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Silicide–carbide composites obtained from alloyed melt infiltration

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Abstract The development of a C_f/(Mo, Ti)Si_2–SiC composite using melt infiltration technique was investigated. C/C preforms and also C_f-felts were infiltrated with an alloyed melt of Si, Ti and $MoSi_2$. The amount of each element was selected so that the melting point of the alloy was lower than 1600 °C. It was then possible to prevent the melt from reacting heavily with the carbon fibers and preserve their reinforcing effect in case of the C/C preforms. After infiltration no residual silicon could be detected in the matrix of the infiltrated C/C composites. The infiltrated C/C samples reached a maximum bending strength of 210 MPa at room temperature. At 1600 °C there is even an increase in their bending strength to 250 MPa. Infiltrated felts showed monolithic and brittle characteristics. Their bending strength at room temperature was not higher than 150 MPa. Because of softening of the residual silicon, the strength of the infiltrated felts was reduced at high temperatures. The felt samples which were infiltrated with an alloyed melt showed higher mechanical strength than pure silicon infiltrated felts both at room temperature and at 1600 °C.

Introduction

Silicon carbide-based composites are increasingly used as advanced ceramics [1]. Because of their excellent mechanical properties, high thermal conductivity and excellent oxidation resistance at low and high temperatures, they become promising engineering ceramics having various gas turbine, regenerator and heat exchanger applications [2, 3]. Since the efficiency of these processes and engines increases at higher temperatures it is of great importance to increase the working temperature of these materials [4]. One of the development techniques for the siliconized silicon carbide (SiSiC) is the melt infiltration process, wherein a melt is infiltrated to a porous preform by capillary forces [5, 6]. Production of highly dense composites in a short time and without considerable dimensional changes is a great advantage of this method [7, 8]. However, due to the softening of silicon which remains in the microstructure after infiltration, the upper limit of the applying temperature of SiSiC ceramics is about 1350 °C [9–12]. To increase this temperature, the preforms can be infiltrated with an alloyed melt. This reduces or completely eliminates the residual silicon and thus the lowering of the mechanical properties around 1400 °C can be avoided [7, 8, 13–15]. In order to improve the mechanical behavior of the infiltrated composite at high temperatures this alloy should contain elements which can form high temperature resistant silicides and carbides while reacting with carbon and silicon. Molybdenum is the most favored element for this purpose because it reacts with silicon to form $MoSi_2$. This material has excellent characteristics like high oxidation resistance and a high melting point [16]. Moreover, $MoSi_2$ exhibits a brittle-to-ductile transition in the range of 900–1000 °C, and above this temperature it shows significant metal-like ductility. Therefore $MoSi_2$ can be used to

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improve the fracture toughness of the infiltrated SiC materials [17]. It is believed that the crack deviation at the SiC–$MoSi_2$ interface is the dominant mechanism in this case [18, 19]. It is also reported that there is a good thermodynamic compatibility between SiC and $MoSi_2$ [18–20]. Some researchers have tried to infiltrate liquid $MoSi_2$ into a porous RBSC (reaction bonded silicon carbide) [21]. The combination of properties of SiC and $MoSi_2$ improves the high temperature mechanical behavior of such composites, but their room-temperature strength suffers from microcracking due to large differences in thermal expansions of SiC and $MoSi_2$ [13, 22]. To overcome this problem one can infiltrate such an alloyed melt into a porous carbon fiber preform in order to prepare fiber-reinforced composites. For this purpose, the infiltrating mixture should have a melting temperature below 1600 °C. Infiltration at higher temperatures causes a heavy reaction between the fibers and the melt and consequently spoils the reinforcing effect of the fibers [23]. The melting point of $MoSi_2$ is 2020 °C, meaning that temperatures of at least 2100 °C are necessary to infiltrate a material with this $MoSi_2$. The melting temperature of the infiltrating alloy should then be reduced by addition of silicon and other elements such as titanium. It has been proven in earlier works that titanium is a suitable choice, regarding high-temperature and oxidation behavior of the composite [13].

