Formation and structure of reaction layers in SiC/glass and SiC/SiC composites

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The structure and composition of interlayers between the fibre and matrix in Nicalon/borosilicate glass and Nicalon/SiC composites depend strongly on their formation mechanism. The applicability of existing models for interface reaction is limited, if the results of electron microscopic characterization are taken into account. The thermodynamic fundamentals illustrated by a volatility diagram of the Si–C–O system reveal that variations in the pressures of O₂, SiO and CO, respectively, are responsible for the occurrence of various phases (carbon, carbon and silica, silica) between the fibre and matrix. The thermodynamic approach yields a four-stage model of layer formation including the active oxidation of SiC.

(Keywords: Nicalon/borosilicate glass; Nicalon/SiC; interlayer formation; volatility diagram; Si–C–O system; transmission electron microscopy)

INTRODUCTION

High-temperature reactions between silicon carbide and oxygen are important for interlayer formation in SiC fibre-reinforced materials. The structure of the interfacial region between SiC fibre and matrix can be very complex, depending on specific reaction conditions such as, for example, temperature, partial pressures of the gaseous species, and matrix composition. The tailoring of such interlayers consequently requires a detailed electron microscopic characterization of both microstructure and microchemistry down to the nanometre scale. The microstructural phenomena revealed by electron microscopy are utilized as the basis for modelling the layer formation, which is additionally necessary for optimizing the structure of the region between fibre and matrix.

The results of two different SiC (Nicalon) fibre-reinforced composite systems are presented. In both systems (Nicalon/borosilicate glass and Nicalon/SiC) carbon-rich interlayers were formed during processing. Materials characterization was carried out using transmission electron microscope (TEM) techniques and

analytical electron microscopy, with the phenomena being discussed in relation to the processing conditions. A four-stage thermochemical model is established to interpret the layer structures.

EXPERIMENTAL

This paper deals with two different material systems: (1) SiC (Nicalon[®]) fibre-reinforced Duran glasses[®] and (2) a composite consisting of SiC (Nicalon) fibres, with an extra carbon coating, and an SiC matrix produced by chemical vapour infiltration (CVI). The SiC (Nicalon) fibre-reinforced Duran glasses (B₂O₃–Na₂O–SiO₂) were produced via sol–gel supported processes, described briefly as follows¹. After thermal desizing the Nicalon fibres were pulled through a suspension consisting of Duran powder and a special sol–gel solution. After drying the impregnated fibres, the fibre plates were stacked to form a prepreg, which was consolidated by hot-pressing in an argon atmosphere.

For the electron microscope investigations, specimens were prepared by cutting thin (< 200 µm) slices 3 mm in diameter, planar grinding and double-mould dimpling down to a thickness of about 10 µm, followed by ion

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Figure 1 Typical structure of the interlayer in a Nicalon fibre-reinforced Duran glass hot-pressed at 1270°C, illustrated by lattice fringe imaging (fibre left, matrix right)

Figure 2 Pores between the carbon-rich interlayer and the matrix

milling (Ar^+ , 5 kV) down to electron transparency. The microstructure investigations were carried out using a JEM 100C transmission electron microscope at 100 kV. Results of microchemical studies by energy-dispersive X-ray spectroscopy (EDXS) as well as electron energy-loss spectroscopy (EELS) were attained using a dedicated field-emission scanning transmission electron microscope (STEM), a VG HB 501 UX, equipped with a serial spectrometer (VG ELS 501) and a light-element X-ray detector (Kevex Quantum)².

For thermodynamic studies, calculations were carried out using the ThermoCalc program and data base³. The volatility diagrams of the Si–C–O system were constructed according to the method of Lou and Heuer^{4,5}.

