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Development of a high temperature C_f/XSi_2–SiC (X = Mo, Ti) composite via reactive melt infiltration

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Abstract

A C_f/(Mo, Ti) Si_2–SiC composite has been developed using the melt infiltration technique. Two types of carbon fiber preforms were infiltrated with an alloyed melt of Si, Ti and $MoSi_2$. In order to prevent the melt from reacting heavily with the fibers and keep the reinforcing effect of the preforms, the melting point of this alloy should be lower than 1600 °C. An induction tube furnace was used to infiltrate the carbon preforms. The carbon preform was mechanically driven into the melt and kept there for 10–15 min. The infiltrated samples were studied using XRD and SEM. Silicon free composites could be obtained using this technique. SiC was the major phase of the matrix. $MoSi_2$ and solid solutions of Si, Mo and Ti could be found in the matrix.

Keywords: Composites; Carbon; SiC; Silicides; Infiltration

1. Introduction

Silicon carbide-based composites have a great potential to be used as advanced cermaics.[1] They possess superior mechanical properties, high thermal conductivity and excellent oxidation resistance at low and high temperatures. Because of their unique properties, these ceramics have attracted attention for a variety of gas turbine, regenerator and heat exchanger applications.[2,3] Efficiency of these motors increases at higher temperatures.[4] Consequently, increasing the working temperature of these materials is of great importance. Siliconized silicon carbide (SiSiC) can be produced by the melt infiltration process, whereby a melt is infiltrated to a porous preform by capillary forces.[5,6] Dense composites can be made by this method in a short time with very little dimensional changes and this is a very important factor in fabricating of heat engine components.[7,8] However the SiSiC ceramics can not be used above 1350 °C. Their working temperature is limited by the softening of residual silicon in the microstructure after infiltration.[9–12] To overcome this problem, the preforms can be infiltrated with an alloyed melt of Si that results in elimination of residual Si after infiltration and consequently a constant mechanical behavior above 1400 °C.[7,8,13–15] Components of these alloys should be able to form high temperature resistant silicides and carbides through reactions with carbon and silicon. This will improve the high temperature mechanical behavior of the infiltrated composite. Among different materials molybdenum is the most favored element because it can react with Si to form $MoSi_2$. This material has excellent high-temperature characteristics with a high melting point and high resistance against oxidation.[16] Moreover $MoSi_2$ exhibits a brittle-to-ductile transition in the vicinity of 900–1000 °C, and above this temperature shows significant metal-like ductility. Therefore it is believed that $MoSi_2$ can improve the fracture toughness of the infiltrated SiC material.[17] In this case the crack deviation mechanism at the SiC–$MoSi_2$ interface is said to be dominant.[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 manufacture $MoSi_2$/RBSC (reaction bonded silicon carbide) by infiltrating a SiC preform with liquid $MoSi_2$.[21] 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 substance. This melting temperature can be reduced by addition of silicon and other substances such as titanium. It has been proven in earlier works that Ti is a suitable

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Table 1
Physical properties of the CF222 and FU-2954 carbon fiber preforms

Preform	Density (g/cm^3)	TEC (K^{-1})	Thermal conductivity (W/mK)	Porosity (%)
CF222	1.6–1.65	$0.8–1.2 \times 10^{-6}$	5 ⊥, 20–40 ||	6–8
FU-2954	0.13–0.15	$2.6–1.2 \times 10^{-6}$	0.3	40–42

choice, regarding high-temperature and oxidation behavior of the composite.[13] Although the combination of properties of SiC and $MoSi_2$ improves the high temperature mechanical behavior of such composites, their room-temperature strength usually suffers from microcracking due to large differences in thermal expansion coefficients of SiC and $MoSi_2$.[13,22] The Use of carbon fiber bodies as infiltration preforms can improve the mechanical properties as a result of the fibers' reinforcing effect. If such fiber preforms are used, the infiltrating mixture should have a melting temperature below 1600 °C. Infiltration at higher temperatures can cause a heavy reaction between fibers and the melt and consequently spoil the reinforcing effect of the fibers.[23]

Aim of this study is to infiltrate a C-fiber preform homogeneously with a Mo–Si–Ti alloyed melt at the temperatures below 1600 °C. The developed composite contains high temperature phases in the matrix and may show constant mechanical properties from room temperature up to 1600 °C. Regarding the investigations on the melting behavior of the infiltrating mixtures, an effective method of infiltration will also be suggested in this work.