The aim of this study is then to infiltrate C/C and C-felt preforms homogeneously with a Mo–Si–Ti alloyed melt at temperatures below 1600 °C, so that the evolving composite contains high temperature phases in the matrix and shows favorable mechanical properties from room temperature up to 1600 °C. The bending strength of the infiltrated samples are measured and compared with the samples infiltrated with pure silicon.

Experimental procedure

The infiltration experiments were carried on with two types of carbon fiber preforms (CF222 and FU-2954, Schunk Kohlenstoff GmbH). The CF222 (C/C Preform) contained long fiber bundles that were oriented in two perpendicular directions. Individual fibers in each bundle were embedded in an amorphous carbon matrix. The fibers were coated with a pyrolithic-carbon layer in order to increase their stability against silicon, so that no significant reaction could take place with the melt below 1600 °C. Some of the physical properties of the carbon fiber preforms are listed in Table 1. The structure of the C/C preforms can be seen in Fig. 1.

The C-fibers in the FU-2954 preforms (felts) were not coated and could react with the melt at their surfaces. This preform had randomly fiber orientation and much higher porosity in comparison to C/C preforms. Figure 2 shows the microstructure of the felts which did not have any intentional fiber texture.

The chemical composition of Si: 50 Wt%, Ti: 14 Wt%, and $MoSi_2$: 36 Wt% was selected for the infiltrating mixture in this study (MoSiTi mixture). For this mixture, $MoSi_2$ Powder (99.5% pure) was mixed with Ti (99.4% pure) and Si (99% pure). $MoSi_2$ and titanium powders were purchased from Alfa Aesar (Karlsruhe, Germany) and silicon powder was obtained from Wacker Chemie (Burghausen, Germany).

An induction tube furnace was used for infiltration. It utilized a quartz glass tube which surrounded the heating zone and permitted the observation of the melting process. SiC-coated graphite crucibles were used as melt sources because of their electrical coupling. Temperature was measured using a W-Rh thermocouple.

The MoSiTi mixture was rapidly heated up to 1100 °C (~50 °C/min) and then with a lower rate of 30 °C/min to 1550 °C. The reactor kept the preform separated from the melt during heating. After the complete melting of the infiltrants the carbon fiber preform was mechanically driven into the melt and kept there for 10–15 min. The infiltrated parts were removed from the crucible and cooled down in the furnace. The phase composition and microstructure of the samples were investigated using X-ray diffraction (Philips PW1710 Diffractometer, Netherlands) and SEM (Camscan Cs-4, U.K.) analysis. The presence of residual silicon in the microstructure was also tested using DTA analyses (Netzsch, Germany). Mechanical properties of MoSiTi infiltrated and also silicon infiltrated samples (C/Cs and felts) were measured using universal testing machine (Zwick 1474, Germany) equipped with a graphite furnace. The bending strength of the infiltrated samples was measured by three-point bending tests at 25 °C and 1600 °C under an inert protective gas.

Results and discussions

SEM studies

The MoSiTi infiltrated C/C obtained at 1550 °C had two quite different microstructures in its exterior and interior parts. While in the fully infiltrated exterior parts (0–2 mm under the surface) all the individual C-fibers were surrounded by the solidified melt (Fig. 3a), only larger capillaries between fiber bundles got infiltrated in the interior parts, leaving the non-reacted C-bundles like isolated

Table 1 Physical properties of the carbon fiber preforms used for infiltration

Preform	Fiber orientation	Density (g/cm^3)	Thermal expansion coefficient (K^{-1})	Thermal conductivity (W/mK)	Porosity (%)
C/Cs	0°/90°	1.6–1.65	0.8–1.2*10^{-6}	5 ⊥, 20–40 ∥	6–8
Felts	Randomly	0.13–0.15	2.6*10^{-6}	0.3	40–42

