JOURNAL OF MATERIALS SCIENCE 31 (1996) 2729–2733

Contact phenomena and interactions in the system $SiC–SiO_2–R_xO_y$ in condensed matter

Part II *Interactions between silicon carbide and silicate glasses at elevated temperatures*

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The contact zone between a silicon carbide monocrystal and silicate glass melt was investigated with the help of a scanning electron microscope, petrographic analysis, infrared spectroscopy, Auger electron spectroscopy, electron spectroscopy for chemical analysis and X-ray diffraction analysis. Silicon carbide may dissolve in glass. When the concentration of carbon atoms in the melt reaches a definite level, oxycarbide phases begin to crystallize. These phases exist at elevated temperatures and then transform to silicon dioxide. Metal cations, constituents of the melt, also may take part in the formation of oxycarbide phases.

1. Introduction

Silicon carbide oxidizes at elevated temperatures in oxygen-containing atmospheres. Pampush *et al.* [1, 2] showed, that sometimes the oxidation of silicon carbide not only leads to the formation of silicon oxide, but also to some new phase. This new phase was identified as silicon oxycarbide. Si–O–C phases were registrated with the help of Auger electron spectroscopy (AES) and infrared absorption spectroscopy during low temperature oxidation of SiC [3]. Lipovitz *et al.* [4] found $Si_xO_yC_z$ in silicon carbide ceramic fibres, manufactured from polycarbosilane polymers. They determined that $Si_xO_yC_z$ has covalent structure using nuclear magnetic resonance (NMR) analysis and electron spectroscopy for chemical analysis (ESCA).

Julbe *et al.* [5] proved the existence of oxycarbide spices during the formation of fibrous silicon carbide from SiO_2–C precursors. The evidence for this was: the shift of Si–O absorption bands in the Fourier transform infrared spectra; a group of peaks intermediate between SiO_2 and SiC in the NMR spectra; the different binding energy of Si_{2p} electrons in the ESCA spectra; significant weight loss of spices during heat treatment (1500 °C, Ar).

Yurkov *et al.* [6] showed that wetting of silicon carbide by melts of silicate glass is chemical in nature. This means that melts of silicate glasses can act as oxidizing agents, but these are more weak than oxygen in air.

Silicon carbide may react with constituents of glasses, giving gaseous products, and it is a well known foam generator in porous glass technology. Silicon carbide may dissolve in melts, giving oxycarbide glasses [7–9].

The aim of the current research is to investigate the interaction of silicon carbide with silicate glass melts.

2. Experimental procedure

Interaction between silicon carbide and the glass melt was investigated primarily in the contact zone. A monocrystal of hexagonal silicon carbide, 10 × 10 mm in length and width, was placed in contact with glass melt S-25-2 (Table I) for 3 h at a temperature of 1500 °C. The crucible with the glass melt and monocrystal was slowly cooled to room temperature. The sample was diamond cut at an angle 30° towards the surface of the SiC monocrystal (plane 0001), so that the width of the contact zone between the monocrystal and the glass was magnified twice. One part of the sample was machine ground, in order to obtain a transparent lapping angle specimen (50 μm thick) for petrographical analysis. The other part was prepared as a lapping angle metallographic specimen for metallographical analysis and scanning electron microscopy (SEM). The specimen was also analysed with the help of electron spectroscopy for chemical analysis (ESCA), Auger electron spectroscopy (AES) and X-ray diffraction (XRD).

The glass powder was mixed with ground SiC monocrystals (grains with average size 0.5–1 mm), in proportion 5:1 by weight. The mixture was heat treated in an oxidizing atmosphere under the same regime. These specimens were analysed by infrared absorption spectroscopy (IAS), ESCA and XRD.

The coating materials of silicon carbide articles after 2500 h (1350 °C) service were also analysed by XRD, IAS, ESCA, SEM, petrographic and metallographic analysis.