2. Experimental procedure

Two types of carbon fiber preforms (CF222 and FU-2954, Schunk Kohlenstoff GmbH) have been used for infiltration experiments. The CF222 includes several fiber bundles that are oriented in two perpendicular directions. Individual fibers in each bundle are embedded in an amorphous carbon matrix. The fibers are coated with a pyrolithic-C layer and it will increase their stability against the melt. They are supposed not to react heavily with the melt below 1600 °C. Some of their physical properties are listed in Table 1. The woven structure of the CF222 can be seen in Fig. 1.

The C-fibers in FU-2954 preform are not coated and can react with the melt at their surfaces. This preform does not have any orientation and has much more porosity in comparison to CF222. Some of their physical properties are listed in Table 1. Fig. 2 shows their non-oriented structure.

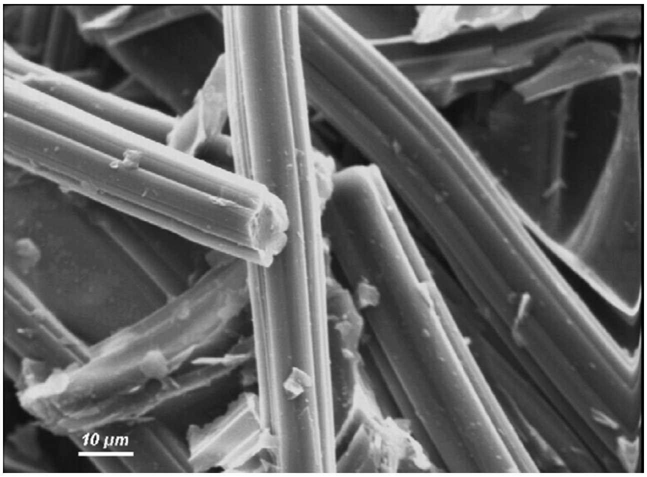

Fig. 2. Non-oriented FU-2954 carbon fibers (SEM, SE).

The infiltrating mixtures with a high $MoSi_2$ content are favorable concerning the high-temperature properties of the composite. On the other hand the mixtures with more than 40% $MoSi_2$ do not melt completely below 1600 °C in this system.

The mixtures should also have an optimized Si content. There should be sufficient Si in the mixtures to help reducing the melting temperature of $MoSi_2$. Adding too much Si will result in some residual silicon in the structure after infiltration, which is not favorable. Commercial $MoSi_2$ powder (99.5% pure) was mixed with Ti (99.4% pure) and Si (99% pure). $MoSi_2$ and Ti powders were purchased from Alfa Aesar (Karlsruhe, Germany) and Si powder was obtained from Wacker Chemie (Burghausen, Germany).

In order to investigate the wetting characteristics of the mixtures, wetting experiments were performed using an optical dilatometer (Hesse Instruments, Germany). Cylindrical samples from different powder mixtures (mixed samples) and also pure silicon have been prepared and put on a carbon fiber plate. The samples and the plate were heated together in a camera-installed tube furnace under vacuum and argon. Volumetric changes of the samples as well as wetting angle at the infiltrant-preform

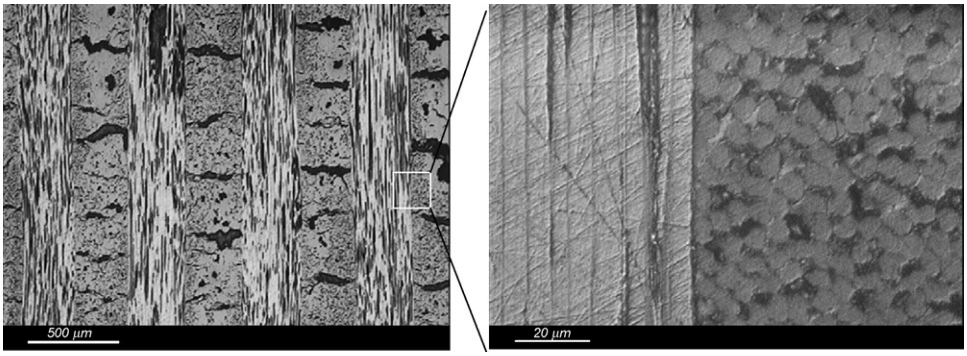

Fig. 1. Woven structure of the CF222 carbon fiber preforms (SEM, BS).

interface were recorded. Microscopic studies were also carried out on the infiltrant-preform interface.