Fig. 1 Woven structure of C/C preforms (SEM, BS)

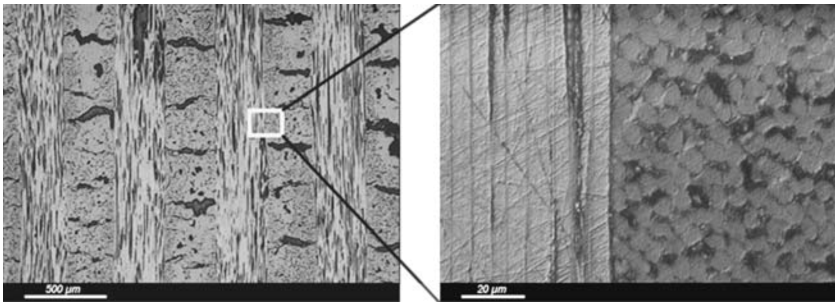


Fig. 2 Randomly orientation of uncoated fibers in felts (SEM, SE)

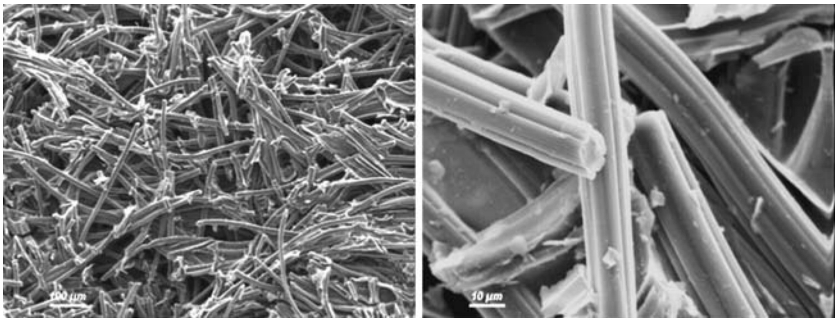
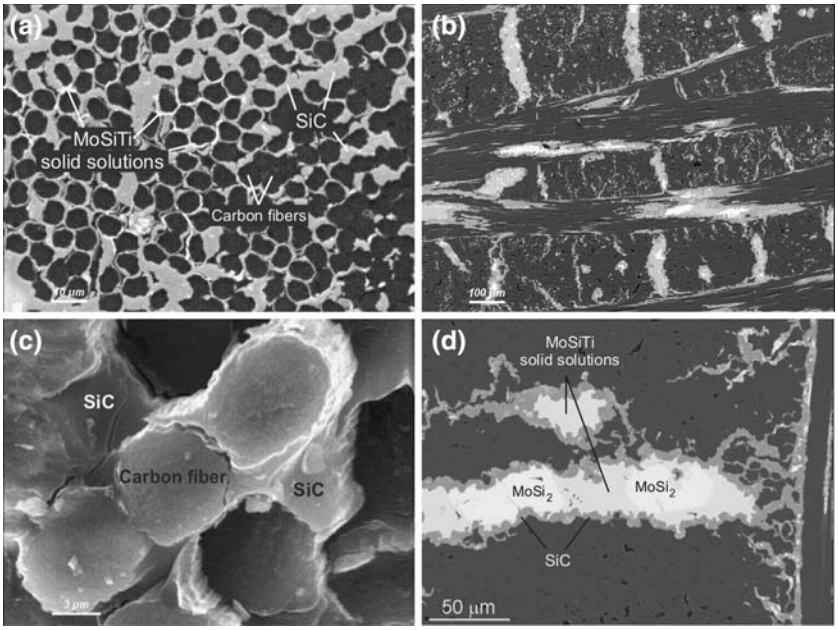


Fig. 3 Microstructure of infiltrated C/C samples (SEM, BS)



islands (Fig. 3b). In the exterior parts, the amorphous carbon in the matrix reacted with silicon from the melt and produced a thin SiC layer around the fibers (Fig. 3c). Apart from SiC, the matrix also included different solid solutions of Mo, Si and Ti as well. $MoSi_2$ grains could be found in the former large pores (Fig. 3d).