RESULTS OF INTERLAYER CHARACTERIZATION

Carbon-rich interlayers between fibres and matrices are known to occur if Nicalon fibres are used to reinforce glasses⁶. The new interphases—carbon and silica—mainly detected by electron microscope techniques are formed by the high-temperature oxidation of the fibre periphery. The formation of the layer is dependent on the constituents of the fibre used. The fibre is characterized by a structure composed mainly of nanocrystalline SiC and amorphous SiC_xO_y ($x + y = 4$) as well as free aromatic carbon aggregates in the case of ceramic-grade Nicalon⁷, which is also important for the layer structure development. *Figure 1* typifies the structure of the interlayer in a Nicalon fibre/Duran glass composite

Figure 3 EDXS line profile across the interface region in a Nicalon fibre-reinforced Duran glass hot-pressed at 1100°C (inset: STEM bright-field image)

hot-pressed at 1270°C. Near the amorphous matrix (on the right side) there are aggregates of graphitic basal layers in a parallel orientation to the interface. The adjoining region of the layer consists of graphite-like ribbons in a cellular arrangement. The cellular structure

Figure 4 EDXS line profile across the sequence of reaction layers (carbon, silica and textured carbon, respectively, in succession) in Nicalon/Duran glass hot-pressed at 1270°C for 30 min (inset: energy-filtered STEM image)

Figure 5 TEM bright-field image of the complex region between fibre and matrix in Nicalon fibre-reinforced SiC (see text)

penetrates into the fibre (on the left side), indicated by the presence of SiC crystallites. Frequently, at the interface between the layer and the matrix there are pores as can be seen in *Figure 2*. Moreover, in composites hot-pressed at lower temperatures (at 1100°C, for example) the matrix near the interface is enriched with silica, as confirmed by EDXS and EELS⁸ (see *Figure 3*). Besides carbon, the interlayer also contains silicon and oxygen probably bound in silica. In the fibre periphery a silicon- and oxygen-rich phase, probably consisting of a silicon oxycarbide, is indicated by studying the energy-loss near edge structure (ELNES) of the Si-L edge⁸. In composites hot-pressed at higher temperatures (such as 1270°C) a silica enrichment on the matrix side has not been detected. Only in the rare case of multiple sequences of interphases an amorphous SiO_x layer has been revealed, which is embedded between two carbon layers (see *Figure 4*)⁹. As in the previous samples, there is a cellular carbon interlayer on the fibre side, whereas on the matrix side there is the additional graphite-like band in parallel orientation to the matrix interface.

A similar reaction layer occurred in the Nicalon fibre-reinforced SiC, although produced via CVI. As *Figure 5* shows, the complex region between fibre and matrix consists of three layers: two carbon layers, with one silica layer in between. The cellular-structured carbon layer on the fibre and the adjoining silica layer result from chemical reactions. In contrast to the Nicalon fibre-reinforced Duran glass, the carbon on the matrix side was deposited at the beginning of the CVI process.

DISCUSSION

Existing models for layer formation and their limitations

A first detailed thermochemical investigation of interphases in Nicalon fibre-reinforced glasses (Nicalon/lithium aluminosilicate (LAS) and Nicalon/calcium aluminosilicate (CAS)) was performed by Cooper and Chyng in 1987¹⁰. In all composites studied carbon-rich reaction layers were detected by transmission electron

microscopy. During hot-pressing the Gibb's free energy is supposed to decrease by oxidation of the SiC crystallites in the outer fibre regions. According to thermochemical considerations, the generation of silicon dioxide and carbon by the following reaction is thermodynamically favoured:

The formation of the carbon-rich layer by the previous reaction is rate-limited by the diffusion of silica constituents from the fibre to the matrix owing to a silica activity gradient, which is determined by the basicity of the matrix glass.

Continuing their STEM studies on Nicalon fibre-reinforced CAS glass ceramics, Bonney and Cooper¹¹ succeeded in modifying the fundamental model. In particular, the microstructural phenomena observed (such as the silica-rich region between the matrix and the nearly pure crystalline carbon layer, and the planar interface between these reaction phases) permitted some new statements to be made about the reaction kinetics. According to Cooper and Chyung, they regarded the reaction (1) as layer formation. Moreover, to explain the planar reaction layer morphology, this reaction was considered a solid-state displacement reaction being rate-limited by the diffusion of oxygen through the silica layer. A planar interface between carbon and silica requires the diffusion of Si^{4+} ions from the fibre via the carbon layer to the interface of silica, where SiO_2 is forming.

