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Processing–microstructure–properties relationships of $MoSi_2$–SiC composites

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Abstract

Silicon carbide green bodies with and without carbon-fibre reinforcement have been infiltrated with $MoSi_2$–Si–X in order to produce high-temperature resistant materials. X is Cr, Ti, Al or B respectively. By adding silicon and one of these components to $MoSi_2$ the melting point is lowered dramatically. The composites therefore could be gained by melt infiltration at max. 1600 °C. During infiltration the additives react within the infiltrated body with carbon or silicon to form high-temperature resistant carbides or silicides. Thermodynamic calculations have been performed to analyse the reactions during infiltration. The infiltration parameters have been studied with respect to the resulting microstructure and properties. By fitting the amount of additives to the quantity of carbon in the SiC-body (or vice versa) no decrease in strength could be observed up to 1500 °C. The fracture toughness can be increased by the use of high-modulus carbon fibres. The most promising X-element for a high-temperature resistant material is titanium. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Infiltration; Microstructure; $MoSi_2$–SiC; Composites; Mechanical properties

1. Introduction

Reaction bonded silicon carbide is a preferred material for high-temperature applications in power engineering.[1,2] Typical applications are, for example burner tubes, nozzles or heat exchangers. To produce this material SiC green bodies with included carbon are infiltrated with molten silicon at about 1500–1600 °C. This results in a reaction of the infiltrating Si melt with the carbon available in the green body so that secondary SiC is created that interlaces the primary SiC particles. The remainder of the silicon melt solidifies during cooling so that a composite of SiC and Si is produced.[3] The advantage of this process is to produce a dense material without any shrinking. This allows the manufacture of large and complex components without expensive post treatment. The low melting point of silicon, however, that results in a rapid decrease in strength at about 1400 °C is a disadvantage here .

To avoid such a decrease in strength various authors tried to replace silicon by high-temperature resistant silicides.[4–8] $MoSi_2$ is very oxidation resistant and thus best suited for this application. It has a melting point of 2020 °C and shows a worth mentioning plastic deformation capacity with subsequent break above 1000 °C due to defects that build up in the lattice.[9–11] Moreover, a glassy SiO_2 layer is produced on the surface in the temperature range of 1000–1600 °C to slow down any further oxidation which leads to a high oxidation resistance.[12,13] Various authors infiltrated SiC–C bodies with $MoSi_2$–Si mixtures at temperatures of about 1700 °C to create composites that still included free silicon. A higher portion of $MoSi_2$ in the mixture resulted in an incomplete infiltration as the melting temperature of the mixture increased considerably.[4,6] Lim et al.[14] infiltrated the SiC–C body first with pure Si, then expelled the remaining Si again at a temperature of 1600 °C and infiltrated it then at 2100 °C with molten $MoSi_2$. By this process they succeeded in producing a material that had even at 1600 °C almost the same strength as at room temperature without showing any cracking due to the different coefficients of thermal expansion.

This paper describes the integration of carbon fibres into the matrix in order to increase the fracture toughness of SiSiC. From literature we know that such fibres are no longer stable at infiltration temperatures above 1600 °C.[15] Without coating the fibres it comes to a reaction between the infiltrating melt and the carbon fibres that will decompose the reinforcement mechanism

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of the fibres. Above 1600 °C even coated fibres are no longer stable in contact with the silicon melt. That is why in the studies described in this paper a third constituent is added to the $MoSi_2$–Si mixtures in order to lower the melting point of the mixture as far as possible to enable an infiltration at temperatures below 1600 °C in order to guarantee the required fibre strength. The constituents added to lower the melting point are to react to carbides with the carbon included in the infiltration body during the infiltration process or with silicon to silicides. The goal is to develop an oxidation-proof material of high fracture-toughness that will be resistant to highest temperatures.