In the interior parts, the silicon from the melt reacted with the carbon on the surface of the carbon bundles to form SiC. This SiC layer acts as a melt penetration barrier and retards the next infiltration steps. It is now the diffusion of silicon atoms via SiC layer that dominates the kinetic of infiltration [24]. On the other hand, as the silicon reacts with carbon, the viscosity of the melt increases on its way into the interior parts of the preform. This will also raise the melting temperature of the melt and cause it to solidify before penetrating into the carbon bundles in the interior parts.

The C_f-felts were fully infiltrated with MoSiTi at 1550 °C. The carbon fibers reacted at their surfaces with silicon from the melt to form SiC. The inner part of the fibers remained non-reacted. The fibers lost their reinforcing effect after reacting with silicon. SiC, $MoSi_2$ and $TiSi_2$ were the main phases in the matrix after infiltration. Since the felts had more and larger pores than C/Cs, more infiltrating materials could react with each other in this sample. On the other hand stability of these C-fibers against silicon was lower than that of C/Cs. Therefore a higher amount of silicon reacted with carbon and relatively more SiC was developed in this sample. Molybdenum and titanium were presented as their silicide forms and not in a solid solution. As it can be seen in the Fig. 4, MoSiTi solid solutions demonstrated a phase separation to form $MoSi_2$ and $TiSi_2$. Free silicon could also be found in the infiltrated felts. This amount of free silicon in the sample could not diffuse through the developed SiC layer to react with the carbon in the given infiltration time.

X-ray analysis

The XRD pattern of an infiltrated C/C sample showed the presence of carbon, SiC, $MoSi_2$ and a phase with the chemical composition of $(Ti_{0.8}, Mo_{0.2})\,Si_2$ in the composite [25] (Fig. 5). A considerable silicon peak could not be detected. Other silicides or carbides like $TiSi_2$, TiC and MoC were also not detected as separate phases. Since there was no residual silicon in the microstructure of this composite, its mechanical properties could not suffer from softening of silicon above 1350 °C.

According to the XRD pattern of the MoSiTi infiltrated felt (Fig. 6), SiC was the main developed phase after infiltration and $MoSi_2$ and $TiSi_2$ were other high temperature phases to be found in this sample. It can also be seen that some free silicon was remained in the microstructure. This is a disadvantage for the high temperature mechanical properties of this composite. In order to reach a composite which is free of residual silicon, the infiltration conditions like time and temperature of the infiltration have to be changed for the felts. A weak characteristic peak of carbon could also be detected by XRD (not shown in Fig. 6).

Differential thermal analysis

The presence of residual silicon in the infiltrated C/Cs was also tested using differential thermal analysis (DTA). Figure 7 shows a comparison between the DTA diagrams of two C/C samples, one infiltrated with MoSiTi and the other one with pure silicon. The silicon infitrated sample showed an endothermic peak at about 1420 °C referring to the melting point of silicon. This indicates that there is still some free silicon in the microstructure after infiltration. In case of MoSiTi infiltrated sample, there was no peak in the related DTA diagram; meaning that the MoSiTi infiltrated

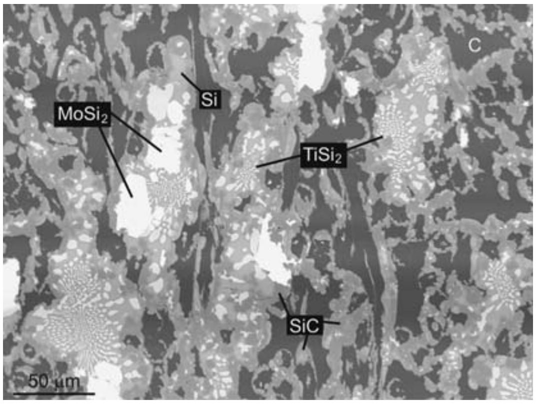


Fig. 4 Microstructure of an infiltrated felt sample (SEM, BS)

