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Preparation and properties of C/C–SiC nano-composites

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Abstract

Recently, there seems to be a great emphasis on the development of advanced thermostructural composites such as C/C–SiC. In these composites the core is made of C/C composite and the surface is protected by a layer of SiC. Due to the different thermal expansions of the two materials, cracking occurs in the top SiC layer. The solution to this problem would be the preparation of gradient composite with SiC present in the matrix phase. In this work various options for the production of the C/C composite with SiC nano-particles dispersed in the matrix were investigated. Such material will enable the production of C/C–SiC composites with gradient structure form the carbon in the core to silicon carbide on the surface and consequently with improved mechanical and thermal properties. Two approaches were used to enable the in situ formation of the SiC nano-particles in the carbon matrix: one was the synthesis of SiC precursors by sol–gel and the other was the use of ceramic forming polymers, which after the pyrolysis form silicon carbide. The preparation of the composites and its influence on the microstructure and the mechanical properties of composites were investigated.

Keywords: Precursors-organic; Composites; Mechanical properties; Carbon; Silicon carbide

1. Introduction

As material requirements become more and more sophisticated, there seems to be a substantially greater emphasis on the development of the advanced thermostructural composites such as C/C, C/SiC and SiC/SiC, because of their high-temperature strength, thermal shock resistance, low thermal expansion coefficient, good thermal conductivity, hardness, abrasion resistance and low density. The excellent mechanical and thermophysical properties of such composites provide many potential applications for these materials, including re-entry shields, rocket nozzles, disc-brakes and prosthetic devices.[1] On the basis of their characteristics such materials are good candidates for the production of brake discs. Discs made out of these composites are much lighter than conventional metallic ones; this reduces the angular momentum of the wheels and the oscillations during shock absorption, leads to improved driving characteristics and reduces the weight of the vehicle. Of course these materials also have their weaknesses. C/C composites are tough and elastic, but have poor resistance to corrosion and wear and have a lower thermal conductivity. Braking discs made out of C/C composites are in use for aeroplane and racing-car brakes, but for use in regular traffic they have a too slow response in the cold and they wear out too quickly. On the other hand, C/SiC and SiC/SiC discs have good corrosion and wear resistance, good thermal conductivity, but for some applications they are too brittle. Nevertheless, they are already used in some expensive sports cars. The brittleness and stiffness become a problem when the discs are thinner, like with motorcycles, when they can break under high loads. The compromise solution is a C/C–SiC composite that unites the good properties of both groups of materials. In the core we have the structure of the C/C composite, which gives the material the desired toughness and elasticity, and on the surface there is a layer of C/SiC composite with good abrasion and oxidation resistance and the desired stiffness, which makes this material ideal for the production of brake discs. One of the possibilities for the preparation of C/C–SiC composites is liquid silicon infiltration (LSI) of a C/C composite.[2,3] The C/C composite is prepared by the polymer infiltration and pyrolysis (PIP) process using phenolic resin. The weaknesses of such C/C–SiC composites are the low thermal conductivity of the C/C core, which leads to large temperature differences between the core and the surface SiC layer and causes the formation of cracks in this layer due to the differ-

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ences in thermal expansion, and the sharp border between the surface SiC layer and the core material, which can also lead to cracking of the SiC layer. A possible solution to the problem would be the preparation of a composite with improved thermal conductivity, which can be achieved with a matrix material containing small SiC particles and a gradient transition from the carbon matrix in the core of the disc to the matrix phase containing increasing amounts of SiC, and then to the SiC surface.