Based on the results obtained from these experiments, one of the mixed samples with the composition of Si: 50 wt.%, Ti: 14 wt.%, and $MoSi_2$: 36 wt.% has been selected as the infiltrating mixture in this study. This powder mixture (MoSiTi) can be completely melted at 1550 °C. The MoSiTi mixture was then pressed to form a tablet using a uniaxial hydraulic press. This tablet was heated up to 1550 °C under argon atmosphere and kept at this temperature for one hour. The microstructure of the molten tablet has been investigated using SEM (Scanning Electron Microscope Camscan Cs-4 (UK)).

According to the last experiments it was necessary to use an effecticve reactor for infiltration experiments. This reactor contains an induction tube furnace and uses a quartz glass tube, which surrounds the heating zone and permits the observation of the melting process. SiC-coated graphite crucibles were used as melt sources because of their electrical coupling potential. 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 rate of 30 °C/min to 1550 °C. The reactor keeps the preform separated from the melt. First after the complete melting of the infiltrants, the carbon fiber preform was mechanically driven into the melt and kept there for 10–15 min.

After taking out and cooling the sample, developed phases were investigated using X-ray diffraction (Philips PW1710 diffractometer, Netherlands) and SEM analysis. The presence of residual Si in microstructure was tested using DTA analyzes (Netsch Gerätebau, Germany) after infiltration.

3. Results and discussions

3.1. Wetting characteristics of the infiltrants

Wetting of the preform by the melt is the most important factor in an infiltration process. The small wetting angles (less than 75°) are favorable for a good infiltration. Optical dilatometry from mixed samples showed that these tablets do not melt properly and also do not wet the carbon fiber plate (Fig. 3a). Silicon tablets, in contrast, melt and wet the preform (Fig. 3b). The geometry of samples changes during heating. These changes can be observed to be shrinkage in the case of mixed samples. Rectangular surface areas of these samples remain unchanged during heating. The wetting angle for these samples will not be less than about 75° at the end of heating. In case of Si samples the geometry undergoes a considerable deformation. It forms a drop of melt at 1600 °C that makes a wetting angle of 39° with the carbon substrate.

Volumetric changes of the samples have been monitored and reported as “shape factor” and “surface area decrease”. Shape factor is a dimensionless parameter usually between 0.5 and 1. It gets the value of 1 when the melt forms an ideal semicircle shape on the wetting surface. Surface area decrease is also a relative dimensionless parameter showing the changes in the surface area of a sample during heating. These changes for a mixed sample and for a Si sample can be seen in Fig. 4a and b. Surface area of the Si sample decreases rapidly after its melting point at 1420 °C. The shape factor of this sample also changes dramatically with the decrease in surface area. The mixed sample keeps its shape almost unchanged even at higher temperatures although a considerable shrinkage can be observed immediately after melting of silicon. After the experiment the porosity of the mixed sample has increased, and its mass decreased compared to the values before and it contained mainly refractory phases rich of Ti and Mo. A thin SiC layer was developed on the carbon substrate. It can be concluded that the molten silicon flows out of the sample and reacts with the carbon substrate at above 1420 °C.