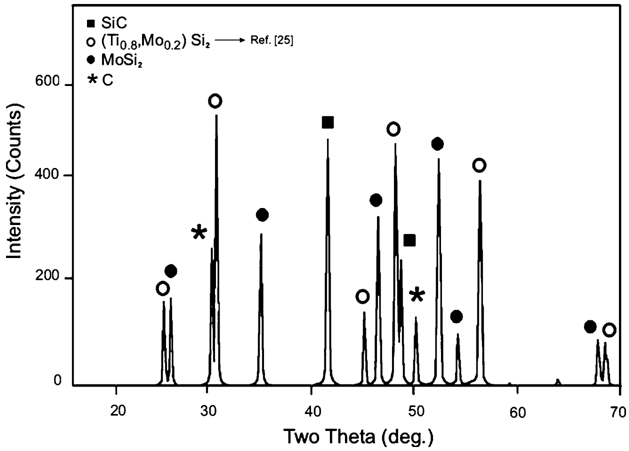


Fig. 5 X-ray diffraction pattern of an infiltrated C/C sample at 1550 °C (Co $k\alpha_{1,2}$, Philips PW1710 Diffractometer)

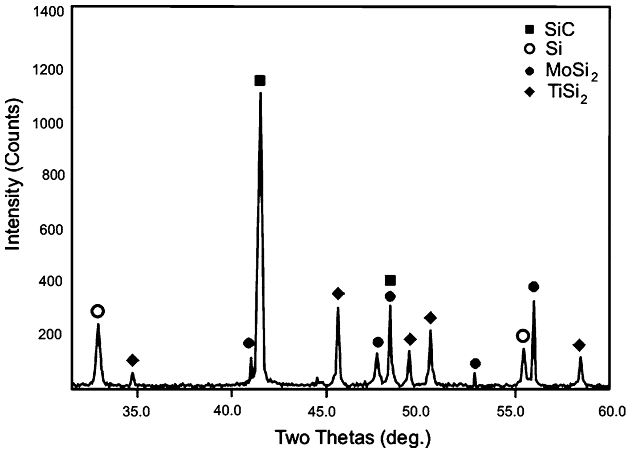


Fig. 6 X-ray diffraction pattern of an infiltrated felt sample at 1550 °C (Co k$\alpha_{1,2}$, Philips PW1710 Diffractometer)

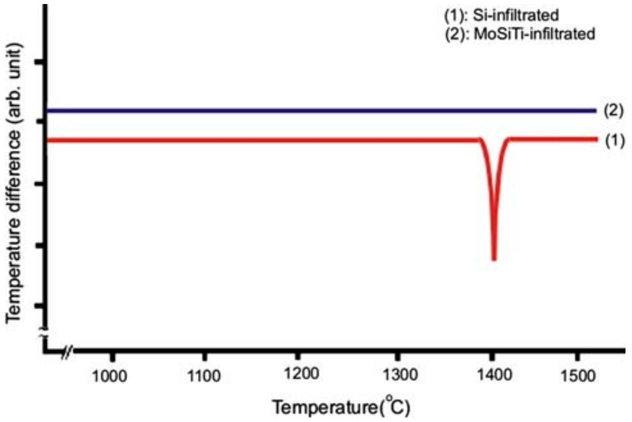


Fig. 7 Comparison between DTA diagrams of silicon infiltrated and MoSiTi infiltrated C/C samples