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3. Results and discussion

3.1. Analysis of the contact zone between silicon carbide and glass

Silicon carbide monocrystals dissolve in the glass melt. The glass darkens as carbon atoms diffuse into it. After 3 h heat treatment of 1500 °C and cooling, the diffusion front could be seen clearly 1.5×10^{-2} m from the monocrystal border of the 0 0 0 1 plane (diffusion of SiC in other directions also takes place). The border between darkened and transparent glass is not strict. Very approximately, the diffusion velocity of carbon atoms in a glass melt of specified composition is about $5 \times 10^{-3}\ \mathrm{m\,h^{-1}}$.

There was no opportunity to determine the diffusion coefficients of silicon carbide or carbon atoms in the glass melt with the help of Auger electron spectroscopy. The general tendency was for a diminishing concentration of carbon from the border of the monocrystal, but the deviation of concentration was large.

The black and transparent zones, having average sizes of 70–150 μm, are clearly seen on the contact zone border between SiC and glass on the transparent specimen, Fig. 1. Inside the black zones new phase crystals exist. The dimensions are 10–12 μm in length and 4–5 μm in width. The crystals are anisotropic and have a short prismatic form. According to petrographic analysis, the refractive index of the new phase is 1.8 (the crystals were too small to determine the refractive index more precisely). In the "black zones" the crystals are surrounded by darkened glass. The refractive index of the new phase differs greatly from all probable forms of crystallization of glass itself (the standard values of refractive index for all forms of silicon dioxide are in the range 1.4–1.65) and of silicon carbide. It is probable that some new phase(s) crystallizes when the concentration of carbon atoms in the melt reaches some definite level.

According to petrographic analysis and XRD (Fig. 2), the glass itself cannot crystallize within the contact zone. A new set of diffraction lines appears on the X-ray diffractogram at 0.444, 0.335, 0.210 and 0.17 nm, that cannot be identified by known substances. Some peaks of the new substance(s) may coincide with peaks of SiC. The same peaks occur on the XRD spectra of the heat treated "ground monocrystals–glass" sample.

New absorption bands appear on the infrared spectra of the heat treated "SiC–glass" at 700, 900 and $1620\ \mathrm{s\,m^{-1}}$, and the band at $1100\ \mathrm{s\,m^{-1}}$ broadens from 1050 to $1250\ \mathrm{s\,m^{-1}}$ (Fig. 3). Pampush reported [1, 2] that a new crystalline phase(s), formed during low temperature oxidation of SiC, gave bands at 1170 and $1200–1230\ \mathrm{s\,m^{-1}}$, i.e. very much like those reported here. Extra bands at 700, 900 and $1620\ \mathrm{s\,m^{-1}}$

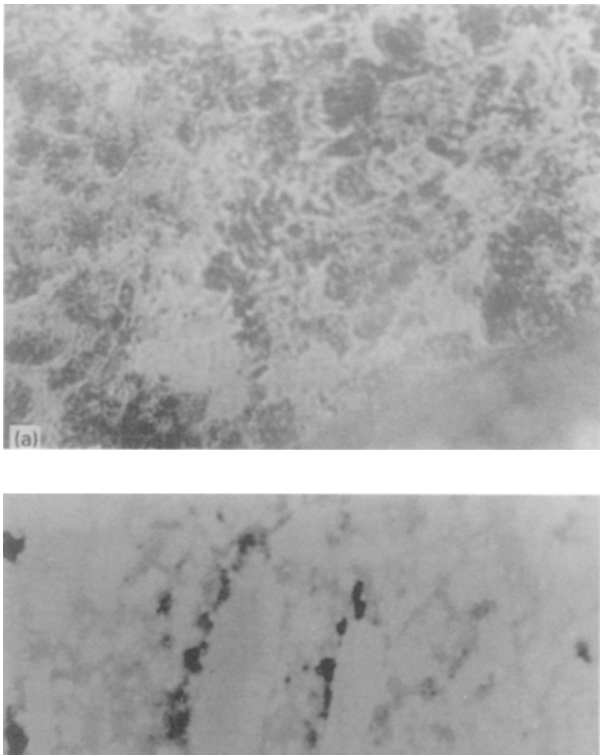

Figure 1 Micrograph of contact zone between silicon carbide monocrystal and glass: (a) transparent specimen (×500), the crystals of the new phase are situated in the black zones, SiC, in the bottom; (b) crystals of the new phase (×3000).