Some other models of layer formation include the passive oxidation of SiC by CO ^{12,13}. Benson *et al.*¹² performed thermodynamic calculations for silica and for silicate glasses with SiC. They distinguished two successive steps in the formation of a carbon layer, depending on the partial pressure of CO. State one is the formation of an initial layer by the reaction of SiC and O_2 , corresponding to the fundamental model of Cooper and Chyung. In stage two the carbon layer formation is controlled by different processes at the interfaces between carbon and its neighbouring phases. At the matrix interface the reaction of carbon with oxygen yields CO, which diffuses to the fibre interface and oxidizes silicon carbide.

These existing models actually explain the main features of the reaction layer but there are some difficulties in interpreting the microstructural phenomena observed, especially for Nicalon/Duran composites hot-pressed at 1100°C.

For example, what is the reason for the experimental observation that a silicon- and oxygen-rich region occurs in the fibre periphery together with SiO_2 enrichment in the matrix near to the interface with the carbon-rich layer? According to Cooper and Chyung, SiO_2 is formed in the fibre periphery and will be transported into the matrix. However, the model by Bonney and Cooper presumes the formation of SiO_2 at the interface between the carbon-rich layer and the silica layer. In the fibre periphery an SiC_xO_y phase with increasing

Figure 6 $\log p_{\text{O}_2}$ – $\log p_{\text{SiO}}$ diagram of the system Si–C–O for 1400 K and a CO pressure of 1 atm

degree of oxidation in approaching the carbon layer exists, as indicated by ELNES studies. This might be a hint of the oxidation of SiC crystallites in the fibre periphery according to Cooper and Chyung. But, at the same time, the matrix near the interface to the carbon-rich layer is enriched with SiO_2 , as predicted by Bonney and Cooper. Furthermore, the interpretation of multiple sequences of carbon and silica is not yet clear. Another problem is the structural differences of carbon, which is not considered in these models.

Thermodynamic fundamentals

The elucidation of the above-mentioned problems requires further investigations into the Si–C–O system. At the temperatures of interest, reactions are possible between the following phases: graphite-like carbon, β -silicon carbide, cristobalite or tridymite, and, finally, gas mainly containing CO, O_2 and SiO ¹⁴. The silicon oxycarbide phase is not considered, because thermodynamic data were not available.

The thermodynamic fundamentals of reactions in the system Si–C–O are comprehensively illustrated by volatility diagrams. The latter are isothermal plots showing the partial pressures of two gaseous species in equilibrium with the condensed phases possible in the system^{4,5}. Moreover, for a gaseous phase consisting of three species the diagram is only valid for a constant pressure of the third gaseous component. The construction of such diagrams for the system Si–C–O is explained in detail in refs 4 and 5. The lines marked simply represent the interdependence of the equilibrium constant and the Gibb's free energy corresponding to the reaction between gas and solid under consideration. The following list presents the reactions described by the lines in the $\log p_{\text{O}_2}$ – $\log p_{\text{SiO}}$ diagram of Figure 6:

Figure 7 Four-stage model of layer formation

Figure 6 is an isothermal plot for 1400 K and 1 atm as the partial pressure of CO. The volatility diagram predicts the different solid interphases (carbon, carbon and silica, and silica, respectively), which may form as a function of the partial pressures of oxygen and silicon monoxide. On inspection of the diagram, the intersection point of lines 4, 5 and 1 is the critical point of the equilibrium between the gas and the solid phases SiC, SiO₂ and C, thus characterizing the critical pressure of SiO in the Si–C–O system required for the stability of SiO₂ in contact with SiC. If the SiO partial pressure is lower than the critical pressure, SiO₂ is unstable in contact with SiC. If SiC is oxidized it forms the volatile SiO (active oxidation). The formation of carbon as the second reaction phase is controlled by the pressures of CO and O₂, respectively. At oxygen pressures lower than the pressure characterizing the equilibrium of carbon and carbon monoxide (marked by R6 in Figure 6), carbon is the only solid reaction phase forming by the active oxidation of SiC [reaction (5)]. If SiC is oxidized at an oxygen pressure higher than the C/CO equilibrium pressure, SiO and CO form. The formation of SiO₂ by SiC oxidation (passive oxidation) is possible at SiO pressures exceeding the critical SiO pressure discussed above.

