Platinum-enhanced graphitisation in sandwich structures of silicon carbide and borosilicate glass

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Abstract

Heat-treated sandwich structures of borosilicate glass and 6H-SiC single crystals (with and without platinum pre-coating) were used as model composites to study the reaction kinetics of the interlayer formation in the system Si–C–O. High resolution and analytical electron microscopical methods revealed a complex interlayer system, mainly consisting of different phases of carbon and silica. A distinct increase in the degree of graphitisation and texturisation of the reaction layer was observed after Pt deposition on the silicon carbide surface, which is attributed to the graphitising effect of both platinum and platinum silicide.

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1. Introduction

The high potential of continuous fibre-reinforced ceramics and glasses is based upon their damage tolerant and quasi-ductile behaviour. However, this can only be achieved by appropriately activating energy-dissipative processes like crack shielding and deflection, debonding and pull-out, which are controlled by the bond strength and sliding resistance in the interlayer regions between fibre and matrix [1–3]. Thus, the optimisation of the mechanical properties of composites with brittle matrices is equivalent to the tailoring of their interlayers.

As we have demonstrated in previous studies [3,5], controlling of the mechanical properties of silicon carbide fibre-reinforced glasses and ceramics is possible by special texturised carbon layers with graphitic basal planes parallel aligned to the fibre/matrix interface. Within the hexagonal basal planes, the planar, trigonal sp^2 -hybridisation of the C-atoms yields strong σ -bonds, whereas perpendicular to these basal planes the electrons of the $2p_z$ -orbitals are forming only weak π -bonds. The resulting anisotropy of properties of graphitic layers allows to control debonding and pull-out [4,5].

As an important precondition for the composite optimisation, the processing of the composites must result in an appropriate structure where matrix and fibres being located in correspondence with the loading geometry of the component. For this joining of the composite partners, processing methods as, e.g. chemical vapour infiltration, pyrolysis of preceramic polymers or hot-pressing are used. During these processes, fibre/matrix interlayers are formed by chemical reactions with very complex structures, depending on the specific reaction conditions such as, e.g. temperature, composition of matrix and fibre, and partial pressures of the gaseous species.

In silicon carbide fibre-reinforced glasses, carbon-rich interlayers are mainly formed by reactions between silicon carbide and oxygen [6–13]. Based on the observed interlayer phenomena, we could explain the layer forming processes by use of volatility diagrams of the system Si–C–O revealing that variations in the pressures of O_2 , SiO and CO are responsible for the occurrence of various phases (carbon, carbon/silica mixtures, silica) between fibre and matrix [14–16]. Thus, we could develop a four-step model of the layer formation [15]. Among the observed phases there is only a marginal portion of textured carbon permitting a controlled pull-out. For enlarging this part of graphitic carbon being parallel aligned to the fibre surface, the mechanism of its formation has to be adjusted. However, on the conventional way comprising oxidation processes this is coupled with an intense formation of pores. An alternative route should be

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opened up by the reaction of SiC with a transition metal, which does not form carbides but catalyses the graphitisation. The catalytic graphitisation by metals has been widely investigated in the last 40 years [17–26]. In spite of this, to the best of our knowledge, there has been no application of the catalytic graphitisation on interlayers in SiC composites so far.

The present paper describes results of new investigations of the reaction kinetics in interlayers between single crystal silicon carbide of the 6H polytype and borosilicate glass. The studies on these model composites reveal details of both, the carbon formation and the effect of platinum on the graphitisation in the interlayer. Structure and chemistry of the reaction layers were studied down to the atomic scale by use of high-resolution transmission electron microscopy (HREM) and spectroscopic techniques including energy dispersive X-ray (EDX) spectroscopy and electron energy loss spectroscopy (EELS) with special respect to the fine structure near the ionisation edge.

2. Experimental details

For the microstructure investigations we used electron diffraction techniques and HREM, carried out in a Philips CM 20 FEG (field emission gun) microscope, operating at 200 keV with a point-to-point resolution of 0.24 nm and equipped with both, a Gatan imaging filter (GIF 200) and an EDX detector enabling the detection of light elements (IDFix-system, SAMx-Germany). So, EDX analysis and EELS with particular emphasis on the energy loss near edge structures (ELNES) could be used to characterise the nanochemistry of the reaction layers. EELS was performed with a microscope working in the scanning transmission mode (STEM), whereas the half width of the zero loss peak was about 0.8–1.2 eV. Series of electron energy loss spectra were recorded by digitally scanning a STEM probe of about 2 nm in diameter across the reaction zones using the Gatan Digiscan model 688. To minimise contamination effects, a cooling specimen holder was used.

