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

Part I *Wetting behaviour of silicate glasses on the surface of silicon carbide at elevated temperatures*

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Wetting behaviour of monocrystal and polycrystalline silicon carbide substrates with melts of 16 silicate glasses was investigated. Different glasses demonstrate various levels of wetting, from no wetting to full wetting. In all cases, wetting of silicon carbide with melts of silicate glass had a chemical nature. Sometimes the drop of molten glass began to bubble. Preliminary treatment of silicon carbide monocrystals affects the wetting behaviour. Varnishing of a primer layer on the silicon carbide substrate may enhance or deteriorate wetting.

1. Introduction

The thermodynamic properties of SiC have been investigated in detail. Investigation of the composition diagrams of silicon carbide are very complicated because of experimental difficulties. The service of silicon carbide articles in oxygen-containing environments leads to the formation of a protective film of silicon oxide, and thus the performance of silicon carbide depends on the coexistence of silicon carbide and silicon oxide.

Ryabchicov [1] investigated the thermodynamic properties of the system $SiC–SiO_2–SiO$ and determined the maximum temperature of coexistance of SiC and SiO_2 to be 2020 K. Experimental data show that the onset temperature of the reaction of SiC and SiO_2 according to Equation 1 is in the interval 1820–1970 K.

$$2SiO_{2\,s,l} + SiC_s = 3SiO_v + CO_v \qquad (1)$$

In real conditions, the impurities shift the equilibrium to the region of lower temperatures.

Silicon carbide refractories came into contact with different melts. The resistance of these refractories is determined by interphase interactions on the border between the SiC_s and the melt. According to Appen [2], the experimental investigations of contact interactions in the systems allow prediction of applications of SiC, and coupled with thermodynamic analysis, could enable contact interactions with different melts to be forecast.

The aim of the present work was to investigate contact phenomena on the border between silicon carbide and melts of glass, as well as to investigate possible interactions between silicon carbide and glasses.

Liquid (melt) can wet a solid surface during interaction of the liquid with a solid, and spread over a surface, or wetting would not occur. There are three main cases of wetting, depending on the value of contact equilibrium angle of wetting, θ, (Fig. 1):

(1). no wetting (bad wetting), $180° < \theta < 90°$;
(2) limited wetting, $90° < \theta < 10°$;
(3) full wetting, no contact equilibrium angle can be registered, and the drop spreads out to form a thin film.

The contact angle of wetting is formed by the surface of the liquid on the solid surface, and is one of the main characteristics of wetting.

The probability of the processes is determined by parameters of the system "solid surface–liquid–gas", where the main parameter is the surface energy of the solid and the surface tension of the liquid, $\sigma_{s,g}$. The thermodynamic criterion of liquid spreading over the surface of a solid is the diminishing free energy of the system, F, due to the increasing surface of contact between the liquid and the solid.

At constant temperature and volume, the change of free energy of the system because of spreading of the liquid is

$$dF = \sigma_{l,g} dS_{l,g} + \sigma_{s,l} dS_{s,l} + \sigma_{s,g} dS_{s,g} \qquad (2)$$

where $\sigma_{l,g}$ etc. are free energies of surface borders (liquid–gas, etc.), S is the surface of the border (liquid–gas, etc.). The spreading of a liquid changes the border surfaces