According to the Si, Ti, Mo ternary phase diagram a closed system of these three elements can be melted congruently at 1350 °C, resulting from a eutectic reaction.[24] For the other points on the phase diagram there will be an incongruent melting; meaning that one of the elements melts first and gradually dissolves the two others. In this case Si is the first element that melts. With an increase of temperature the two remaining elements dissolve gradually in the Si. This process will end in a homogeneous liquid solution (above the liquidus line). Any physical or chemical removal of Si from this system can delay the melting or even prevent it until very high temperatures. A

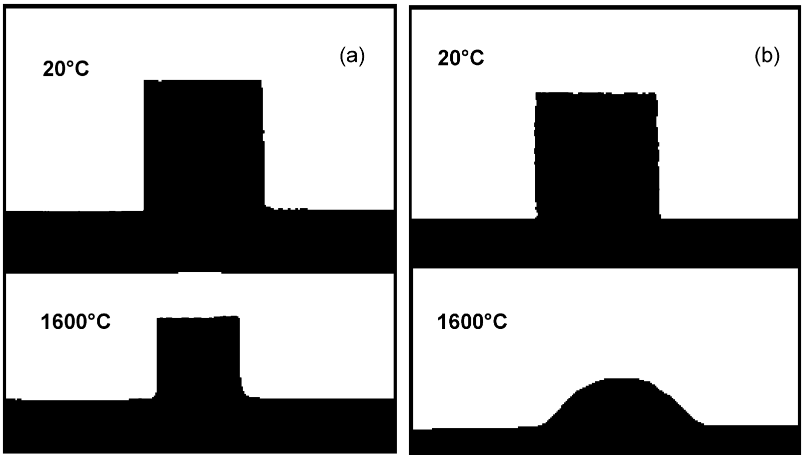

Fig. 3. Deformation of mixed and Si samples placed on C-preform while being heated up to 1600 °C under argon atmosphere; (a) mixed sample, (b) Si sample.

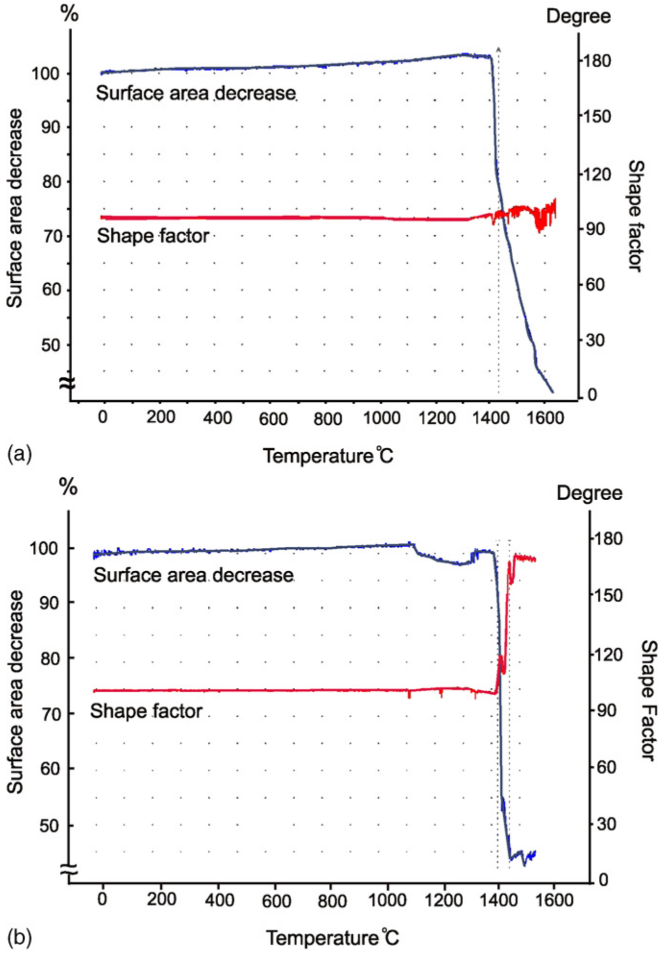

Fig. 4. Dilatometric changes of the infiltrants while heating up to 1600 °C under argon atmosphere. (a) mixed sample, (b) Si sample.

very important result can be obtained from these experiments: In order to complete the reactions between the different phases in the powder mixture. Silicon should be prevented from leaving the mixture till 1550 °C. In other words there should be no contact between the infiltrants and the preform before this temperature. In order to do this, an effective infiltration reactor has been designed and built in this work.