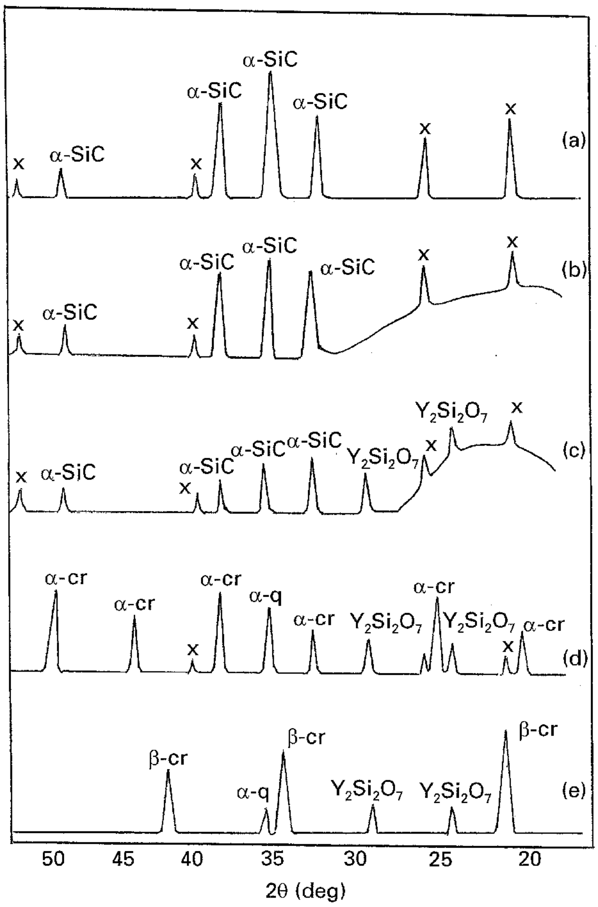

Figure 2 X-ray diffractogram of: (a) contact zone between silicon carbide monocrystal and glass; (b) heat treated (1500 °C, 3 h) SiC–glass; (c) heat treated (1500 °C, 3 h) SiC–SiO_2–Y_2O_3 coating (d) heat treated (1400 °C, 2500 h) SiC–SiO_2–Y_2O_3 coating; (e) heat treated (1400 °C, 2500 h) SiC–SiO_2–Y_2O_3 coating; after additional treatment. (α-cr) α-crystobalite; (β-cr) β-crystobalite; (α-q) α-quartz and (X) oxycarbide phase(s).