Table 1
Compositions of the infiltration mixtures (X = Cr,Al,B,Ti)

Infiltration constituent sample designation	$MoSi_2$ (wt.%)	Si (wt.%)	X (wt.%)
MoSiCr1	63.2	19.1	17.7
MoSiCr2	52.4	31.0	16.6
MoSiCr3	66.5	14.1	19.4
MoSiAl2	43.6	48.6	7.8
MoSiB1	45.9	50.8	3.3
MoSiB2	76.2	21.1	2.7
MoSiTi1	22.5	56.8	20.7
MoSiTi2	36.0	49.9	14.1
MoSiTi5	33.3	20	46.7

2. Thermodynamic considerations

2.1. Selection of suitable infiltration mixtures

To infiltrate $MoSi_2$–Si mixtures at temperatures below 1600 °C such mixtures must contain about 97 at.% Si (84.8 wt.%). But it is impossible to include as much carbon into the green body to be infiltrated that all the silicon will react to silicon carbide. That is why a further element X should be added apart from Si so that a ternary $MoSi_2$–Si–X mixture with a lower melting point will develop. The element X should react during the infiltration with carbon to high-temperature resistant carbides or with silicon to silicides. This involves in particular the elements Al, B, Cr and Ti.

The compositions suited for the infiltration in the ternary systems Mo–Si–Al, Mo–Si–B, Mo–Si–Cr and Mo–Si–Ti must be within a phase range that produces $MoSi_2$ during solidification. The composition must be completely molten at a maximum temperature of 1600 °C and the ternary constituents must build up during cooling carbides or silicides that are resistant to highest temperatures. The compositions have been selected by evaluating ternary diagrams and by melting tests.[16] From Table 1 you may see a summary of the compositions that have successfully been used.

2.2. Calculation of the phase formation upon infiltration

For a better understanding of the reactions between an infiltrating melt and the carbon available in the infiltration body computer calculations have been done by the computing program equiTherm 4.0.[17] The program calculated the respective equilibrium phase compositions that are obtained at a reaction of 100 g melt with a certain carbon quantity. This allows study of the thermodynamic resistance of individual phases in presence of carbon (depending on the carbon quantity). The problem was that the program knows only compositions of certain stoichiometry while in reality often mixed phases occur. That is why these calculations may give only a rough evaluation on the reactions in presence of carbon. With regard to the stability of $MoSi_2$ these calculations are of special importance as other molybdenum silicides or molybdenum carbides show a clearly lower oxidation resistance.

Here, the results of the calculations for the melts MoSiCr2 and MoSiTi1 are to be shown as an example. The results of the calculations on MoSiB1 are not useful as the database does not include any molybdenum borides whose formation will lead to completely different results indeed in reality. For the composition MoSiAl2 the program calculation starts from the development of Al_4C_3 that will not arise in reality, however, because of the prevailing kinetic conditions.

2.2.1. The MoSi2–Si–Cr–C system

Without the presence of carbon a MoSiCr2 melt (see Table 1) will solidify to $MoSi_2$, $CrSi_2$ and Si according to the calculation (Fig. 1). If 100 g of melt reacts with up to 5 g carbon the free silicon reacts with carbon to SiC [Eq. (1), Fig. 1]. In case of more carbon content (up to 8 g) there will be an additional reaction of silicon bound in $CrSi_2$ with carbon to SiC. Instead of chromium disilicide the compositions Cr_5Si_3 and CrSi will occur that contain less silicon [Eq. (2), Fig. 1]. Among them Cr_5Si_3 is the more stable one. By adding more carbon (up to 11 g on 100 g melt) CrSi as well as $CrSi_2$ will be decomposed in favour of Cr_5Si_3 in order to build up SiC from Si and carbon [Eq. (3), Fig. 1]. If 100 g melt are brought into contact with more than 11 g (but less than 17 g) carbon $MoSi_2$ will be decomposed while bulding up SiC (the Si of $MoSi_2$ reacting with the carbon) and the composition Mo_5Si_3 which contains less silicon (Eq. (4), Fig. 1].

If 100 g melt react with more than 17 g carbon all silicides will decompose to build up SiC from Si. Cr will react to Cr_3C_2 and Mo reacts to MoC and Mo_2C. From these considerations we see that above a certain available carbon quantity the $MoSi_2$ decomposes, although it should be the main portion of the matrix as it has the best oxidation resistance of the arising Mo phases.