In the literature we found a method for preparing a layered C/SiC coating for oxidation protection and improved mechanical properties using chemical vapour deposition (CVD).[4] Another useful method is CVI, in which the composite material is prepared by changing the matrix from C in the core to SiC on the surface by changing the precursors that determine the C-to-SiC ratio.[5] Other methods for the preparation of C/SiC composites mainly involve the use of organometallic precursors that form SiC during the pyrolysis and are used for the impregnation of carbon fibres or fabrics during the preparation of the composite. The latest generation of polymeric precursors are used for the impregnation of carbon fibres or fabrics and after pyrolysis form SiC with an efficiency of around 75–85 wt.%. These precursors are easy to use and give excellent products, but they are relatively expensive and can only be used for high-tech components in the military and aerospace industries. Kotani et al.[6] describe new, cheaper precursors based on polyvinylsilanes (PVS), which are easy to synthesise and also form SiC after pyrolysis. However, in this case the product is not stoichiometric, there is always some free carbon present. However, in the case where PIP is combined with reactive sintering[7] or LSI,[8] where silicon reacts with carbon to form SiC, such free carbon is needed in the matrix. Another possibility for obtaining more free carbon in the matrix phase after pyrolysis is the mixing of polymeric precursors with precursors that form carbon, i.e., phenolic resin. SiC precursors can also be synthesised using the sol–gel method tetraethoxysilane (TEOS). The hydrolysis product is mixed with phenolic resin and pyrolysed. During pyrolysis the SiO_2 reacts with carbon, and SiC is formed.[5–11] These precursors are much cheaper but the stoichiometry of the SiC formed depends on the ratio of the SiO_2 and carbon formed during the pyrolysis. The difference is also in the temperature of the pyrolysis, which in this case has to be higher than 1000 °C.

In this work several options for the production of the material based on C/C composite with SiC nano-particles dispersed in the matrix were investigated. Such material will enable the production of C/C–SiC composites with gradient structure from the carbon in the core to silicon carbide on the surface and consequently with improved mechanical and thermal properties. The carbon matrix phase also containing SiC nano-particles was prepared by two techniques: one was the synthesis of SiC precursors by sol–gel from tetra-ethyl-*ortho*-silicate and phenolic resin and the other was the use of ceramic forming polymers, which after the pyrolysis form silicon carbide. The preparation of such C/C–SiC nano-composites and the influence of microstructure and composition on physical properties of composites were 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. Sample CMC 50/50 was prepared by impregnation of fabrics by ceramer produced via sol–gel procedure from phenolic resin (resolic type; Fenolit, Slovenia), TEOS (Acros Organic, USA), absolute ethanol (Carlo Erba Reagenti, Italy) and deionised water with the addition of concentrated HCl (37 wt.%; Merck, Germany) as a catalyst. 35.5 wt.% of water was mixed with 33 wt.% of ethanol and 1.5 wt.% of HCl. Thirty weight percent of TEOS was added and the solution was mixed for 5 min to obtain stable sol which was mixed with phenolic resin for additional 10 min. The name 50/50 denotes the mass ratio between phenolic resin and SiO_2-gel used for the preparation of the ceramer. Sample CMC 03 was manufactured using KiON Ceraset polysilazane (KiON Corp., USA) as the matrix material, and the sample CMC 15 was prepared with Starfire QS polycarbosilane (Starfire Systems, USA) as the matrix precursor. All of the samples were prepared by polymer infiltration and pyrolysis process with the minimum of five subsequent impregnations and pyrolysis cycles. The carbonisation conditions were as follows: 950 °C, 2 h, heating rate 2° min^{-1} in Ar gas. Additional heat treatment at 1600 °C for 2 h in flowing argon with heating rate 20° min^{-1} was conducted to allow the matrix phase to crystallise. Liquid silicon infiltration of the samples was conducted at 1600 °C for 2 h in Ar using silicon powder. All the samples were characterised by XRD diffraction (D4 Endeavor, Bruker AXS, Germany), scanning (JSM-5800, JEOL, Japan) and transmission (JEM-2000 FX, JEOL) electron microscopes, and the flexural strength was measured by three-point bending test with a span length of 80 mm (model 1362, Instron, UK).