Sandwich structures have been made by merging HF-cleaned single crystals of 6H-SiC and plates of borosilicate glass (Fiolax® Schott Glaswerke, Mainz, Germany) [27]. The sandwich size was typically 10 mm × 10 mm × 4.4 mm, containing SiC-crystal slides (3 mm × 3 mm × 0.38 mm) made from wafers, produced by the modified Lely technique (SiCrystal AG, Eschenfelden, Germany) with the polished wafer surfaces being C-terminated (000 $\bar{1}$). For producing the sandwiches, glass plates were stacked below and above the SiC single crystals, placed in alumina crucibles, and positioned in a horizontal mullite tube furnace which was equipped with a continuous gas-supplying system and a ZrO₂ oxygen sensor including a Pt/PtRh thermocouple. Using this sensor near the sample, both the partial pressure of oxygen and the temperature could be monitored. All experiments were performed under argon flow (4 l h⁻¹).

For the first series of tests, uncoated 6H-SiC crystal slides were merged into the borosilicate glass at 1164 °C. The second series of tests comprises sandwich structures made of 6H-SiC slides, which were coated with a thin layer of pure platinum of about 5 nm in thickness before merging into borosilicate glass at 977 °C. By positioning a tantalum foil inside the tube, the partial pressure of oxygen could be reduced to about 10⁻⁹ Pa at 1164 °C or 10⁻¹³ Pa at 977 °C while heating-up the furnace with a ramp of 200 K h⁻¹ to the maximum temperature, which was kept for 30 min before cooling-down again with 200 K h⁻¹.

For transmission electron microscopy, specimens have been made using a refined cross-section technique. After fixing the sandwiches with Si-blocks, slides of about 1 mm in thickness were cut, embedded in wax and divided into small parts, containing the SiC/glass interface of interest in the centre. After grinding and dimpling, these parts were subsequently glued on Cu rings. The thinning to electron transparency has been performed by ion milling using the precision ion polishing system PIPS 691 (Gatan Inc.).

3. Results and discussion

In both kinds of annealed sandwiches, i.e. with uncoated and with Pt-coated 6H-SiC, at the interface between the SiC and the glass partitioned interlayers were formed having a thickness of 100–150 nm and with the main components (i) sp²-hybridised C and (ii) SiO₂. However, the microstructural and chemical peculiarities of the reaction zone appear rather differently.

3.1. Interlayers in specimens of uncoated 6H-SiC and borosilicate glass

The features of these interlayers are demonstrated in the HREM image (Fig. 1). The atomic 6H polytype structure of the silicon carbide can clearly be recognised by alternating bright/dark contrasts (which are induced by a small crystal tilt away from the $\langle 11\bar{2}0 \rangle$ zone axis [28,29]) corresponding to the six-fold stacking of the atomic planes. Each dot represents a SiC dipole. The interface between the reaction layer and the SiC shows terraces on the nanometer scale which are adjoining both the inhomogeneously thick amorphous layer of SiO₂ (on the left and right of Fig. 1) and an additional, only 5 nm thick interlayer (in the middle part of Fig. 1), which is adjacent to the amorphous carbon zone (on the top) extending to the glass. The narrow layer consists of turbostratic carbon having the basal planes nearly parallel oriented to the (000 $\bar{1}$) plane of the SiC. Thus, even at the high reaction temperature of 1164 °C, the formation of texturised turbostratic carbon is shown to be limited to the region between carbon and silica, whereas the most part of the layer occurs amorphous. This indicates a mechanism of formation of turbostratic carbon via an intermediate step of CO generation as we have shown in [15,27]. Firstly,

Fig. 1. Details of the interlayer consisting of amorphous carbon (C_a) and amorphous silica (S_a) with a lamella of graphitic carbon (C_g) near to the step-like interface to the 6H-SiC.

by reduction of SiO_2 , carbon of the layer is transformed into CO. Then, on cooling from the heat-treatment temperature, carbon re-precipitates turbostratically from the CO gas according to the Boudouard equilibrium. This is also emphasised by our observation of pores in the region between amorphous carbon and silicate glass with lamellae of graphitic basal planes parallelly arranged to the surface of the pores. However, for the required graphitisation of the complete interlayer the total amount of carbon of the layer should be consumed, which would result in a violent formation of pores. Thus, the mechanism of formation of turbostratic carbon via carbon monoxide is inapplicable for the generation of texturised turbostratic interlayers with thicknesses greater than approximately 5 nm.

3.2. Interlayers in specimens of Pt-coated 6H-SiC and borosilicate glass

In contrast to the findings discussed above, the investigations on structures with Pt-coated 6H-SiC show a significant graphitisation of the whole carbon layer.