2.2.2. The $MoSi_2$–Si–Ti–C system

According to the program calculations a melt composition MoSiTi1 (see Table 1) will solidify to Si, $TiSi_2$, $MoSi_2$ and TiSi without the presence of carbon (Fig. 2). Here it is shown very clearly that the program calculations are only conditionally applicable as from the ternary diagram we see that apart from Si and $TiSi_2$ there is a ternary solid solution of $MoSi_2$–$TiSi_2$ available. From the calculated results you may nevertheless see that preferably the free Si reacts with the carbon. SiC builds up from the titanium disilicide, beside which a titanium silicide TiSi of lower silicon content originates [Eq. (1), Fig. 2]. If more carbon is available for reactions (>15 g/100 g melt) the titanium silicides will be decomposed by building up SiC and TiC [Eq. (2), Fig. 2]. Above a carbon content of about 30 g per 100 g melt $MoSi_2$ will be decomposed by building up SiC and Mo_5Si_3 [Eq. (3), Fig. 2]. Contrary to the Mo–Si–Cr–C system $MoSi_2$ becomes instable in presence of C only when all titanium silicides have reacted with carbon to SiC and TiC. If the melt reacts with even more carbon also Mo_5Si_3 will no longer be stable and SiC and molybdenum carbides will be formed [Eqs. (4) and (5), Fig. 2].

3. Experimental procedure

3.1. Sample preparation

As green bodies for the infiltration commercial isostatically pressed SiC materials with 6.8 wt.% carbon and a density of 2.17 g/cm^3 (Tece, Selb, Germany) have been used. For tests where SiC fibres or higher carbon portions were added, these SiC green bodies have been crushed and the powder gained has been mixed with the respective fibres or soot portions (flame soot FL101, Degussa, Hanau, Germany, medium grain size $d_{50}=95$ nm). These batches have been stirred with a moulding auxiliary (0.5% polyvinyl alcohol solution, 0.7 ml on 3.5 g material), filled into a mould and pre-compressed in a lever press by about 2 MPa. Thereafter the sample has been removed from the mould and recompressed isostatically at 200 MPa. Various fibre materials have been used for short fibre reinforcement. They had been made available by Schunk-Kohlenstofftechnik GmbH, Gießen, Germany. Among them was a low-modulus fibre with relatively high graphitization, called HTA fibre, on the one hand, and a high-modulus fibre of Mitsubishi, on the other.

The green bodies have been infiltrated with the mixtures listed in Table 1 using the powders mentioned in Table 2. Both pressed powder pellets and pre-molten samples were used for this purpose. A detailed description of the sample manufacture is given by Meier.[18] Crucible systems were used for the infiltration. They

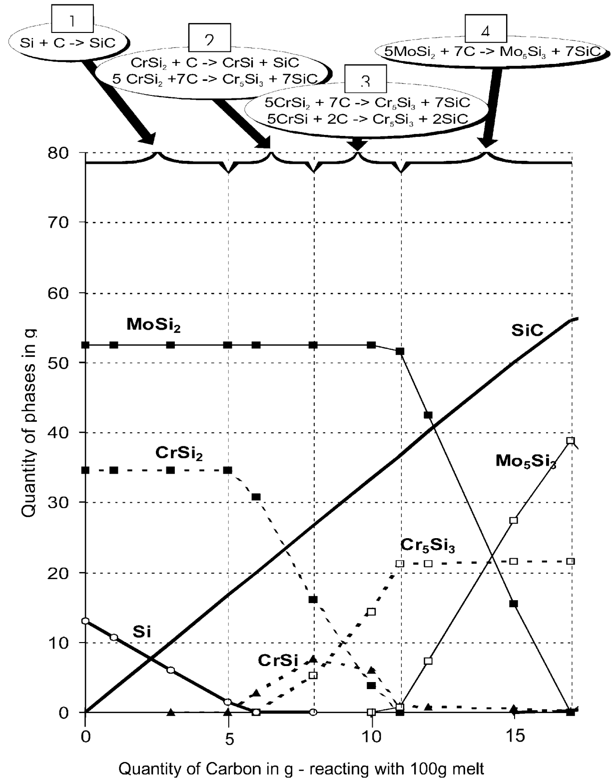

Fig. 1. Phase compositions resulting from thermodynamic calculations in the $MoSi_2$–Si–Cr–C system.