$$dS_{l,g} = dS_{s,l} - dS_{s,g} \qquad (3)$$

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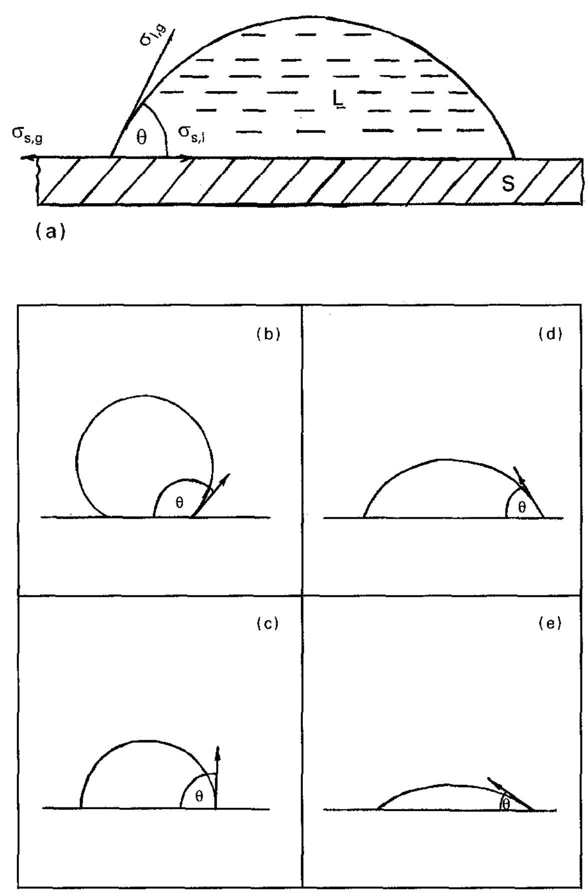


Figure 1 Wetting behaviour: (a) surface forces at equilibrium of a drop of melt on a solid substrate; (b) no wetting; (c, d) limited wetting; (e) full wetting.

and the condition for spontaneous spreading is

$$\sigma_{l,g} + \sigma_{s,l} - \sigma_{s,g} < 0 \qquad (4)$$

At equilibrium the free energy of the system should have a minimum value, $dF = 0$, and the contact equilibrium angle of wetting

$$\cos\theta = (\sigma_{s,g} - \sigma_{s,l})/\sigma_{l,g} \qquad (5)$$

The work of adhesion characterizes the bond forces of the liquid and solid and equals the work of separation of the liquid and solid along the interphase border. It also characterizes the interaction of two condensed phases at a square of contact

$$W_a = \sigma_{s,g} + \sigma_{l,g} - \sigma_{s,l} \qquad (6)$$

Combining with Equation 5 gives

$$W_a = \sigma_l(1 + \cos\theta) \qquad (7)$$

The greater the interaction of the contacting phases, the greater is the value of the work of adhesion. The work of cohesion, W_c, characterizes the interaction of the particles of one phase. An isothermal separation of the volume of a liquid into two parts, the work of cohesion and the work of separation, give two values of surface tension

$$W_c = 2\sigma_{l,g}/2 \qquad (8)$$

Thus the equation for the contact angle may be rewritten

$$\cos\theta = (2W_a - W_c)/W_c \qquad (9)$$

The equation shows that the value of the contact equilibrium angle of wetting is determined by a balance of forces of attraction of the liquid to the solid surface and the forces of mutual attraction of particles of the liquid. The wetting behaviour may now be represented as:

1. no wetting, $W_a < 1/2W_c$;
2. limited wetting, $W_a > 1/2W_c$;
3. full wetting, $W_a > W_c$.

The work of adhesion is always positive, because between bodies of any nature, forces of molecular attraction always act, and contact angles are always lower than 180 °, thus it is impossible to realize full unwetting. The lower the work of cohesion (and surface tension of a liquid), the easier is the process of wetting. For full wetting, it is necessary that the work of adhesion should be at least twice the value of the surface tension of the liquid.

2. Experimental procedure

The wetting experiments were performed using the "sitting drop" method in air in the temperature range 1000–1450 °C. We investigated the wetting behaviour of silicon carbide by glass melts used in the electronic industry in Russia [3]. The compositions and characteristic temperatures of the glasses are given in Table I. The glass nomenclature is that used in the electrovacuum industry of Russia; the first number of the series, S, corresponds to the coefficient of linear expansion; e.g. linear coefficient of expansion of glass S-48-1 is $48 \times 10^{-7}\,K^{-1}$.