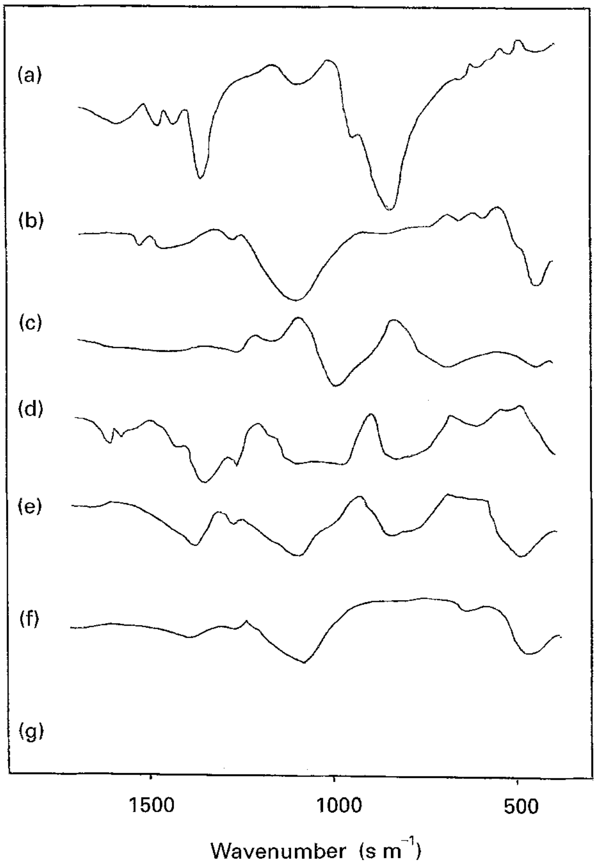

Figure 3 Infrared spectra of: (a) silicon carbide monocrystal; (b) S-25-2 glass; (c) data of Pampush *et al.* [12]; (d) heat treated (1500 °C, 3 h) SiC–glass; (e) heat treated (1400 °C, 2500 h) SiC–SiO_2–Y_2O_3 coating; (f) heat treated (1400 °C, 2500 h) SiC–SiO_2–Y_2O_3 coating after additional treatment.

may appear, owing to carbon atoms in the structure of the glassy phase, that cannot occur in the process of low temperature oxidation [1].

X-ray photoelectron analysis was performed on the silicon carbide monocrystal before and after Ar-ion etching and on the contact zone between SiC and glass (after Ar-ion etching). The line shapes of silicon, carbon and oxygen are shown on Fig. 4. Table I reports the Si_{2s}, C_{1s} and O_{1s} electron binding energies in the specimens and standard data [10].

The carbon peak before treatment is not symmetrical: it presents .a shoulder, corresponding to carbon atoms linked to oxygen, that is present on the panorama spectrum. After treatment the carbon peak becomes symmetrical. The same is true for the silicon peak.

After treatment in ethyl alcohol, residual carbon and traces of SiO_2 remain on the surface of the SiC monocrystal (the former may be absorbed gaseous CO_2). Only after ion etching (Ar) does the SiC surface become clean.

C_{1s} and Si_{2s} peaks of the etched contact zone between SiC–glass are split. Besides the 285.3 eV peak, corresponding to the Si–C bond, the 287.5 eV peak is seen. The latter may be attributed to a carbon atom in the Si–O–C bonding in the glass structure and oxycarbide phases. Si_{2s} atoms have binding energy values of 151.5, 156.7, 158.3 and 159 eV. The first value corresponds to the Si–C bond; the last value to the Si–O bond; intermediate values may be attributed to the Si–O–C bond in the crystalline (oxycarbide crystals) and non-crystalline state (solidified glass). The oxygen peak will not broaden, nor have any shoulders.

So, silicon carbide may dissolve in some glasses, having no reaction with the gaseous products. In certain conditions oxycarbide phases crystallize in the melt. This data is in agreement with [1, 2]. Homeny and coworkers reported about fully amorphous oxycarbide glasses [7, 8]. Imon *et al.* [9] reported that carbon atoms will not form individual oxycarbide phases, but enhance crystallization of known phases. Sol–gel synthesis promotes the formation of oxycarbide glasses with concentrations of carbon up to 18% [11].

Metal cations may promote formation of Si–O–C bonding in the melt. Metal cations may take part in the formation of an oxycarbide structure, as occurs in SiAlON-related systems.

3.2. Analysis of coatings on silicon carbide materials

Coating materials of silicon carbide articles, that work at elevated temperatures, undergo changes. The composition of the S-25-2 glass and SiC particles, and yttria–silica compositions with SiC, were analysed after 3, 1000 and 2500 h heating at 1400 °C.

During the first 3 h the composition "glass–SiC", as well as 'yttria–silica–SiC", in thin layer coatings transforms as described above for the bulk compositions. According to petrographic analysis, in glass with refractive index 1.471, there are crystals of silicon carbide and a substance with a refractive index of 1.8, i.e. the product of interaction between the silicon carbide and silicon oxide. The average size of the oxycarbide particles is 1–2 μm. It is located around crystals of silicon carbide in the form of aggregation occupying 10–15% of the area.

Si–O–C absorption bands appear on the infrared spectra. On the "glass–silicon carbide" coating diffractogram peaks appear at 0.444, 0.335, 0.210 and 0.17 nm; in the case of the "silica–yttria–silicon carbide" composition, only two peaks appear at 0.335 and 0.210 nm. Silicon carbide partly dissolves in the glass melt and oxycarbide phases begin to grow (Fig. 2).

