showed that the samples prepared by using the phenolic-resin-silica precursor were more porous and contained larger amounts of inhomogenities. For that reason the new set of samples was prepared with more attention paid to the preparation step. The results of the flexural-strength measurements of the new, more homogenous samples, before and after the crystallisation thermal treatment, are presented in **Table 1**.

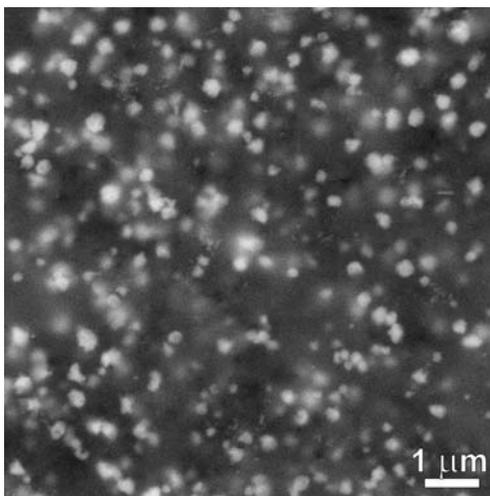


Figure 4: SEM microstructure of a carbon matrix showing nanosized precipitates

Slika 4: Mikrostruktura matrične faze, v kateri so vidni nanometrski izločki

The flexural strength of the samples prepared from the phenolic-resin-silica precursor is somewhat higher than that of the carbon-carbon composite prepared by using just a phenolic resin (sample CMC 100/0). These results are somewhat in contrast with the results of a similar study by Chen-Chi et al.⁷ The presence of the silicon in the amorphous matrix changes the structure of the carbon-fibre-matrix interface and influences the strength. From the results it can also be seen that the crystallisation heat treatment further improves the strength of the composites prepared with the ceramer. The reasons for that are most probably the increased strength of the matrix phase as well as the increased strength of the interface between the fibres and the

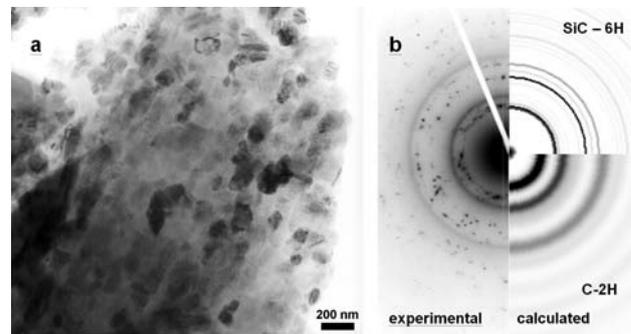


Figure 5: a) TEM microstructure showing nano-precipitates in the carbon matrix, b) experimental and calculated electron-diffraction patterns

Slika 5: a) TEM-posnetek, ki prikazuje nanoprecipitate v ogljikovi matrici, b) eksperimentalna ter izračunana elektronska difrakcija

Table 1: Flexural strength of the samples (SD) after their preparation via PIP and after additional heat treatment at 1600 °C for 2h in the flowing Ar

Tabela 1: Upogibne trdnosti vzorcev (in standardna deviacija) po pripravi preko PIP in dodatni termični obdelavi pri 1600 °C 2h v pretoku Ar

| | CMC 100/0 | CMC 70/30 | CMC 60/40 | CMC 50/50 |
|--|-----------|-----------|-----------|-----------|
| Flexural strength after PIP (SD), MPa | 59 (4) | 62 (5) | 67 (5) | 69 (6) |
| Flexural strength after heat treatment (SD), MPa | 58 (3) | 68 (5) | 72 (6) | 73 (4) |

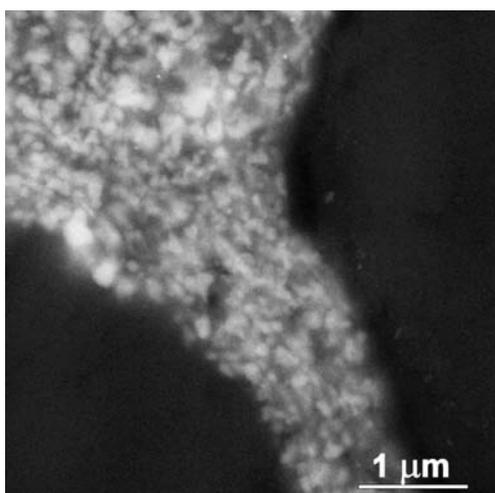


Figure 6: SEM microstructure of the carbon fibre/matrix interface
Slika 6: Mikrostruktura fazne meje matrica/vlakno

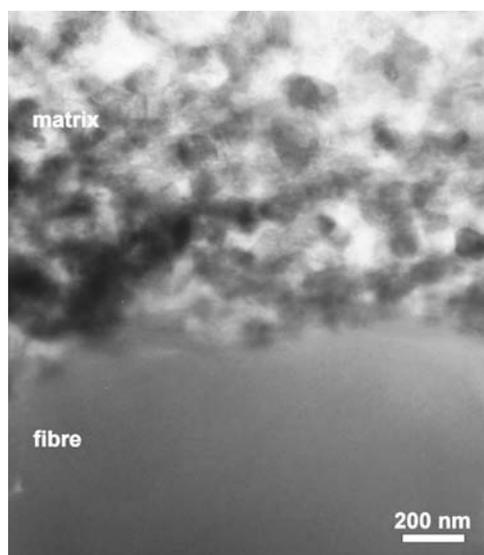


Figure 7: TEM microstructure of the carbon fibre/matrix interface
Slika 7: TEM-posnetek fazne meje matrica/vlakno

matrix, resulting from the precipitation of the silicon-carbide particles around the fibres. In **Figure 6** the fibre/matrix interface of the CMC 50/50 sample is shown. The interface of the sample containing silicon carbide shows the presence of the SiC particles at the matrix-fibre interface that is influencing the strength of the interface resulting in a higher strength of the composite. The interface was analysed using also the trans-

mission electron microscope to verify the presence of the SiC particles at the interface. The micrograph of the interface between the fibre and the SiC particles containing the matrix is presented in **Figure 7**. It can be seen that the SiC particles are precipitating at the interface without any phase visible in between. Obviously, the interface between the matrix and the fibres is changed, which is affecting the mechanical properties of the composite. The bonding is stronger, but not too strong, so the pull-out of the fibres is still visible on the fracture surfaces of the samples. This effect is also the reason for high strength and toughness of these composite materials.

4 CONCLUSIONS

The preparation of the C/C-SiC composites is possible by replacing the phenolic resin with a phenolic-resin-silica ceramer. In the case of the phenolic-resin-silica ceramer the matrix phase contained nanoprecipitates of SiC after the crystallisation heat treatment at 1600 °C in an inert atmosphere. The changing of the matrix phase improved the mechanical properties of the composites, which was attributed to the change in the interface between the matrix and the fibres. The silicon-carbide particles precipitating from the silicon containing a matrix are present directly at the interface increasing the bonding strength between the matrix and the fibres. The presence of the SiC particles on the interface was also confirmed by the TEM microscopy.

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