Assuming a closed system, reactions (3) and (5) prove that one O₂ molecule will form two SiO molecules at the most, leading to a real ratio of partial pressures $p_{\text{SiO}}/p_{\text{O}_2}$ of ≤ 2 (refs 4 and 5). This is illustrated by the isomolar

line, dashed in the diagram. Only the parameters to the right of this line are physically attainable. At the intersection of the isomolar line and line 4 pressure conditions are attained that are necessary for SiO₂ to form away from the SiC surface. But this O₂ pressure is not sufficient to exceed the equilibrium p_{SiO} defined by the triple point. Only at higher p_{O_2} is passive oxidation possible, which forms CO.

For Nicalon fibre-reinforced glasses it is assumed that p_{SiO} depends on p_{O_2} at the interface between fibre and matrix. Thus, for layer formation reactions (2) to (5) are important, as the isomolar line restricts the interpretation of the volatility diagram. However, further investigations are necessary to prove the significance of the isomolar line for the layer formation process at the interface between fibre and matrix, because the real pressures at the reaction front are not known.

The four-stage model of layer formation

The thermodynamic considerations discussed above are the fundamentals of the model which will briefly be explained in the following (see Figure 7). At the beginning of the four-stage process an oxygen pressure given on the lower right of the diagram is assumed at the interface to the fibre, which is supplied by the oxygen dissolved during glass preparation. Thus, an SiO₂ film on the fibre is forming by reaction (2) (stage 1). This film

grows until its diffusion barrier effect causes a reduced oxygen pressure at the fibre which is lower than the pressure for the equilibrium of silicon carbide, silica and gas. Thus, SiO₂ is unstable in contact with SiC. Reaction (3) forming SiO and CO occurs in *stage 2* of the layer formation process. Away from the interface to the fibre the ratio of the partial pressures $p_{\text{SiO}}/p_{\text{O}_2}$ indicated by the intersection of the isomolar line and line 4 is exceeded, with SiO₂ forming and the oxygen partial pressure at the fibre decreasing further. In *stage 3* of the layer formation process, carbon is stable at the interface to the fibre and is formed by the active oxidation of SiC, reaction (5). At the end of stage 3, a porous region and an SiO₂ film have formed on the fibre next to the carbon layer. On cooling the composite from the hot-pressing temperature (*stage 4*), carbon precipitates according to the following reaction from the CO-containing atmosphere of the pores

Carbon formed is texturally depositing on the surface of the pore, resulting in an orientation of the graphitic basal planes nearly parallel to the pore surface as *Figure 2* shows. Depending on the location of the pores, multiple layers of carbon and silica have occasionally been observed. In contrast, that part of carbon formed by the SiC oxidation [reaction (5)] is added to the structural units of carbon in the fibre periphery. The primary carbon aggregates of graphitic basal planes are arranged around the SiC crystallites of the fibre, creating the cellular texture of most of the carbon in the reaction layer.

CONCLUSIONS

The layer forming processes in Nicalon fibre-reinforced composites are reactions between silicon carbide and oxygen. The conditions of layer formation are discussed using the volatility diagram of Si–C–O, which illustrates the dependence of the condensed phases on temperature, pressure and composition of gaseous species. The diagram proves that carbon-rich layers may form by the active oxidation of SiC to SiO and C in the fibre periphery. Moreover, the previously favoured passive oxidation associated with the formation of SiO₂ and C is

found to depend strongly on certain pressures of O₂, SiO and CO. Differences in the partial pressures due, for example, to the growth of diffusion barriers are the reasons for the division of the layer forming process into successive stages. Interlayer phenomena, revealed by various electron microscope techniques, have been explained by a four-stage model.

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