The contact equilibrium angle of wetting was registered on a film at a magnification × 10. According to Visotskis and Appen [4] the equilibrium between the surface forces in a drop of silicate glass on a metal plate takes place after 30–40 min exposure at a fixed temperature. Each experiment was repeated three times. The calculation of contact equilibrium angle of wetting was made according to the formula

$$\theta = 2\,\mathrm{arctg}(2H/d) \qquad (10)$$

where H is the height and d is the diameter of the drop.

In Part I of this work the substrates were monocrystals of hexagonal α-SiC (the 0 0 0 1 plane), prepared by the method of Lely [5]; dimensions 10×10^{-6} m. In Part II, the substrates were polycrystalline silicon carbide materials with porosity of 19% and 28% and an average grain size 10–100 μm and 100–2000 μm (Table II).

The surface of a silicon carbide monocrystal was analysed using electron spectroscopy for chemical analysis (ESCA) before and after argon-ion bombardment (etching).

TABLE I Chemical composition and characteristic temperatures of glasses (T_g corresponds to viscosity $10^{12.3}$ Pa s, T_p to 10^{10} Pa s and T_s to $10^{6.65}$ Pa s

Glass	Composition wt %											(°C) T_g	(°C) T_p	(°C) T_s
	SiO_2	B_2O_3	Al_2O_3	ZnO	BaO	CaO	MgO	Na_2O	K_2O	Li_2O	CeO_2			
S-25-2	78.2	19.5							2.3			560	635	821
Pyrex	80.6	12.0	2.0			0.3	0.06	4.0	1.0			535	615	820
S-37-1	57.6		25.0			7.4	8.0		2.0			485	740	806
S-37-2	70.0	27.0						1.4	1.0	0.6		485	590	732
S-37-3	70.0	26.5						1.0	1.4	0.4	0.7	470	615	748
S-38-1	68.8	26.5	1.6					2.5	1.6			445	570	732
S-39-3	57.0	10.0	17.0		8.5	5.0	2.5						775	918
S-40-1	74.8	18.0	1.4					4.2	1.6			500	610	765
S-48-3	54.0		18.5	6.0	8.0	13.5							730	810
S-50-1	25.0	30.0	20.0		25.0							470	620	680
S-52-1	68.7	19.0	3.5					4.4	4.4			522	585	720
S-52-2	68.3	18.0	8.0	3.0				3.4	3.6	0.7		492	577	720
S-60-1	53.5	7.0	12.0	7.5	7.0	4.5	2.0	4.5	1.5	0.5		560	630	770
E	54.0	10.0	15.0			17.0	4.0					630	700	785
SP-4	85.5	11.0	1.5					0.5	1.5				650	
SP-5	78.5	15.0	2.0					1.5	3.0				620	
SP-6	78.0	14.5	1.75					1.75	4.0				600	

TABLE II Characteristics of the polycrystal materials, used as substrates

Material	Grain size (μm)	Porosity (%)	Composition (wt %)				
			SiC	Si	C	SiO_2	Fe_2O_3
Coarse-grained	100–2000	28	98.97	0	0.3	0.6	0.13
Fine-grained	10–100	19	98.75	0.1	0.2	0.85	0.1

3. Results and discussion

3.1. Wetting behaviour of silicon carbide monocrystals

X-ray photoelectron analysis (XPA) was performed on a silicon carbide monocrystal before and after argon-ion etching and on the contact zone between SiC and the glass (after argon-ion etching). The line shapes of silicon, carbon and oxygen are shown in Fig. 2.

The carbon peak before treatment is asymmetrical; it presents a shoulder, corresponding to carbon atoms linked to oxygen, which is present on the panorama spectrum. After treatment, the carbon peak becomes symmetrical. The same picture is found for the silicon peak.

After treatment in ethyl alcohol, residual carbon remains on the surface of the SiC monocrystal (it may be absorbed gaseous CO_2), and traces of SiO_2 are also found. Only after argon-ion etching does the surface of SiC become clean.