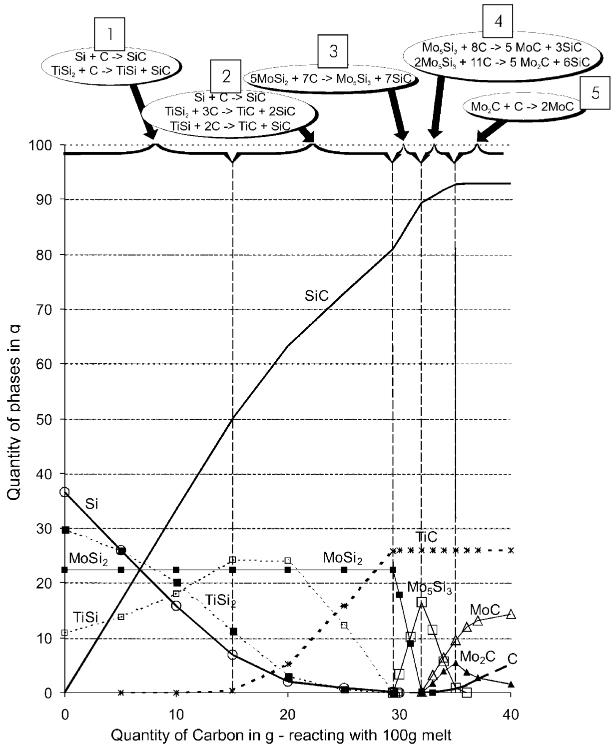

Fig. 2. Phase compositions resulting from thermodynamic calculations in the $MoSi_2$–Si–Ti–C system.

Table 2
Powders used for the infiltration mixtures

Material	Chemical purity (wt.%)	Grain size d_{90} (μm)	Supplier
$MoSi_2$	> 98.0	10	H.C. Starck, Goslar
Si	> 99.0	85	Merck, Darmstadt
Cr	99.0	44	Alfa Aesar, Karlsruhe
Ti	> 99.0	80	Alfa Aesar, Karlsruhe
Al	99.0	22	Alfa Aesar, Karlsruhe
B	95.0	45	Alfa Aesar, Karlsruhe

consisted of one BN outer crucible (65 mm diameter, 90 mm height) and three BN inner crucibles (53 mm diameter, 25 mm height). The outer crucible was closed by a BN cover and placed in a pressure sintering furnace of KCE company (type FPW100/150–2200–100LA, with C-heating conductors and C-fibre lining). The heating rate in vacuum was up to 1200 °C 20 K/min. Above this temperature the heating rate was 10 K/min until the required infiltration temperature was reached. The holding time at the final temperature was according to the respective trial 10–120 min. When about 1500 °C was reached the gas supply was opened and a pressure of 20 bar Argon was created in the furnace. The cooling was done without control at a rate of about 20 K/min down to 1000 °C and by about 5 K/min cooling rate down to room temperature. After the cooling the excessive solidified melt that surrounded the samples was ground off by means of a diamond wheel (grain 200).

3.2. Sample characterisation

The density and open porosity of the infiltrated materials have been determined according to Archimedes' principle (DIN 51065 and 51056). The depth of infiltration was measured by a light microscope (Zeiss, type Axiophot) to find the average values at different spots of the sample. The phases built up during the infiltration have been EDX-analysed by means of a scanning electron microscope (Jeol, type JSM U3). By using this quantitative X-ray microanalysis the proportions of single elements can be determined in different parts of a sample. On this basis various mineral phases can be estimated.

The high-temperature resistance of the infiltrated samples has been examined by a differential thermal analysis (Netzsch, type STA 429). To determine the oxidation resistance the SiC samples were ground into rectangular shapes and the surfaces of the samples were measured by a slide gauge. These samples were oxidized while laying on Al_2O_3 prisms in air at 1200 and 1400 °C, respectively, and for different holding times (Naber-Industrieofenbau, type LHT 16 R17) and their gain in weight was determined in mg/cm^2.