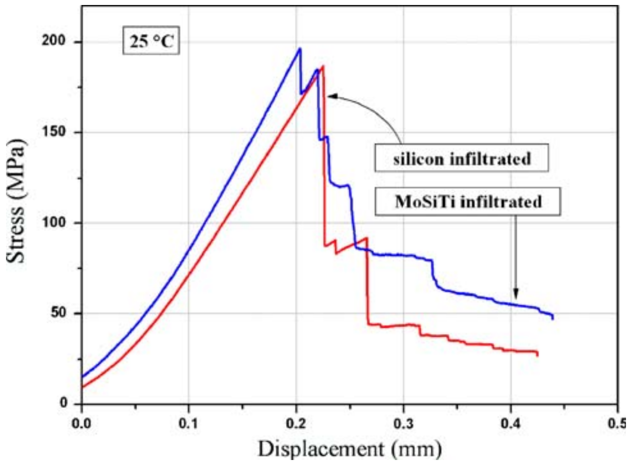


Fig. 8 Room-temperature bending test of a MoSiTi infiltrated C/C compared with a silicon infiltrated C/C

C/Cs do not contain any free silicon in the microstructure and they can demonstrate favorable mechanical behavior up to high temperatures. According to these results the application temperature of these composites can be considerably increased by using the infiltrating mixtures like MoSiTi instead of pure silicon.

Measurement of mechanical properties

In order to evaluate the mechanical properties of the infiltrated samples, four groups of samples were prepared using the infiltration reactor. The different preform-infiltrant combinations and the related bending strengths are summarized in Table 2.

It can be seen that the bending strength of infiltrated C/C samples was higher than that of infiltrated felts both at room temperature and at 1600 °C. This is because of the high volume fraction of carbon fibers (V_f) in these samples. According to the Eq. 1 these fibers can withstand the applied stresses after the matrix is fully cracked [26]. This means the fibers control the mechanical properties of the infiltrated C/C.

$$V_f \geq \frac{1}{1 + \frac{\sigma_f}{\sigma_m} - \frac{E_f}{E_m}} \tag{1}$$

In this Equation, E is the Young's modulus, σ is the strength, and the indexes f and m are related to fibers and matrix respectively. Since both the silicon infiltrated and the MoSiTi infiltrated C/C samples contained the same fibers with the same volume fraction there was also no considerable difference between their mechanical behaviors. As it can be seen in Fig. 8, both of these samples underwent a rupture at applied stress of about 200 MPa, while the loading point was displaced about 0.2–0.3 mm at 25 °C. No catastrophic failure could be observed in both cases. Small differences could be related to the matrix

Table 2 Three-point bending strength of the infiltrated samples at 25 °C and 1600 °C

Samples	Bending Strength (MPa)*	
	25 °C	1600 °C
C/C + MoSiTi	199 ± 3	244
C/C + Si	206 ± 19	246
Felt + MoSiTi	150 ± 7	85
Felt + Si	123 ± 4	56

* Three measurements at 25 °C, one measurement at 1600 °C

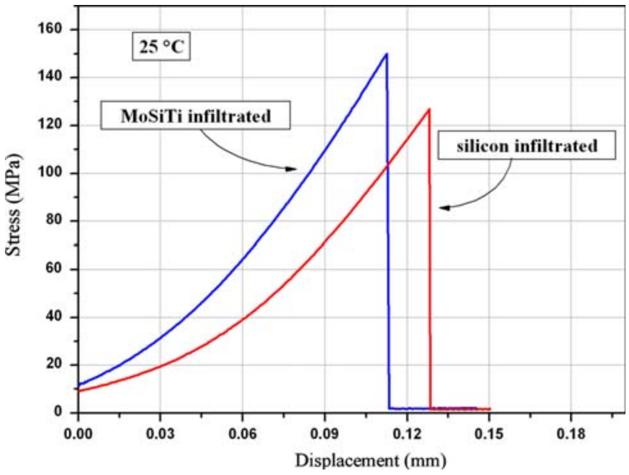


Fig. 9 Room-temperature bending test of a MoSiTi infiltrated felt compared with a silicon infiltrated felt