As can be seen in Fig. 2, lamellae of graphitic basal planes with a distance of 0.344 nm are generated at the interface to the SiC as well as within the adjacent reaction layer. In addition, the basal planes of these graphitic lamellae were parallel oriented to the $(000\bar{6})$ plane of the 6H-SiC. This corresponds to the diffraction pattern taken from both SiC and layer, presented in Fig. 3. The diffraction ring of the (0002) graphene sheets of the layer clearly shows brightened arcs being aligned with the $[000\bar{1}]$ di-

rection of 6H-SiC, indicating a preferred orientation of the graphitic basal planes within the reaction layer. However, as will be shown later, it is not pertinent to refer to a straight catalysing effect of the platinum on the graphitisation. First, the nanochemical peculiarities of the interlayer region shall be considered. Fig. 4 shows EDX-profiles of carbon, oxygen, silicon and platinum acquired along the line which is marked in the STEM bright-field image (on the bottom of Fig. 4). Within the layer, the trends of the signals of carbon as well as of silicon and oxygen indicate high contents of carbon and probably silica. The platinum, which is concentrated in particles, shows correspondingly distinct signal peaks at the particles located within the layer and at the interface to the borosilicate glass.

3.2.1. Reactions of Pt and SiC

The platinum-containing particles were formed by the reaction between platinum and silicon carbide. Presumably the first step of this reaction is the significant disintegration of SiC (Eq. (1)) indicated by the graphitic lamellae penetrating into the $(000\bar{6})$ -planes of the 6H-SiC

as marked by arrows in Fig. 2. By expansion of this graphitic lamellae, some pieces of the silicon carbide are peeled off from the wafer surface and can finally be found within the reaction layer as demonstrated by the silicon carbide flake in the middle part of Fig. 2.

In the next step platinum interacts with silicon which was formed by the SiC disintegration. Thus, platinum silicide

Fig. 2. Pt-enhanced disintegration of 6H-SiC yielding to both the cleaving of the SiC interface and the formation of graphitic lamellae being nearly parallel aligned to the (0006) plane of 6H-SiC. Arrows represent the graphitic lamellae penetrating into (0006) planes of 6H-SiC.

can be generated (Eq. (2)) and finally precipitated near the SiC surface.

Summarising both steps yields Eq. (3), the reaction between Pt and SiC forming silicide and carbon.

Fig. 3. Diffraction pattern from reaction layer and 6H-SiC with arrows marking widened arcs in the 0002 diffraction ring of the graphene sheets within the layer (specimen of Pt-coated 6H-SiC and borosilicate glass).

Fig. 4. EDX spectroscopy profiles recorded along the line marked in the STEM bright-field image, inserted below; arrows point to Pt-enrichment in particles. The thin epoxy region within the reaction layer is a preparation effect.

Fig. 5. Particle of Pt_xSi_y in a trough of the 6H-SiC indicating reaction processes between SiC and Pt.

Fig. 5 shows details of the formation of platinum silicide at the attacked silicon carbide surface. Within a trough of the SiC (excavated by the reactions with the platinum), a particle of platinum silicide can be seen. It shows lattice fringes with a distance of 0.31 nm, which does not correspond to any lattice spacings of elemental platinum as demonstrated in Table 1, but can be attributed to any of the platinum silicides PtSi , Pt_2Si , or $\text{Pt}_{12}\text{Si}_5$, which is also shown in Table 1. First nanoanalytical measurements via ELNES in correspondence with quantum-chemical calculations give hints to a preference of the silicide Pt_2Si [30]. This would also be in agreement with the observation that the presence of C in the Pt–Si–C system (as in our case) favours the formation of metal-rich silicides [31].

3.2.2. Graphitisation mechanisms

To exclude possible influences of glass constituents on the Pt-enhanced graphitisation additional specimens were

made by heat-treatment of Pt-coated 6H-SiC at 977 °C in Ar (partial pressure of oxygen about 10^{-13} Pa) without a borosilicate glass matrix. Fig. 6 shows details of the interfacial reactions of these specimens. As indicated by arrows, silicide particles grown into the silicon carbide can be detected at the wafer surface. However, as the most interesting feature, atomic planes of graphite, aligned parallel to the particle surface, can clearly be seen at the silicide surface being opposite to the SiC, on the left of the upper part of Fig. 6. Thus, the silicide formation at the interface to the SiC is coupled with the generation of carbon which possibly diffuses through the silicide to the opposite particle surface, where it is precipitated as graphitic carbon.