To measure the four-point bending strength of the infiltrated SiC samples according to DIN 51110 an equipment of INSTRON (type 8562 H 1805) has been used. The measurement of the fracture toughness according to EN 843–1 was done by means of samples with a saw cut. Three measurements have been done for each measuring point. If these measurements resulted in a standard deviation of more than 5% from the average value further measurements were done (up to a maximum 12 measurements per measuring point).

4. Results and discussion

4.1. Influence of the infiltration conditions on the microstructure

When infiltrating SiC with included carbon it is to be observed that after the melting of the infiltration mixtures the porous solid bodies are first covered by the molten mass. The latter penetrates the infiltrated body in a second step then (Fig. 3). That is why even for only slightly infiltrated samples the surfaces have normally less prosity than the interior. For the penetration velocity of the melt into the porous SiC green body and for the depth of penetration the infiltration conditions (composition of the infiltration mixture, way of powder preparation, infiltration temperature, holding time and pressure) are of decisive influence. It is not always a higher infiltration temperature that results in a more intense infiltration. With an increasing infiltration temperature respectively infiltration time in particular the melting point lowering constituents evaporate from the powder mixture. With low portions of admixtures (i.e. for MoSiAl, see Table 1) the viscosity of the melt will increase even with growing infiltration temperatures which leads to a clearly worse infiltration result and thus to a higher porosity (Fig. 4). For mixtures with high portions of melting point lowering constituents (i.e. MoSiTi1, see Table 1) the evaporations will hardly affect the viscosity. Here the viscosity becomes lower with increasing temperatures, the infiltration will be more complete and the porosity share will decrease. From the light-microscopic pictures in Fig. 4 it is clearly to be seen that even for an insufficient infiltration the edges of the samples have less porosity than the interior thanks to the infiltration process described in Fig. 3.

Because of the fibre stability problem mentioned above and of the maximum infiltration temperature of 1600 °C predetermined by this problem the mixtures used for infiltration may partly be selected only from a small range of compositions. In order to achieve that the melting point lowering constituents react to high-temperature resistant carbides or silicides during the infiltration the carbon content of the SiC green body must be very exactly adjusted. If the carbon content is too low not all the con-

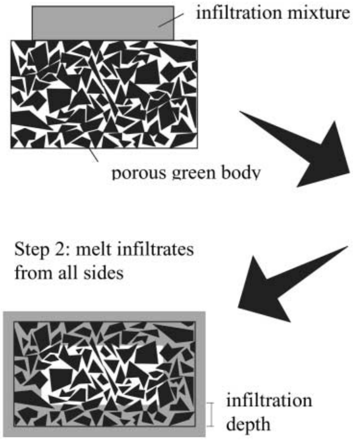

Fig. 3. Schematic view of the infiltration process of SiC with metallic melts.

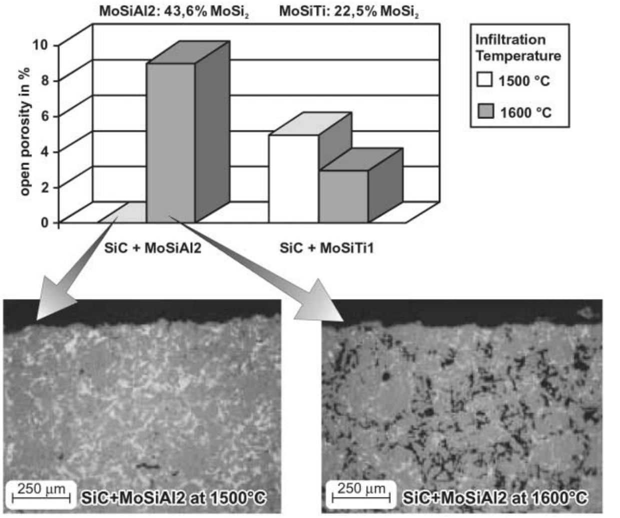

Fig. 4. Open porosity and microstructure as a function of the infiltration temperature for different SiC/$MoSi_2$–Si–X materials (black: porosity, dark grey: SiC, grey: solidificated melt).