After 1000 h oxycarbide phases began to disappear (as shown by XRD). Petrographic analysis shows that the total amount of the oxycarbide phase diminishes up to 3–5%; some glassy phase particles remain in the carbon structure. The Si–O–C bands (as shown by IAS) remain constant.

Silicon dioxide crystallizes to α-crystobalite (average diameter 1 μm) and partly to α-quartz, that remains unchanged up to 2500 h. In the case of the "yttria–silica–SiC" composition, yttrium silicate, $Y_2Si_2O_7$, of 3–5 μm dimension also crystallizes. The diffractogram peaks of α-crystobalite are shifted, showing the existence of carbon solid solution (and probably other atoms) in the lattice of crystobalite. It is presumed that this fact plays a major role in the stabilization of α-crystobalite. This picture remains up

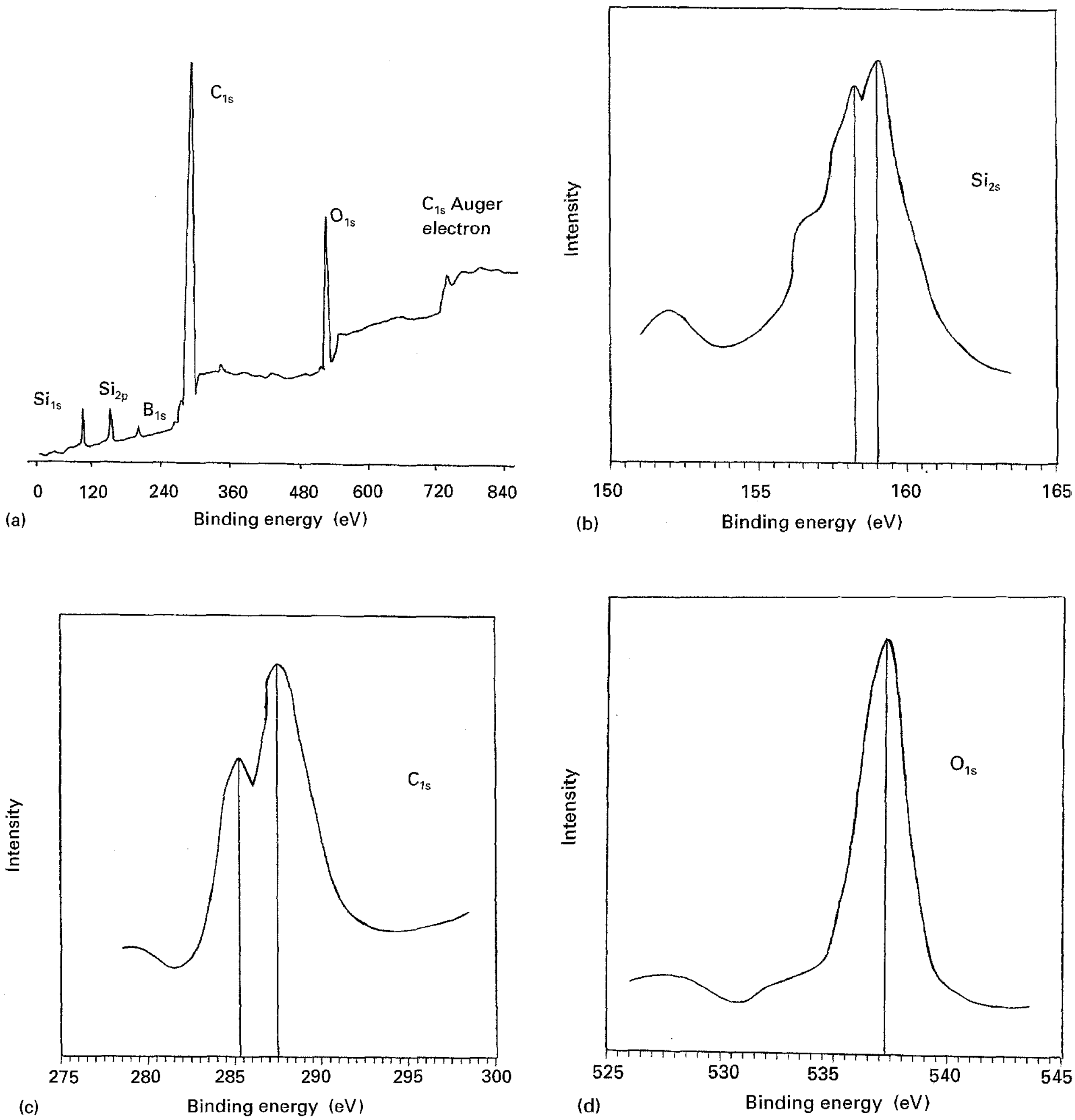

Figure 4 Photoelectron spectra of: (a) contact zone silicon carbide monocrystal–glass; (b) contact zone SiC–glass, peak Si_{2s}; (c) contact zone SiC–glass, peak C_{1s}; (d) contact zone SiC–glass, peak O_{1s}; (e) $SiC–SiO_2–Y_2O_3$ coating (2500 h, 1400 °C), peak Si_{2s}; (f) $SiC–SiO_2–Y_2O_3$ coating (2500 h, 1400 °C), peak C_{1s}.

to 2500 h. The only difference is that the Si–O–C bonds become weaker.