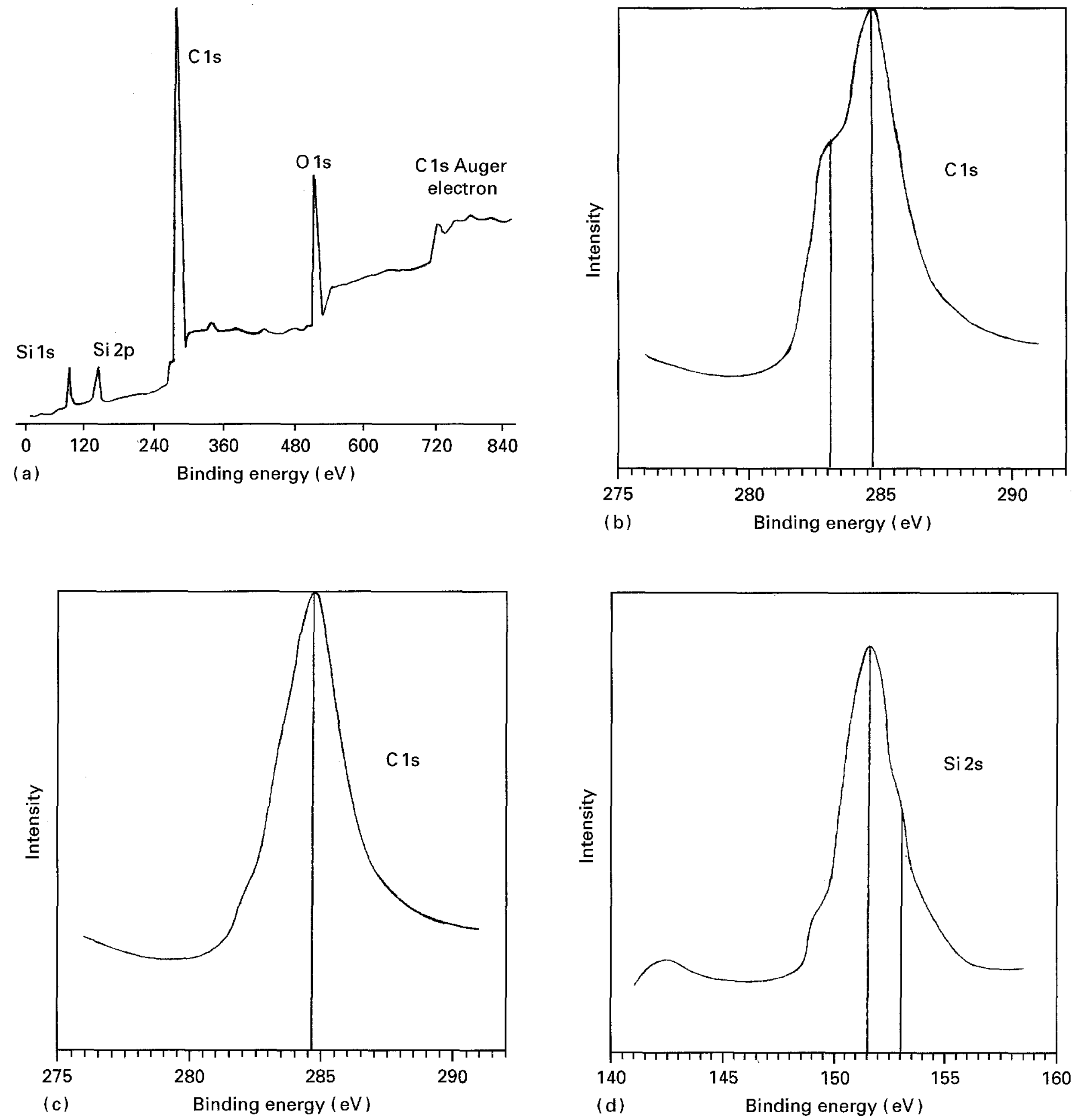
The experiment showed a variety of types of behaviour of glasses on a plate of a SiC monocrystal (Fig. 3a, b). Melts of glasses S-37-2, S-38-1, SP-6, SP-5 did not wet the plate of SiC monocrystal at all in the interval 1000–1500 °C (the contact equilibrium angle of wetting did not change with temperature and equals 120°–80°).