3. Results and discussion

In Fig. 1 the microstructure of CMC 50/50 sample, prepared from phenolic-resin–silica ceramer after PIP and after crystallisation heat treatment, is presented. Carbon fabrics surrounded with bright homogenous matrix phase are visible in Fig. 1a. Some porosity and inhomogeneity is also present and there is also almost no brighter, silicon-rich phase present in-between the fibres in the fabric. The reason for this is the relatively high viscosity of the phenolic-resin–silica ceramer used for the impregnation of the fabrics and the spaces between the fibres were not well filled. They are only filled later, during the re-impregnation of the composite with pure phenolic resin. After heat treatment (Fig. 1b) the precipitation of small particles (bright phase) in the matrix can be observed. The matrix phase also contains large amount of free carbon (dark phase).

The TEM investigation of the matrix phase before the crystallisation heat treatment did not show the presence of any crystalline phases, the matrix is completely amorphous. After the crystallisation heat treatment small nanometric grains were found in the matrix phase (Fig. 2). Electron diffraction patterns of nanocrystalline material, consisting of broaden circles, could not be easily analysed; thus, simulated electron diffraction patterns of possible candidates were calculated[12] and compared to

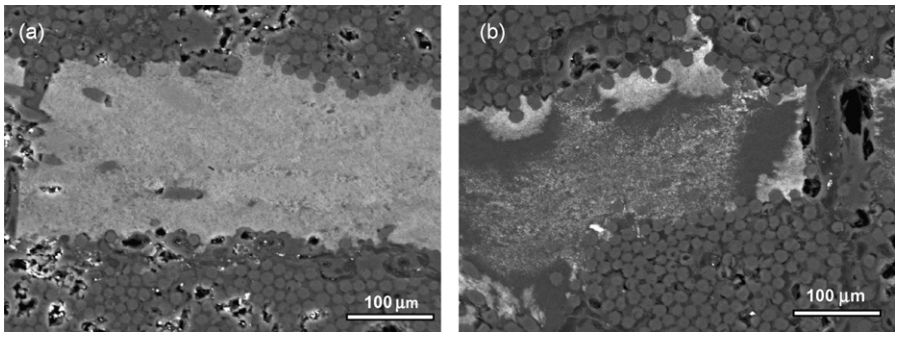

Fig. 1. The microstructures of CMC 50/50 after preparation via PIP (a), and after additional heat treatment at 1600 °C for 2 h in flowing Ar (b).

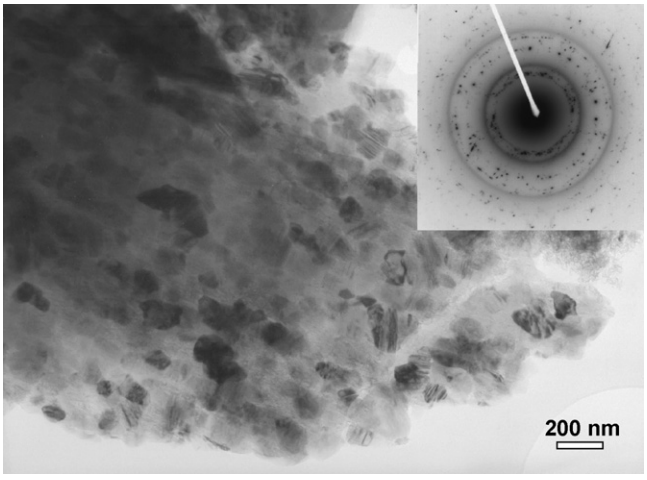

Fig. 2. The microstructure and diffraction pattern of CMC 50/50 matrix phase after additional heat treatment at 1600 °C for 2 h in flowing Ar.