ESCA spectra (Fig. 4) also show that Si–O–C bonds exist in the coating materials after 2500 h heat treatment. The Si_{2s} peak at 158.2 eV corresponds to the Si–O–C bond, but it is broad and has a shoulder, so there may be variants of bonding. The Si_{2s} peak at 155.5 eV may be responsible for participation of the yttrium cation in the Si–O–C bonding. There is no Si–C bonding in the material. The C_{1s} peak is very complex. There is binding energy at 287.5 eV, that corresponds to the Si–O–C bond, and bonds at 289.0 and 289.3 eV, may also be caused by the participation of the yttrium cation in the Si–O–C bond.

Mechanical stabilization may also play a significant role in the process. The coating material after 2500 h heat treatment was withdrawn from the SiC plate, ground and additionally treated at 1450 °C for 2 h. XRD showed full transformation of α-crystobalite to the β-modification (Fig. 2e), with a particle size of 20–40 μm.

4. Conclusions

1. The silicon carbide monocrystal may slowly dissolve in some glass melts; the process may take place without gaseous products.
2. An oxycarbide phase(s) begins to crystallize when the concentration of carbon atoms in the melt reaches a definite level.
3. An oxycarbide phase(s) may exist at elevated temperatures; after 1000 h at 1300–1400 °C it