3.2. *Characterisation of the infiltrating mixture*

According to the last results, the phase developments and reactions, which take place in the infiltrating mixture during heating should be studied before infiltration. Among different powder mixtures one of them which could satisfy the above mentioned conditions has been selected (MoSiTi mixture). Fig. 5 showes the microstructure of MoSiTi mixture after heating up to 1550 °C under argon atmosphere. $MoSi_2$ is localized in the center of the white big grains. This white big grains are relatively well distributed all around the sample. Solid solutions of Si, Mo and Ti with different chemical compositions surround the $MoSi_2$ in each grain. Concentration of Ti in these solid solutions is high at exterior parts of the grain and it is low in the center. Residual silicon is not present in this sample. Si is present only in combination with Ti and Mo. Semi quantitaive chemical analyzes concerning some points on this sample are presented in Table 2. It is clear to see that all of the phases have reacted with each other. It can be concluded that the MoSiTi sample is completely molten at 1550 °C.

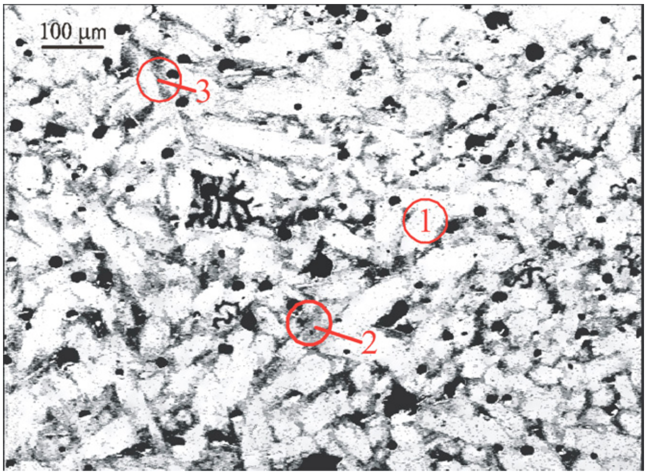

Fig. 5. MoSiTi tablet, molten at 1550 °C under argon atmosphere (SEM, BS).

3.3. *Evaluation of the samples after infiltration*

3.3.1. *SEM studies*

The MoSiTi infiltrated CF222 samples obtained at 1550 °C have two quite different microstructures in their exterior and interior parts. While in the fully infiltrated exterior parts (0–2 mm under the surface) all the individual C-fibers are surrounded by the solidified melt (Fig. 6a), only bigger capillars between fiber bundles get infiltrated in the interior parts (Fig. 6b), leaving the non-reacted C-bundles like isolated islands. In the exterior parts, the amorphous carbon in the matrix has reacted with silicon from the melt and produced a thin SiC layer around the fibers (Fig. 6c). Apart from SiC, the matrix also includes different solid solutions of Mo, Si and Ti as well. Big $MoSi_2$ grains can be found in the former large capillary pores (Fig. 6d).

In the interior parts, the SiC layer on the surface of the C-bundles which is produced through a reaction between silicon and carbon acts as a melt penetration barrier and retards the next infiltration steps. It is then the diffusion of Si atoms via SiC layer that dominates the kinetic of infiltration.[25] On the other hand, as the Si reacts with C the viscosity of the melt increases on its way into the interior parts of the samples. This will also raise the melting temperature of the melt and cause it to solidify before penetrating into the C-bundles in the interior parts.

Table 2
Chemical composition of some points on the molten MoSiTi tablet

Molten MoSiTi tablet	Si (wt.%)	Ti (wt.%)	Mo (wt.%)
Point 1	43.6	24.5	31.5
Point 2	44.5	42.16	8.64
Point 3	49.38	45.14	5.48