Almost absolute wetting is demonstrated by glasses S-37-1, S-40-1, S-50-1, S-52-2, S-60-1. Other glasses have intermediate values between absolute wetting and no wetting, with contact angles $30° < \theta < 60°$.

The glasses have different softening points (Table I) and viscosities (Fig. 4) but, in general, the wetting ability did not correlate with viscosity. For example, glasses S-37-1 and S-38-1 have almost equal viscosities at all temperature intervals. Glass S-37-1 demonstrates absolute wetting behaviour at 1400 °C ($\theta = 7°$), but the contact equilibrium angle of wetting of the melt of glass S-38-1 at 1300 °C on SiC monocrystal is 105° whilst at 1450 °C it diminishes to 60°.

Therefore the different wetting behaviour of glasses on SiC must be linked with the chemical composition or with chemical interactions on the surface of the silicon carbide.

In some cases it was possible to see "bubbling" of a drop of glass (dotted lines in Fig. 1). This "bubbling" is linked with the reaction of SiC with components of the glass, producing gaseous products, although there may be other causes (e.g. gases, dissolved in the crystals). "Pyrex" glass bubbles in contact with silicon carbide only in the interval 1150–1260 °C, then the bubbling ceases and the glass exhibits normal wetting behaviour. Glass S-52-1 bubbles in all temperature intervals beginning from 1300 °C. General analysis of the wetting curves of silicon carbide monocrystals shows that common wetting behaviour is a slow monotonic diminishing of contact equilibrium angle. Sometimes there may be steps on the wetting curves,



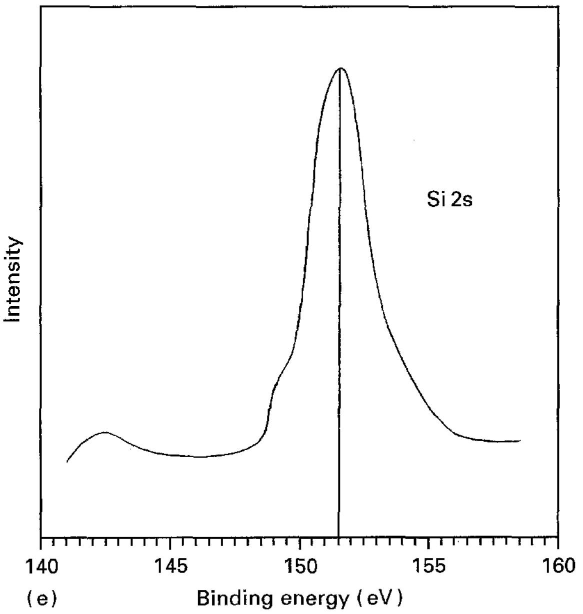


Figure 2 Photoelectron spectra of the surface of silicon carbide monocrystal: (a) unetched surface; (b) C'_{1s} peak, unetched surface; (c) C'_{1s} peak, etched surface; (d) Si'_{2s} peak, unetched surface; (e) Si'_{2s} peak, etched surface.

as in the case of glasses S-37-3 or E. The other type of behaviour is monotonic reduction of the contact angle of wetting, followed by a rapid fall (S-50-1, S-48-3, S-60-1). Sometimes a drop began to bubble.

The specific work of adhesion was calculated according to Equation 7. Surface tensions of glass melts were calculated according to the method given by Appen [2].

The molar work of adhesion was calculated as

$$W_{\mu} = W_a S_{\mu} = W_a(\mu/\rho)^{2/3} N^{1/3} \qquad (11)$$

where S_{μ} is the surface of monomolecular level of 1 mol substance, μ and ρ are the molar weight and density, and N is Avogadro's number.