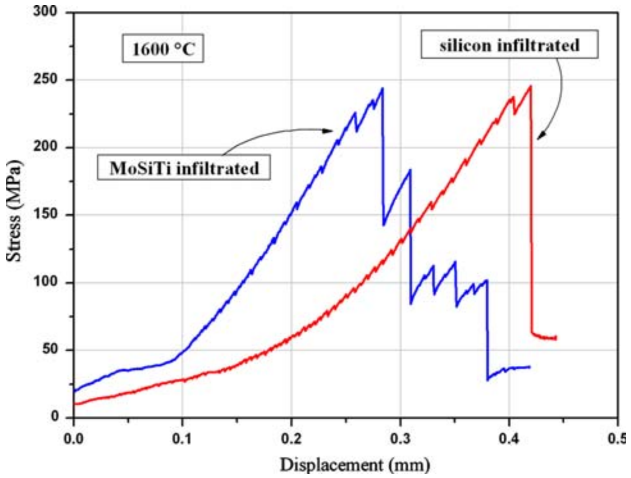


Fig. 11 Bending test of a MoSiTi infiltrated C/C compared with a silicon infiltrated C/C both measured at 1600 °C

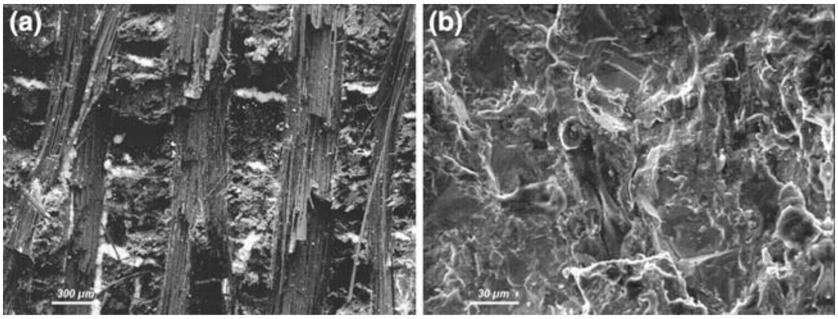
phases. The matrix of the MoSiTi infiltrated sample has less ductile phases than the silicon infiltrated sample. It also suffers from microcracks resulting from different thermal expansion of the phases being present.

Stress–displacement curves for infiltrated felts at room temperature are demonstrated in Fig. 9. The samples showed brittle behavior with a catastrophic failure at the end. MoSiTi infiltrated sample had a higher strength because it contained phases with higher Young's moduli and strength in the microstructure. It should be noted that the fibers lost their interface with the matrix phases and these matrix phases controlled the mechanical properties of the composite. Comparing the bending fracture surfaces from the MoSiTi infiltrated C/Cs and felts (Fig. 10a, b), one can understand the role of fibers and matrices more clearly.

At 1600 °C the strength of infiltrated C/Cs increased for both silicon infiltrated and MoSiTi infiltrated samples (Fig. 11). This is due to an increase of carbon fibers' strength with rising temperature. Such an increase in the strength of different C/C composites was also observed by other authors [27, 28]. At 1600 °C both of the silicon infiltrated and MoSiTi infiltrated samples showed higher values of loading point displacement in comparison to room-temperature tests. MoSiTi infiltrated samples showed higher deformation. This is due to the increase of the ductility of $MoSi_2$ at high temperatures. Large increase in the deformation of silicon infiltrated sample is resulted from partially melting of the matrix phases.

The bending strength of the infiltrated felts was reduced at 1600 °C compared with the room-temperature value (Fig. 12). This is because of the residual silicon in the microstructure of both of these samples. But it is important to see that the bending strength of MoSiTi infiltrated felt was still considerably higher than the silicon infiltrated felt. SEM analysis revealed grain growth and recrystallization processes in the microstructure of MoSiTi infiltrated felt after heat treatment at 1600 °C (Fig. 13). Crystallization of secondary microfibers and also growth of primary crystals help the composite to withstand higher applied stresses. If the residual silicon in MoSiTi infiltrated felts can be removed through optimizing the infiltration time and temperature, this microstructure can be favorable for high temperature application of such composites.