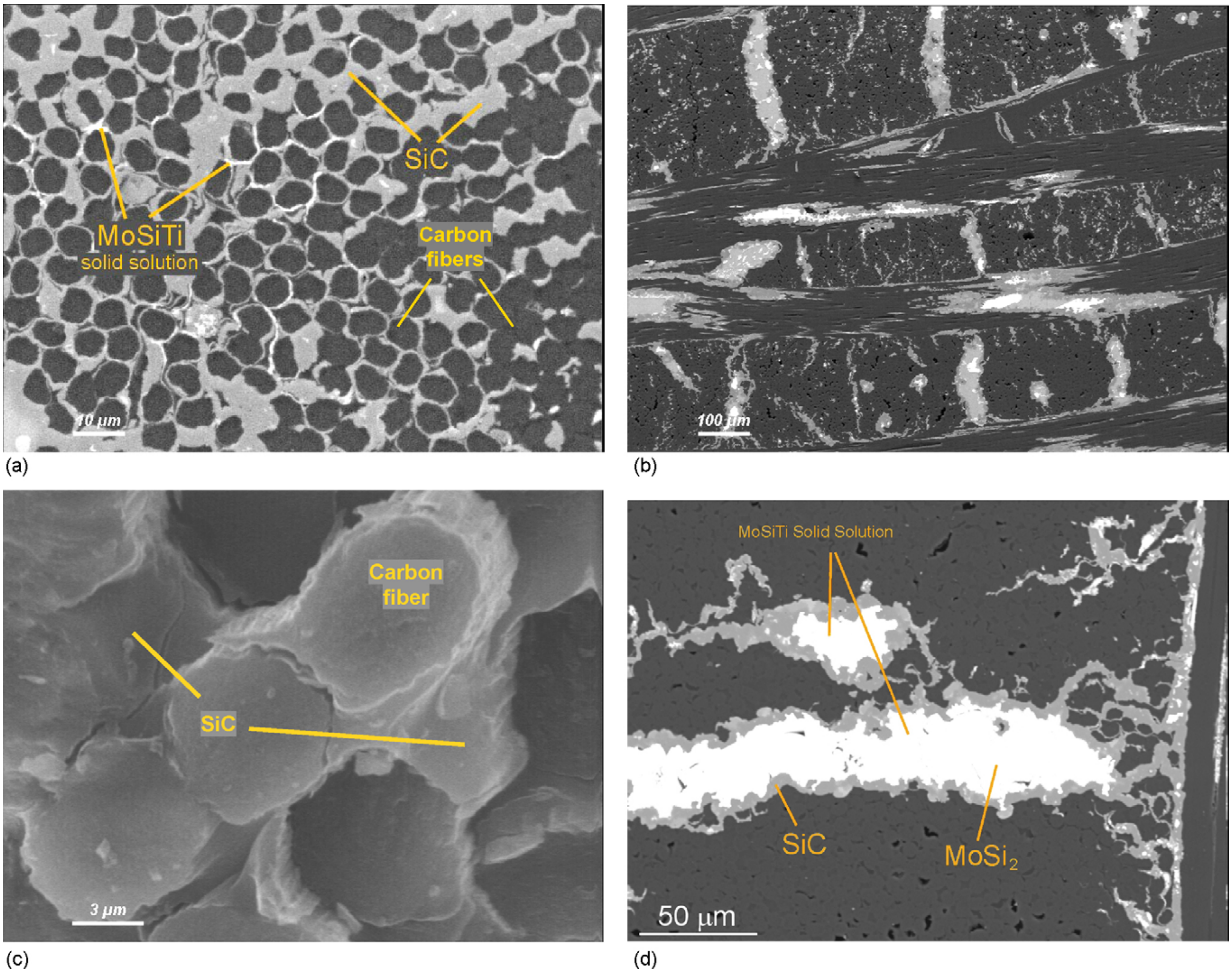

Fig. 6. CF222 carbon fiber preform infiltrated with MoSiTi. (a) Fully infiltrated CF222 in the areas close to the surface (SEM, BS), (b) partially infiltrated CF222 in the interior areas of the samples (SEM, BS), (c) SiC layer resulted from the reaction between the amorphous carbon in the matrix and the silicon around the fibers (SEM, SE), (d) big $MoSi_2$ grains and MoSiTi solid solutions formed in the former large capillary pores (SEM, BS).