The value of molar work of adhesion enables physical wetting (due to the orientational interaction or

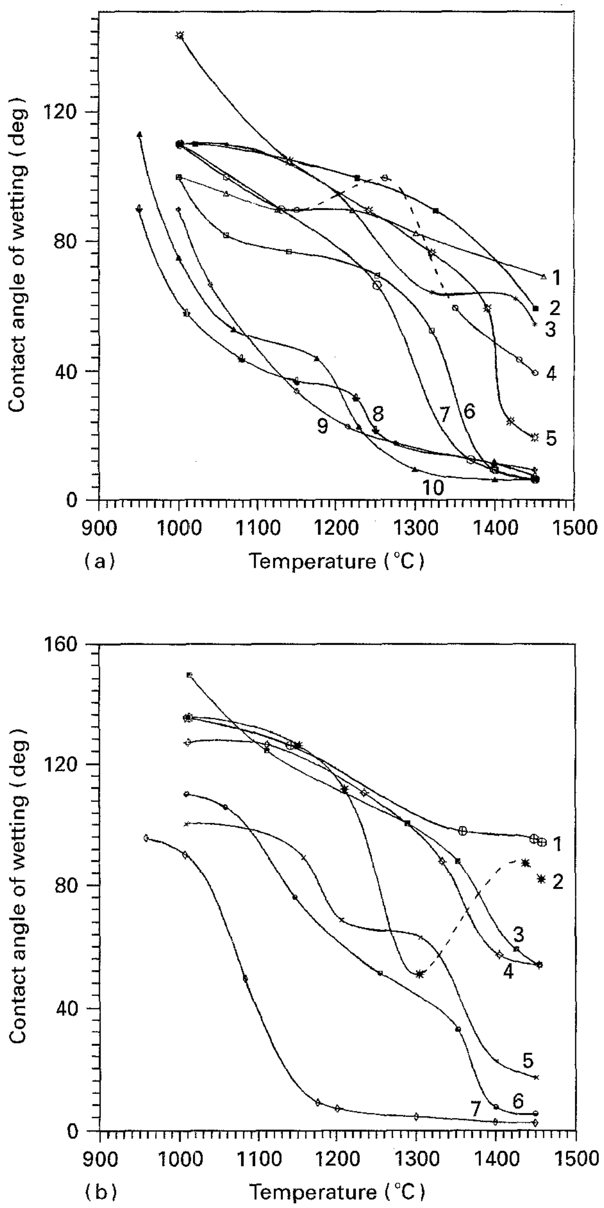


Figure 3(a, b) Temperature dependence of the contact equilibrium angle of wetting of silicon carbide monocrystal with melts of silicate glasses. (a) (1) S-37-2, (2) S-38-1, (3) S-25-2, (4) Pyrex, (5) S-48-3, (6) S-37-1, (7) S-39-3, (8) S-50-1, (9) S-40-1, (10) S-37-3. (b) (1) SP-6, (2) S-52-1, (3) SP-5, (4) SP-4, (5) E, (6) S-52-2, (7) S-60-1.

Van der Vaals forces) to be distinguished from chemical wetting (due to interaction of constituents of the melt with the substance of the substrate).

The energy of physical wetting is small, parts or units of kJ mol^{-1} [6], whereas the energy of chemical wetting is of the order of hundreds of kJ mol^{-1}.

The wetting of silicon carbide with melts of silicate glasses has a chemical nature (Table III). Even in the cases of almost no wetting (e.g. glass SP-6), molar work of adhesion reaches values of 383–1086 kJ mol^{-1}. So we may say, that during the wetting the chemical interaction of an SiC plate with constituents of the glasses takes place.

The other feature of the chemical nature of wetting is the rather sharp dependence of molar work of adhesion on temperature [6]. The value of the molar work of adhesion of wetting of silicon carbide with silicate glasses is at least doubled for a temperature rise of 400 °C (Table III).