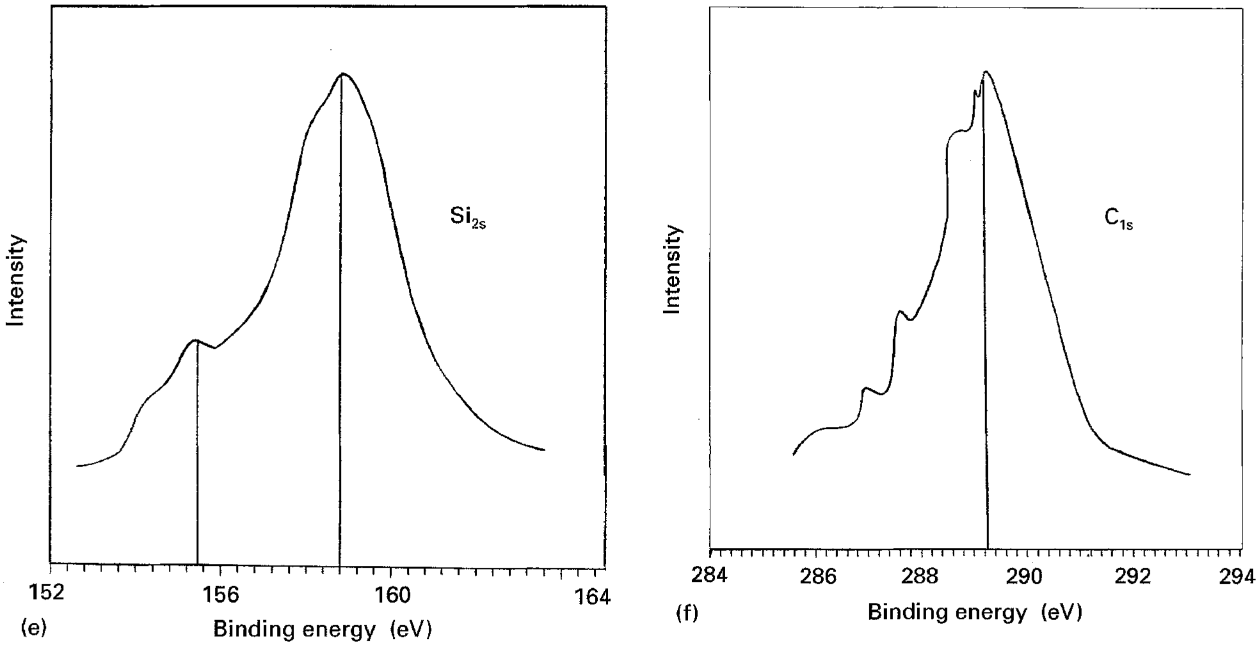

Figure 4 (continued)

TABLE I Electron binding energies (eV) of Si$_{2s}$, C$_{1s}$, O$_{1s}$ electrons from ESCA spectra of the SiC monocrystal, contact zone "SiC–glass", SiO_2–SiC–Y_2O_3 coating and literary data

	Silicon carbide		α-quartz [10]	Contact zone SiC–glass	Coating	Si$_x$O$_y$C$_z$ [5]	Graphite [10]
	Unetched crystal	Etched crystal					
Si$_{2s}$							
	149.3	149.3	153.5	151.5	158.2		
	151.5	151.5		156.7	155.5		
	153.0			158.3			
				159.0			
C$_{1s}$							
	283.2	284.7		285.3	287.0	283.2	284.3
	284.7			287.5	287.6	284.4	
					288.0		
					289.3		
O$_{1s}$							
	537.3		537.3		537.3	533.8	

disappears, giving α-crystobalite and carbon dioxide. The carbon atom may be in solid solution in the structure of the α-crystrobalite, playing a stabilizing role.

Acknowledgements

The authors thank Dr N. M. Vankina and Dr S. M. Varnakov (Institute for Technical Glass, Moscow) for ESCA measurements; Dr N. Popova (Mendeleev University) for petrographic analysis and Mrs M. Marukhina (Mendeleev University) for making transparent lapping angle specimens and photos.

References

1. R. PAMPUSH, W. PTAK, S. JONAS and J. STOCH, *Mater. Sci. Monogr.* **6** (1979) 435.
2. *Idem, ibid.* **10** (1982) 674.
3. B. O. YAVUG and L. HENCH, *Ceram. Eng. Sci. Proc.*3 (1982) 596.
4. J. LIPOVITZ, H. A. FREEMAN, R. T. CHEN and E. R. PRACK, *Adv. Ceram. Mater.* **2** (1987) 121.
5. A. JULBE, A. LARBOT, C. GUIZARD, L. COT, T. DUPIN, J. CHARPIN and P. BERGES, *Eur. J. Solid State Inorg. Chem.* **26** (1989) 101.
6. A. L. YURKOV, B. I. POLYAK, E. V. SHURIGINA and T. V. MURAHVER, *J. Mater. Sci. Lett.* **11** (1992) 1107.
7. J. HOMENY, G. NELSON and S. W. PONLIK, *J. Amer. Ceram. Soc.* **70** (1987) 114.
8. J. HOMENY, G. NELSON and S. RISBUD, *ibid.* **71** (1988) 386.
9. M. M. IMON and H. S. RISBUD, *J. Mater. Sci. Lett.* **5** (1986) 397.
10. V. I. NEFEDOV, "Rentgenoelectron Spectroscopy of Chemical Substances" (Chemistry, Moscow, 1984) p. 255 (in Russian).
11. H. ZHANG and C. G. PANTANO, *J. Amer. Ceram. Soc.* **73** (1990) 958.

Received 23 February
and accepted 5 September 1994