FU-2954 preforms got fully infiltrated with MoSiTi at 1550 °C. The carbon fibers reacted at their surfaces with Si from the melt to form SiC. The interior parts of the fibers have been remained non-reacted. But the fibers have lost their reinforcing effect after reacting with silicon. SiC, $MoSi_2$ and $TiSi_2$ are the main phases in the matrix after infiltration. Since the FU-2954 sample has more and bigger pores than CF222, more infiltrating material has come to the reaction in this sample. On the other hand stability of these C-fibers against the Si is lower than the fibers in CF222. Therefore a higher amount of silicon has reacted with carbon and relatively more SiC has been developed in this sample. Mo and Ti are presented as their silicide forms and not in a solid solution. As it can be seen in the Fig. 7, MoSiTi solid solutions undergo a phase separation that produces $MoSi_2$ and $TiSi_2$ in the structure. Residual silicon can also be found in the infiltrated FU-2954 samples (light gray areas surrounded by SiC in Fig. 7). This amount of free Si in the sample could not diffuse through the developed SiC layer and react with the carbon in the given infiltration time.

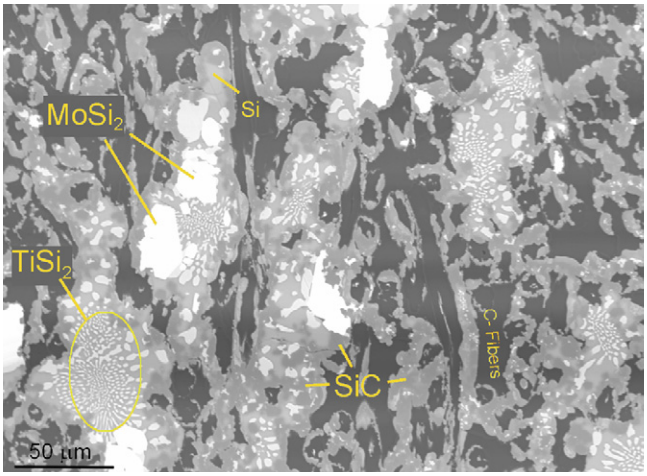

Fig. 7. Microstructure of an infiltrated FU-2954 (SEM, BS). Carbon fibers in the perform react heavily with silicon and can not reinforce the matrix.

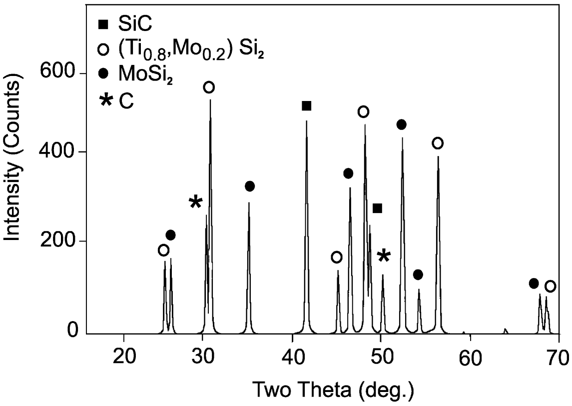

Fig. 8. X-ray diffraction pattern of MoSiTi infiltrated CF222 sample, infiltration temperature: 1550 °C, (Co $k\alpha_{1,2}$ Philips PW1710 diffractometer).

3.3.2. X-ray analysis

The XRD pattern of a MoSiTi infiltrated CF222 sample showed the presence of carbon, SiC, $MoSi_2$ and a solid solution with the chemical composition of $(Ti_{0.8}, Mo_{0.2})\ Si_2$ in the composite (Fig. 8). A considerable Si peak could not be detected. Other silicides or carbides like $TiSi_2$, TiC and MoC were also not detected as a separate phase. Since there is no free Si in the structure of this composite, its mechanical properties may not suffer from softening of Si above 1350 °C.

According to the XRD pattern of the MoSiTi infiltrated FU-2954 sample (Fig. 9), SiC is the main developed phase after infiltration and $MoSi_2$ and $TiSi_2$ are the other high temperature phases to be found in this sample. It can also be seen that the free silicon has been remained in the structure. This is a disadvantage for the high temparature mechanical properties of this composite. In order to reach to a Si-free composite, the infiltration conditions like time and temperature of the infiltration may have to be changed for the FU-2954 samples. A weak characteistic peak of C could also be detected by XRD (not shown in Fig. 9). Obviously there is much less carbon in this sample in comparison to CF222 with oriented C-fiber bundles.