These findings are strong hints to a mechanism denoted as metal-mediated graphitisation [26] corresponding to the metal-mediated crystallisation of silicon and germanium [26,37–39]. In these cases, not only metals act as mediating agents but also their compounds like silicides. Thus, e.g.

Table 1
Interplanar distances d of Pt and of the silicides Pt_3Si , $\text{Pt}_{12}\text{Si}_5$, Pt_2Si , and PtSi with those values marked, which correspond to the measured distance of 0.31 nm

Pt [32]	Cubic	Pt_3Si [33]	Cubic	$\text{Pt}_{12}\text{Si}_5$ [34]	Tetragonal	Pt_2Si [35]	Tetragonal	PtSi [36]	Ortho-rhombic
d (nm)	(hkl)	d (nm)	(hkl)	d (nm)	(hkl)	d (nm)	(hkl)	d (nm)	(hkl)
0.227	(111)	0.274	(101)	0.307	(321)	0.329	(101)	0.307	(011)
0.196	(002)	0.224	(111)	0.299	(420)	0.298	(002)	0.302	(110)
0.139	(202)	0.194	(002)	0.279	(411)	0.279	(110)	0.296	(002)

Fig. 6. Reaction zone in annealed, Pt-coated 6H-SiC (without glass matrix) showing silicide particles, which were grown into the 6H-SiC. Note the graphitic carbon precipitated at the particle interface opposite to that with the SiC (above epoxy).

the silicide NiSi_2 mediates the crystallisation of amorphous silicon [39]. This mechanism of crystallisation is supposed to be based on both (i) dominant diffusion of nickel atoms through the silicide and (ii) silicide disintegration. At the interface to the crystalline silicon, the silicide NiSi_2 disintegrates producing nickel and silicon. The silicon atoms then arrange to form the crystalline silicon lattice, whereas the nickel atoms diffuse to the opposite interface between the silicide and the amorphous silicon with re-forming of the silicide NiSi_2 .

The driving force for the phase transformation is the reduction of the free energy associated with the transformation of metastable amorphous silicon into stable crystalline silicon. In analogy, for the graphitisation being mediated by metals the amorphous carbon is considered to dissolve within the metal by diffusion, resulting in a supersaturation with respect to the more stable graphitic phase due to the higher free energy of the amorphous state. Subsequently, a nucleation of graphite can take place, with growth of graphite by diffusion of carbon through the metal [26]. Thus, in our case, the relative diffusivities of Pt, Si and C through the silicide should be the key parameters, which determine the graphitisation kinetics. However, no data are currently known to the authors about this problem. Nevertheless, studies of diffusion couples of the system Pt–SiC have shown the mobility of Si in Pt_2Si to be somewhat higher than that of Pt [40]. Moreover, the carbon product of the reaction between SiC and Pt has been considered to be non-diffusing

by assuming an uniform carbon activity of 1. However, the difference in the chemical potential of amorphous carbon and graphitic carbon has to be taken into account as it represents the driving force for the diffusion of carbon from the amorphous to the graphitic phase.

This state of knowledge permits to suppose only a rough model of graphitisation as described below, comprising the formation of silicide at the interface between the particle and the silicon carbide as well as the disintegration of platinum silicide at the interface between the particle and the reaction layer (cf. Fig. 7, labelled 1). At the latter interface platinum atoms are formed by the silicide disintegration, which will

Fig. 7. Scheme of the graphitisation mechanisms being supposed to take place in sandwich structures of Pt-coated 6H-SiC and borosilicate glass: 1—metal-mediated graphitisation; 2—Pt-catalysed stacking of graphitic lamellae (see text).

diffuse through the silicide to the interface with the carbide. Here, Si and C are generated by the Pt-enhanced disintegration of the SiC. While Si atoms are consumed by the Pt₂Si formation, C atoms diffuse through the silicide to the opposite interface with the reaction layer, where they precipitate to form graphitic lamellae. This suggestion of formation and disintegration of Pt₂Si is also emphasised by elemental gradients, which have been found in Pt/6H-SiC-reaction couples at the interfaces of Pt₂Si to both the silicon carbide and the adjacent carbon layer [41]. Pt₂Si regions near the 6H-SiC has been described to be enriched in Si, whereas those near the C layer are Pt-rich.

Complementary and prior to the above process, another graphitising mechanism can be assumed to be active in the carbon formed at the SiC interface. As shown schematically in Fig. 7, labelled 2, this mechanism presumably takes place parallel to the formation of silicides, that means, immediately after the Pt enhanced SiC disintegration. It is conceivable that Pt atoms affecting the disintegration of the SiC also catalyse the formation of the stacks of graphitic basal planes arising from the former (000 $\bar{6}$) planes of the 6H-SiC, which seem to be partly displaced by the expanding graphitic lamellae.