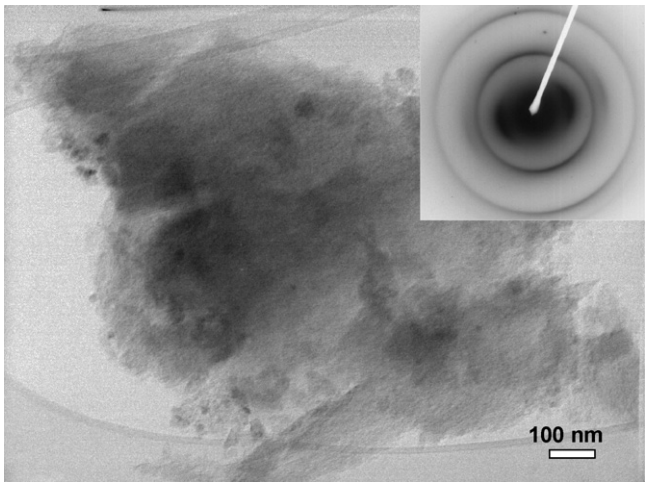

Fig. 4. The microstructure and diffraction pattern of CMC 03 matrix phase after additional heat treatment at 1600 °C for 2 h in flowing Ar.

the experimental diffraction patterns. Based on these calculations it was concluded that nanocrystals have the structure of 6H silicon carbide.

Fig. 3 shows the microstructure of the CMC 03 composite prepared from a polysilazane ceramic precursor. The microstructure of the sample after the PIP process (Fig. 3a) is much more homogeneous than the previous one, the bright phase is also visible between the fibres in the fabrics. After the crystallisation thermal treatment there is no phase separation visible, as with the previous case, but the matrix phase starts to decompose at this temperature and there are a lot of pores and cracks present in the structure.

However, the TEM analysis showed no trace of crystalline phases in the matrix, only very small crystallites of carbon are present as can be concluded from the diffraction pattern (Fig. 4).

The microstructure of sample prepared using polycarbosilane polymer as a matrix forming precursor (sample CMC 15) is presented in Fig. 5. After final carbonisation step, the composite shows some inhomogeneity regarding the matrix phase. After the PIP process there are two phases visible in the matrix: one, a little darker continuous phase in-between the fibres and between the islands of other, brighter phase. The composition of the two matrix phases could not be distinguished by means of EDX analysis. After the heat treatment at 1600 °C, the matrix

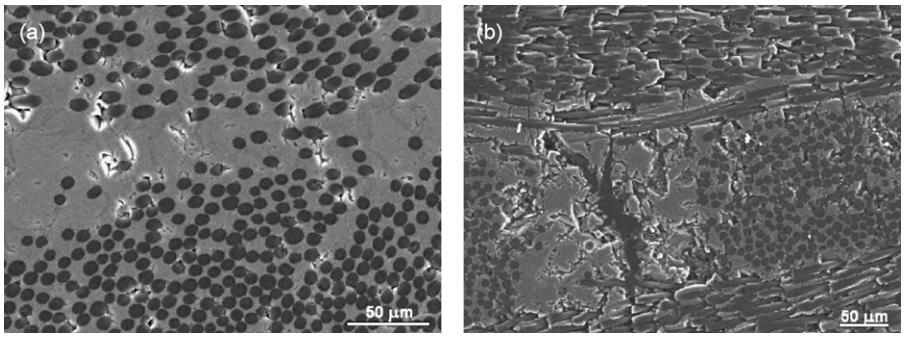

Fig. 3. The microstructures of CMC 03 after preparation via PIP (a), and after additional heat treatment at 1600 °C for 2 h in flowing Ar (b).

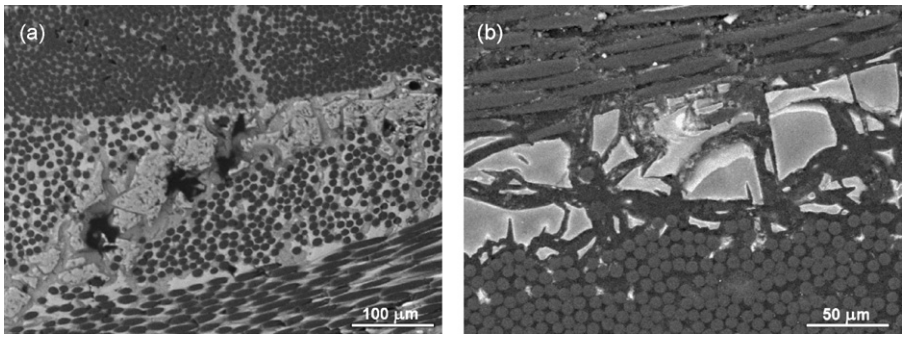

Fig. 5. The microstructures of CMC 15 after preparation via PIP (a), and after additional heat treatment at 1600 °C for 2 h in flowing Ar (b).