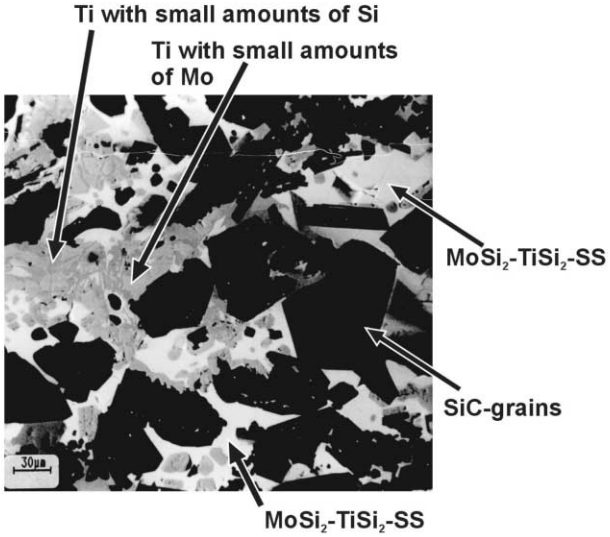

Fig. 5. SiC +40 wt.% C, infiltrated at 1600 °C with MoSiTi1 (polished surface, SEM, BSE).

stituents added for lowering the melting point may react to high-temperature resistant carbides or silicides and there will be a low-melting silicon rest phase built up in the structure that affects the high-temperature resistance in a negative way (see Section 4). Too high carbon content will lead to thermally instable connections as already discussed in Section 2. Fig. 5 shows the microstructure of a sample whose carbon content has been increased up to 40 wt.% leading after infiltration with MoSiTi1 at 1600 °C to a microstructure with 4 vol.% free silicon.

4.2. *Influence of the microstructure on the mechanical properties of the infiltrated SiC–$MoSi_2$–Si–X materials*

For the high-temperature resistance of the infiltrated materials the quantity of remaining silicon phase in the microstructure is decisive. Even small quantities that will soften at about 1410 °C (melting point of silicon) which leads to a rapid decrease in strength (Fig. 6). As to SiSiC with 18 vol.% free silicon the strength decreases very quickly at the melting point of silicon as is well known. The material type infiltrated with MoSiTi1 (Table 1) includes apart from a number of other compositions $<4\%$ free silicon by volume in the microstructure. Due to the very different thermal expansion coefficients of the newly formed phases ($\alpha_{SiC} = 4.5 \cdot 10^{-6}$ K^{-1}, $\alpha_{MoSi2} = 8.1 \cdot 10^{-6}$ K^{-1}) micro-cracks occur in the microstructure which reduce the room temperature strength considerably compared to SiSiC (Fig. 6). Despite the low proportion of free silicon the strength decreases rapidly at temperatures around the silicon melting point. If the development of a silicon phase is prevented like in this case by changing the infiltration mixture towards compositions of lower silicon content (MoSiTi5, see Table 1, by increasing the infiltration temperature to 1800 °C) a constant strength up to 1500 °C (upper measurement limit of the equipment) is obtained. This strength is however only half the RT strength of SiSiC, which is again due to micro-cracking in the microstructure because of big differences in the heat expansion behaviour of the individual phases.

In further investigations SiC powders with different grain size distributions and different carbon types shall be used in order to avoid cracking. In previous papers on SiSiC it has already been shown that by fitting these sizes to each other the cracking during solidification can be minimized.[3]

As known from literature it is possible that during the infiltration of SiC/C green bodies with included carbon short fibres the fibres may be attacked by the infiltrating melt. The decomposition happens more rapidly the lower the graphitization degree (and thus the crystal order) of the fibres. Despite a high graphitization degree