3.2.3. Effect of oxidation processes

Finally, the effect of oxygen, which diffuses from the borosilicate glass into the SiC, has to be discussed. Fig. 8a presents a set of EEL spectra taken at points along the line in the STEM bright-field image on the right. From the up-

permost spectrum to the lowermost one, the energy loss near edge structures of both the Si-L₂₃ edge and the C-K edge change, indicating a modification in the chemical bonding of the respective elements. Further on, an additional O-K edge occurs within the layer. The distinct B-K edges within the spectra from the layer hint to a diffusion of boron species from the glass to the SiC.

The upper of the background-subtracted spectra recorded in the interlayer (Fig. 8b) appears quite similar to that of silica showing an onset at about 104 eV and two distinctly split peaks at about 108.5 and 115.5 eV [42]. This clearly demonstrates the high content of SiO₂ in the reaction interlayer. Moreover, regions of high content of SiO₂ (marked by dark grey filling) and those of low content of SiO₂ alternate, whereas the reverse applies to the content of carbon. This is demonstrated in Fig. 8b showing background-subtracted spectra from both interlayer regions, normalised to the maximum intensity of the first plasmon peak after the C-K edge. Corresponding to these analytical electron microscopy findings, HREM very clearly shows cellularly arranged lamellae of graphitic stackings, which are embedded into an amorphous SiO₂ matrix (Fig. 9). Consequently, in sandwich structures with glass such oxidation effects have to be considered parallel to the reaction processes with platinum. Thus, at the interface to the 6H-SiC at least two competing processes can take place—the reaction of SiC with oxygen;

and that one with platinum discussed above (Eq. (3)).

Actually, the scenario at the silicon carbide surface will be determined by the kinetics of these interacting processes:

Fig. 8. (a) Set of electron energy loss spectra recorded along a line from the 6H-SiC to the interlayer (inset: STEM bright-field image); (b) background-subtracted spectra within the layer.

Fig. 9. HREM image of an interlayer region showing regularly arranged graphitic lamellae embedded into an amorphous matrix, a flake of 6H-SiC (on the top), and a Pt-containing particle (on the left).

If the oxidation prevails, then the products of Eq. (4) (silica and carbon) isolate the platinum or the platinum silicide, which has been already formed, and silicide particles are included into the reaction layer, as observed.

The formation of the alternate regions of silica and carbon within the reaction layer is assumed to be caused by the oxidation of the silicide particles themselves forming silica and platinum.

Thus, oxygen could initiate a cycling of the formation of silicides (Eqs. (2) or (3)) and that of platinum (Eq. (5)), which is equivalent to the decoupling of the formation of carbon (by the Pt-enhanced disintegration of SiC Eq. (1)) and the formation of silica (by the silicide oxidation Eq. (5)).

4. Conclusions

For the first time, the metal-mediated graphitisation was applied for structuring of interlayers in heat-treated silicon carbide/glass sandwiches. The microstructure and the nanochemistry of the reaction layers between carbide and glass were studied down to the atomic scale by HREM and spectroscopic techniques.

The carbon of the whole layer has been found to be significantly graphitised by the effect of platinum. Thus, the layer consists of a cellular net of lamellae of graphite basal planes embedded in a silica matrix. A number of the lamellae is aligned parallel to the (000 $\bar{6}$) plane of the 6H-SiC wafer resulting in a distinct texturisation of the carbon. The platinum is concentrated in particles located at the attacked surface of the SiC, within the layer, and especially at the interface to the glass. Both, the attacked SiC surface and the particles, which appear to consist of Pt_xSi_y and especially of Pt_2Si , indicate a reaction between Pt and SiC.

The procedure of layer formation has been shown to be very complex. It comprises processes induced by platinum as well as oxidation processes by oxygen diffusing from the glass to the SiC. The first step of the reaction of Pt and SiC appears to be the Pt-enhanced disintegration of SiC, which is indicated by graphitic stackings penetrating into the (000 $\bar{6}$) planes of the 6H-SiC. In this early stage of layer formation, the Pt-atoms could affect also the formation of graphitic lamellae from amorphous carbon being generated by the disintegration of SiC. Most of the platinum seems to react with silicon (the second product of the SiC disintegration) forming a silicide. These silicide particles mediate the graphitisation of the carbon products of both the reaction of SiC and Pt and the SiC oxidation. Thus, the observed enhancement of the graphitisation appears to be caused by a complex of combined effects of platinum and of a platinum silicide-mediated solution-precipitation mechanism.

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