phase undergoes severe decomposition; from the microstructure analysis it can be concluded that the darker phase, which was in-between the fibres, evaporated and only islands of brighter matrix phase remained in the sample. The reason for such extensive degradation of the matrix phase probably is a large volume change during transformation to SiC, namely the density of the matrix phase after pyrolysis is around 1.8 g/cm^3 and the density of SiC is 3.2 g/cm^3.

TEM analysis of the matrix phase showed the presence of SiC nano-precipitates in the matrix, similar to those observed in the matrix prepared from phenolic-resin–silica creamer (Fig. 6). The structure of these precipitates was confirmed to be SiC by analysis of selected area diffraction pattern also shown in Figure.

The TEM investigation of the matrix phases of all three samples before crystallisation heat treatment at 1600 °C for 2 h in flowing argon did not show the presence of any crystalline phases, the matrix is amorphous, or the crystallite size is below 1 nm, which is in accordance with the findings of other authors.[13–15] The results from the TEM analysis were also confirmed by XRD analysis of the composites. In Figs. 7 and 8 the diffraction patterns of the samples after PIP process and after crystallisation thermal treatment at 1600 °C are shown, respectively. After PIP no crystalline phases were observed, besides the wide signal of carbon, which is in case of CMC 50/50 and CMC 15 the sum of the signals of fibres and matrix phase, that

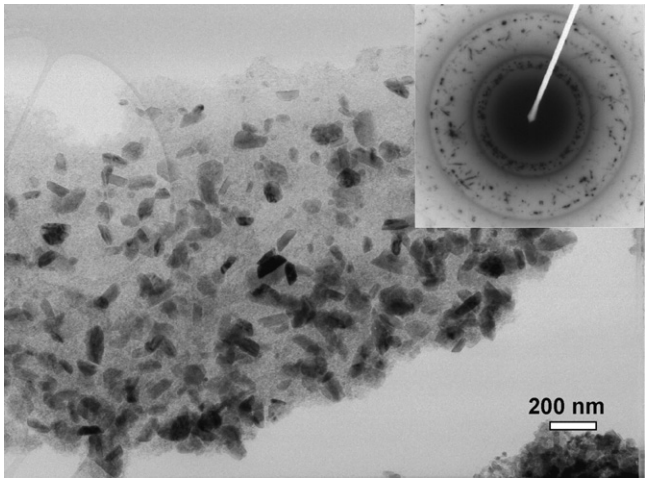

Fig. 6. The microstructure and diffraction pattern of CMC 15 matrix phase after additional heat treatment at 1600 °C for 2 h in flowing Ar.

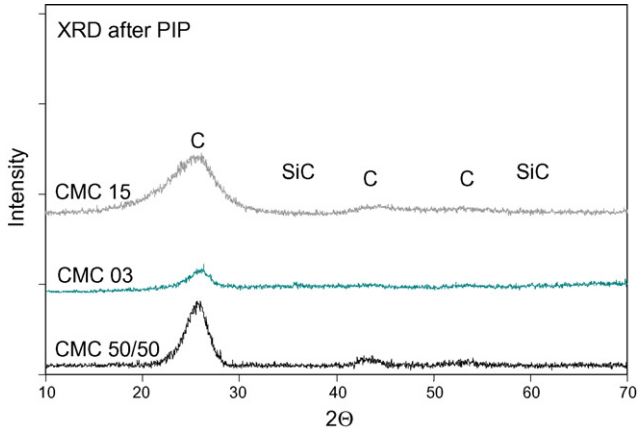

Fig. 7. XRD analysis of the samples after preparation by PIP.

both show very low crystallinity, whereas in the case of CMC 03, there is only a low signal of carbon, presumably originated from the fibres only. After crystallisation thermal treatment, the formation of SiC was confirmed in samples prepared form phenolic-resin–silica ceramer and polycarbosilane, whereas the sample prepared from polysilazane did not show any crystalline phases.