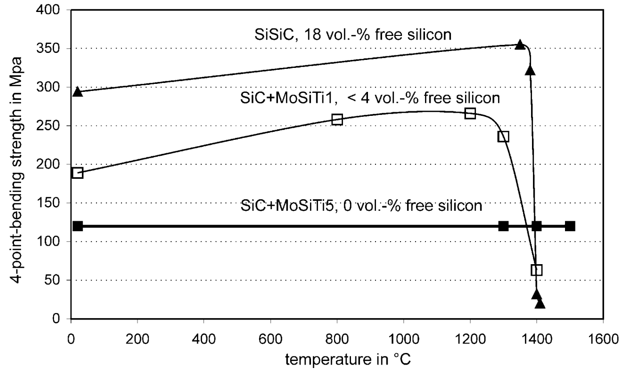

Fig. 6. Bending strength vs the temperature of SiC+6.8%C, infiltrated with various compositions of the $MoSi_2$–Si–Ti system (standard deviations are max. 10% of the average values).

fibres may be attacked more easily by a lower oriented coating and will decompose then as much as lower oriented fibres. Vice versa, coatings made from higher oriented carbon (PyC coatings) applied on lower oriented fibres may protect them against the attack of the infiltrating melt. In the infiltration trials described in this paper only the high-modulus carbon fibres of Mitsubishi with a particularly high graphitizing degree and thus high crystal order have been stable with all the used melts and can therefore be used in a reasonable way for the short fibre reinforcement. The low-modulus fibres HTA are only stable for an infiltration with MoSiAl2 or MoSiTi1 melts. Their use for a short fibre reinforcement is not reasonable, however, as they are bonded so firmly into the matrix that the desired fibre pull-out will not be achieved upon breaking whereas the fibres will break through smoothly. Accordingly, these fibres will neither increase the strength nor the K_{IC} value of the infiltrated SiC materials. Unlike that a fibre pull-out is achieved with the short fibre reinforcement by high-modulus carbon fibres and an increase in strength as well as a higher stress intensity factor K_{IC} is to be observed (Fig. 7). Too high fibre proportions, however, will lead to a pre-damage of the material due to the great differences in heat expansion already in the production and thus to clearly lower strength values. The mixture with the best fibre resistance has always been used as an infiltration mixture for the determination of the strength and the K_{IC} value.

4.3. Oxidation behaviour of $SiC–MoSi_2–Si–X$ materials

The oxidation behaviour of the $SiC–MoSi_2–Si–X$ materials is on the one hand characterized by the formation of oxide films on the surface consisting of SiO_2 and the ternary constituents and on the other by the formation of MoO_3 with its relatively high vapour pressure. The samples infiltrated with MoSiAl2, Si, MoSiB1 and MoSiTi1 show a parabolic weight gain versus time in the first 170 h at 1400 °C (Fig. 8). The same behaviour has been observed at 1200 °C. Diffusion of oxygen through the SiO_2 layer formed at the surface of the samples is the rate controlling step in the beginning of the oxidation experiments and therefore

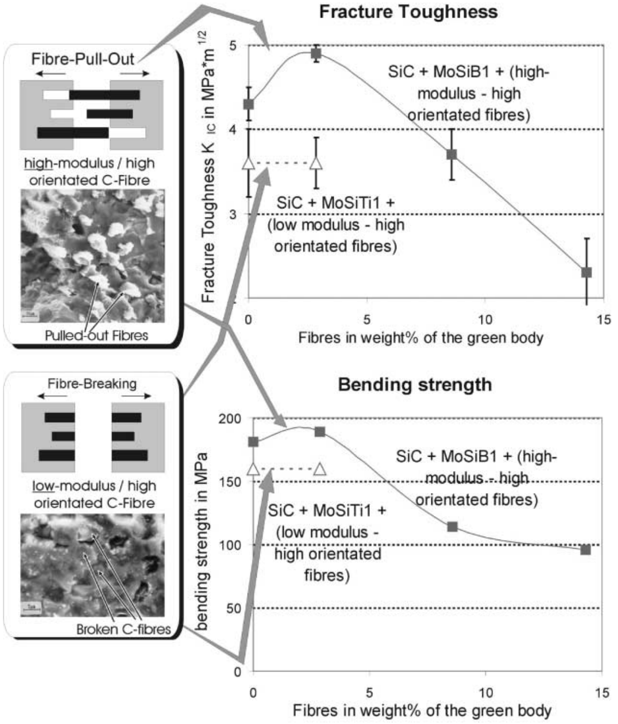

Fig. 7. Fracture toughness and bending strength of short fibre reinforced SiC–MoSi2–Si–X materials.

$$\frac{\Delta m}{A} = k \cdot \sqrt{t} \tag{1}$$

with

Δm = weight gain; A = surface area; k = parabolic oxidation rate constant; t = time.