Fig. 10 Fracture surfaces of the C/Cs (**a**) and felts (**b**) infiltrated with MoSiTi after breaking in a three point bending test at room temperature under argon atmosphere (SEM, SE)



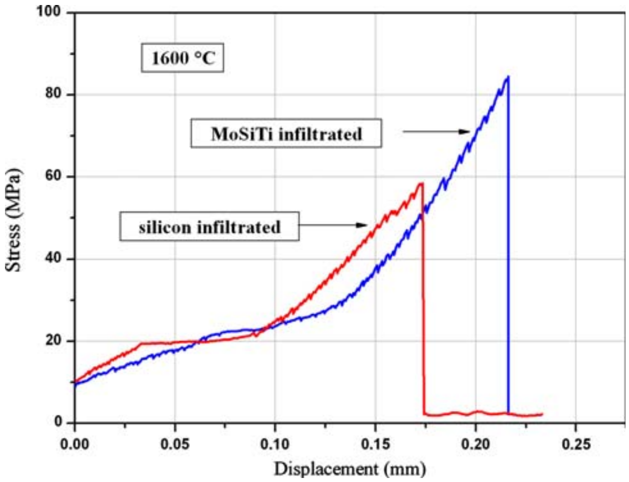


Fig. 12 Bending test of a MoSiTi infiltrated felt compared with a silicon infiltrated felt both measured at 1600 °C

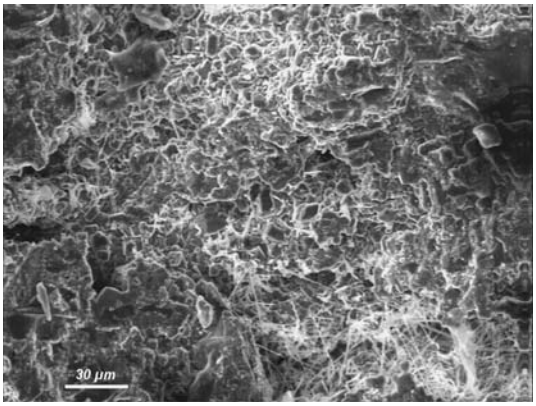


Fig. 13 Fracture surface of the MoSiTi infiltrated felt after breaking in a three point bending test at 1600 °C under argon atmosphere (SEM, SE)

Conclusions

According to the results it is possible to infiltrate a carbon fiber preform with an alloyed melt of Si, Ti and $MoSi_2$ at temperatures below 1600 °C. Under applied conditions, the final C/C composite was free of residual silicon. In case of infiltrated felts and in order to reach a silicon-free composite, time and temperature of the infiltration have to be optimised. The Py-C coated fibers in C/C showed a good resistance against the melt and a weakly bonded interface with the matrix after infiltration. In contrast, the carbon fibers in the felts reacted heavily with the melt and produced monolithic ceramic composites whose room-temperature mechanical properties suffer from microcracking in the microstructure.

Investigations into the mechanical behavior of MoSiTi infiltrated and silicon infiltrated C/Cs and felts released very interesting results. For the C/C samples it was observed that the fibers control the mechanical properties of the final composite and so the bending strength of MoSiTi infiltrated C/C samples was very close to that of silicon infiltrated C/C samples. Strength of these samples was increased at 1600 °C. This was related to an increase of the strength of the fibers themselves.

In case of infiltrated felts the mechanical behavior of the final composite showed to be controlled by the matrix. MoSiTi infiltrated samples were stronger than silicon infiltrated ones both at room temperature and at 1600 °C.

At 1600 °C both of the felt samples showed a sharp decrease in their strengths. This was due to softening of the silicon at elevated temperatures. In a direct comparison, MoSiTi infiltrated samples were stronger at 1600 °C which was due to microstructural effects. Recrystallization and growth of crystals were observed in both types of infiltrated felts. As well as SiC crystals, secondary $MoSi_2$ micro-fibers were found in the MoSiTi infiltrated samples.

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