The results of mechanical properties measurements, presented in Table 1 together with mass loss after crystallisation

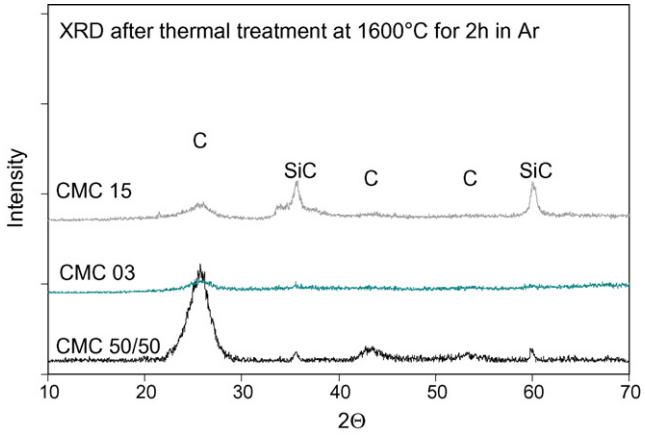

Fig. 8. XRD analysis of the samples additional heat treatment at 1600 °C for 2 h in flowing Ar.

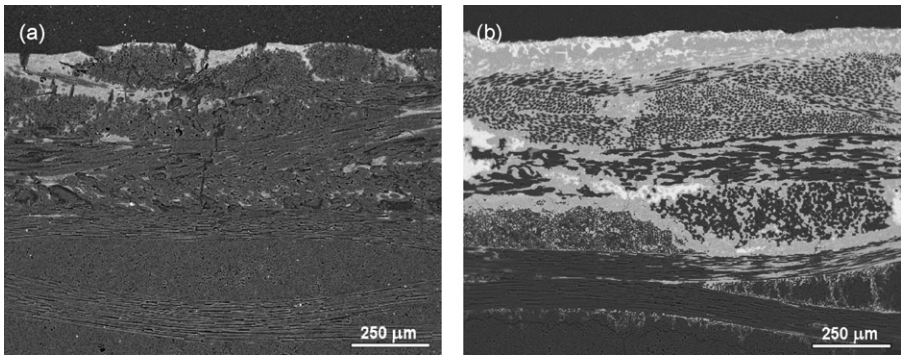

Fig. 9. The microstructures of C/C–SiC composites with gradient structure after the preparation via PIP (a), and after liquid silicon infiltration (b).

heat treatment, are in accordance with microstructural observation. The mass loss of the samples prepared using ceramic forming polymers is confirming the decomposition of the matrix phase already observed by the microstructure analysis. The flexural strength of the CMC 50/50 samples is comparable to the strength of C/C composite prepared only using phenolic resin as a matrix phase, which is 58 MPa. Values for the CMC 03 and CMC 15 samples are much higher, 124 MPa and 94 MPa, respectively. Values are actually in the range requirement for the braking discs. After the crystallisation heat treatment at 1600 °C the strength of the CMC 50/50 sample did not worsen, in spite of a noticeable weight loss. This is not the case with the samples prepared with ceramic forming polymers. Severe degradation of mechanical properties was observed in the latter case, which was also observed by Berbon and Calabrese,[16] who tested the samples prepared with Starfire polycarbosilane. According to their observations, the reason for this is the debonding between the fibres and the matrix phase, also observed in our samples. Actually, the strength of the CMC 15 samples could not be measured because of the delamination of the composite due to decomposition of matrix phase. However, the use of the composites prepared using ceramic forming polymers for the production of disc-brakes would be possible since the structures of the composites after PIP process are very homogenous and the strength values are high enough, but the crystallisation step would have to be omitted. In that case the thermal properties, as well as friction and wear of these new composites, should be further investigated.