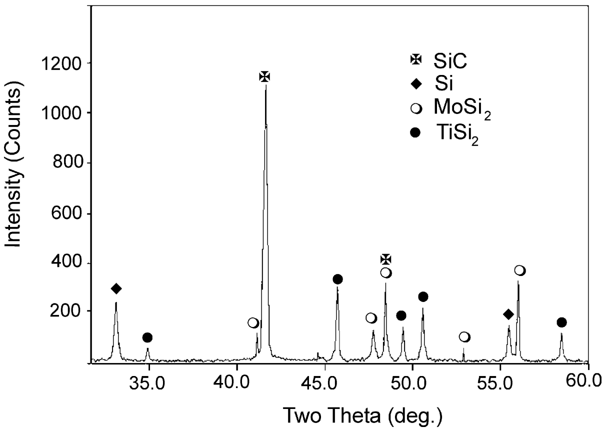

Fig. 9. X-ray diffraction pattern of MoSiTi infiltrated FU-2954 sample, infiltration temperature: 1550 °C, (Co $k\alpha_{1,2}$ Philips PW1710 diffractometer).

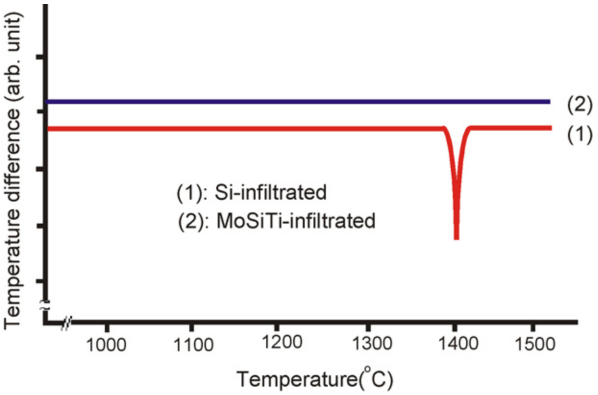

Fig. 10. Comparison between DTA curves of Si infiltrated and MoSiTi infiltrated samples.

3.3.3. Differential thermal analysis

The presence of free silicon in CF222 samples was also tested using differential thermal analysis (DTA). Fig. 10 shows a comparison between the DTA diagrams of two CF222 samples, one infiltrated with MoSiTi and the other with pure Si. The silicon infitrated sample shows an endothermic peak at about 1420 °C referring to the melting point of silicon. This indicates that there is still some residual silicon in the structure after infiltration. In case of MoSiTi infiltrated sample, there is no peak in the related DTA diagram. This suggests that the MoSiTi infiltrated CF222 preforms do not contain any residual silicon in its microstructure and they can demonstrate constant mechanical behavior up to high temperatures. According to these results the application temperature of the SiSiC parts can be increased considerably by using the infiltrating mixtures like MoSiTi instead of pure silicon.

4. 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. It is very important to prevent any contact between the preform and the infiltrants before the infiltrants are completely molten. Immediately after 1420 °C molten Si can penetrate into the pores of the preform before it reacts completely with other infiltrants. It will leave some refractory phases outside and it is not possible to infiltrate them at 1550 °C. That means the use of mixtures with lower silicon contents does not necessarily help to get a Si-free composite after infiltration at 1550 °C. Carbon fibers in CF222 carbon fiber preforms do not react heavily with the melt under the applied conditions. SiC, $MoSi_2$ and a solid solution with the chemical composition of $(Ti_{0.8}, Mo_{0.2})\ Si_2$ are the main phaes in CF222 infiltrated samples. Under optimized conditions, the final CF222 composite can be free of residual silicon. FU-2954 carbon fiber preforms get fully infiltrated with MoSiTi and show a monolithic structure after infiltration. As well as SiC, there are $MoSi_2$, $TiSi_2$, free silicon and non-reacted carbon in the microstructure of these composites. In order to reach to a Si-free composite, time and temperature of the infiltration may have to be changed for the FU-2954 samples.

Investigations on the mechanical behavior of infiltrated CF222 and FU-2954 samples are proposed for future study.

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