From the parabolic oxidation rate constant the activation energy of these materials can be calculated as follows:

$$k = k_0 \cdot \mathrm{e}^{-(E_{\mathrm{A}}/RT)} \tag{2}$$

$$\Rightarrow \ln k = \ln k_0 + (-E_{\mathrm{A}}/RT) \tag{3}$$

with E_{A} = activation energy.

For the oxidation of SiSiC an E_{A} of about 266±19 kJ/mol and for MoSiAl2/ SiC an E_{A} of 256+32 kJ/mol has been estimated from an Arrhenius plot ln k vs $1/RT$ after oxidation experiments at 1200 and 1400 °C. The comparable values confirm the conclusion that the mechanism of oxidation of these two materials seems to be very similar. For the MoSiB1 and MoSiTi1 infiltrated materials the scatter of data was too big for a reliable calculation. The reason for this wide scatter of data may be the fact that the evaporation of MoO_3

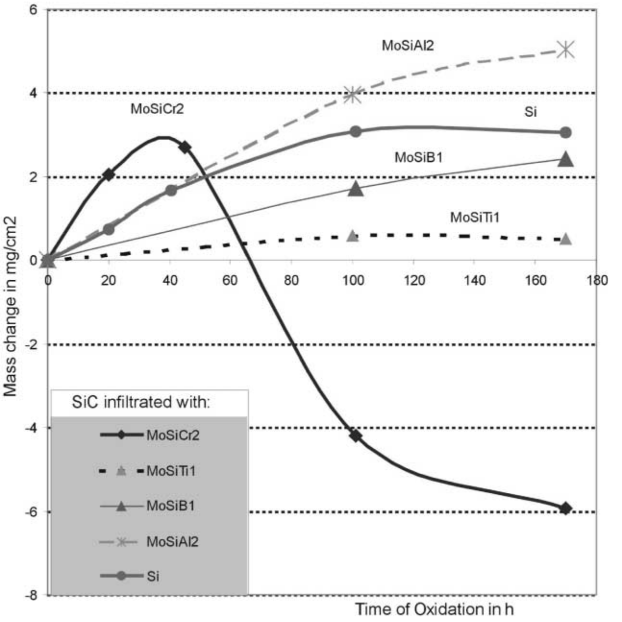

Fig. 8. Oxidation behavior of silicon carbide infiltrated with different molybdenum compounds.

leads to weight losses in the materials. MoSiCr2, for example shows this weight loss especially at oxidation times above 40 h. This material cannot be used for high temperature applications. MoSiTi1 is the most oxidation resistant material within this group of composites and shows even a better behaviour than SiSiC.

5. Conclusions

Within the frame of these studies it could be shown that it is possible to produce a SiC–$MoSi_2$ carbon fibre composite material by infiltrating the carbon fibres at 1600 °C. This was possible by using suitable ternary melting point lowering elements. High-modulus fibres of Mitsubishi in connection with a suitable infiltration medium make a small increase of the fracture toughness recognisable. The melting point lowering elements react to high-temperature resistant silicides or carbides upon infiltration. The use of titanium (even at an infiltration temperature of 1800 °C in this case) allowed to produce a material without any free silicon that maintains its strength up to 1500 °C. Problems are raised by the fact that due to different expansion coefficients of the various microstructural constituents cracks are produced during cooling that result in a lower strength level. That is why a continuation of the studies is planned in order to minimise the problem of cracking upon cooling by varying the SiC grain size distribution and by using different carbon types and thus to optimise a high-temperature resistant C-fibre reinforced composite material with high fracture toughness.

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