To check the possibility of the preparation of the gradient C/C–SiC composite using the prepregs impregnated with the phenolic-resin–silica ceramer, that proved only suitable for use in combination with LSI, regarding the thermal stability as well as price, prepregs impregnated with phenolic resin containing various amounts of silica precursor were stacked into composite. The structure of such material after the PIP process is presented in Fig. 9a. The gradient structure of the matrix phase is visible, in the core of the disc the matrix consists only of carbon, while towards the surface the amount of bright, silicon-rich phase is increasing. This sample was also impregnated with liquid silicon to prepare gradient C/C–SiC composite. The results are presented in Fig. 9b. The resulting microstructure is indeed gradient, with relatively smooth transition from the carbon core to silicon carbide surface. The structure of composite prepared by LSI of pure C/C composite is presented in Fig. 10 for comparison. In this composite, the transition from pure C/C composite to SiC surface is too sharp which is causing intensive cracking of the surface layer due to thermal expansion mismatch.

Table 1
Flexural strength and mass loss of samples after preparation via PIP and after additional heat treatment at 1600 °C for 2 h in flowing Ar

	CMC 50/50	CMC 03	CMC 15
Strength after PIP (MPa)	55	124	94
Strength after heat treatment (1600 °C, 2 h Ar) (MPa)	59	54	–[a]
Mass loss after thermal treatment (%)	6	25	32

[a] Immeasurable.

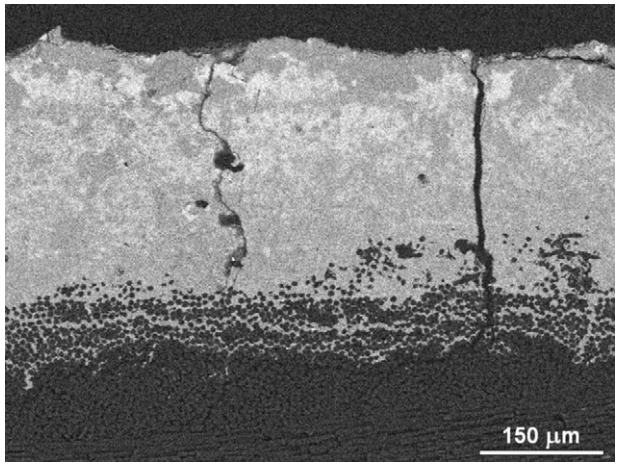

Fig. 10. The microstructures of C/C–SiC composite prepared with LSI of conventional C/C composite.

4. Conclusions

The preparation of C/C–SiC composite is possible by substituting the phenolic resin either with a phenolic-resin–silica ceramer prepared by sol–gel or by a ceramic forming polymer. Phenolic-resin–silica ceramer and the Starfire polycarbosilane lead to the formation of SiC in the matrix, during crystallisation

thermal treatment at 1600 °C, in the form of small, nanometric grains. In the KiON polysilazane matrix no crystalline phases were observed after this thermal treatment. However, when polymer precursors were used, the crystallisation thermal treatment leads to the decomposition of the matrix phase and the subsequent worsening of mechanical properties, which is not the case when phenolic-resin–silica ceramer was used. All these results indicate the phenolic-resin–silica ceramer as the most suitable candidate for the preparation of C/C–SiC composites with C–SiC matrix that will lead to improved thermal properties of the composite if the process will be combined with liquid silicon infiltration for the preparation of dense SiC surface layer. If however the ceramic forming polymers are used for the production of materials for disc-brakes, that would also be possible since the structures of the composites after PIP process are very homogenous and the strength values are high enough, the crystallisation step would have to be omitted. In that case the thermal properties, as well as friction and wear of these new composites, should be further investigated.

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