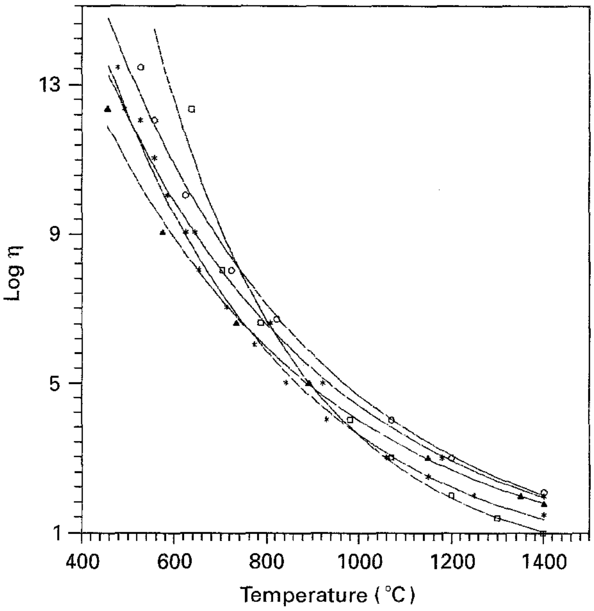


Figure 4 Plot of log viscosity (Pa s) of some glasses versus temperature. (*) S-52-1, (○) Pyrex, (□) E, (*) S-37-1, (▲) S-38-1.

The next experiment was carried out in order to examine the influence of additives (or the constituents of the melts) on the wetting behaviour. The oxides BaO, ZnO, SrO, CoO (well-known promoters of adhesion) were added in amounts of 5, 10, 20 wt % to glasses S-25-2 and S-37-1. The compositions were heat treated in order to obtain new glasses. Glass S-25-2 exhibited moderate wetting; glass S-37-1 showed excellent wetting, but only above 1400 °C (Fig. 3).

The addition of ZnO and CaO promoted "bubbling" of a drop of glass S-25-2 on contact with SiC (Fig. 5) (if the drop is bubbling, the curve is dotted). Additions of BaO and SrO significantly decreased the contact angle of wetting. There was no monotonic dependence of the decrease of contact angle of wetting of the glass with increase in the amount of additions at a given temperature. Increasing the amount of additions up to 20% leads to a decrease of the contact angle of wetting.

Additions of BaO, SrO, CoO, ZnO to glass S-37-1 did not promote bubbling (Fig. 6). The effect of the additions on the decreasing equilibrium angle of wetting is not high. The best results are obtained in the case of additions of CoO and ZnO. Barium oxide plays almost no role in the decreasing contact angle of the melt. Class S-37-1 contains rare-earth oxides CaO and MgO, but no boron oxide. Probably the addition of oxides with mixed valences, ZnO and CoO, changes the activity of boron ions in the melt of S-25-2.

At the same time it should be noted that the value of molar work of adhesion is almost unchangeble, because it is not a strict criterion. It is doubtful if, in one case the molar work of adhesion is bigger, it means that the chemical interaction should proceed at a greater rate. Usually it monotonically increases with increasing temperature. (Probably, it may be possible to link the value of molar work with the Gibb's free energy. However, in order to do this, it is necessary to understand which component reacts with the silicon carbide.)

TABLE III Work of adhesion (specific and molar) of glass melts to the surface of silicon carbide monocrystal

Glass	Temperature (°C)	Work of adhesion		Glass	Temperature (°C)	Work of adhesion	
		Specific ($N m^{-1}$)	molar ($kJ m^{-1}$)			Specific ($N m^{-1}$)	molar ($kJ m^{-1}$)
S-25-2	1000	0.204	908	Pyrex	1000	0.195	870
	1060	0.191	849		1060	0.244	1086
	1200	0.259	1154		1150	0.291	1295
	1320	0.397	1767		1260	0.238	1060
	1425	0.400	1780		1350	0.429	1910
	1450	0.433	1929		1450	0.500	2224
S-37-1	1000	0.353	1572	S-37-2	1000	0.227	1012
	1060	0.484	2155		1060	0.249	1109
	1140	0.516	2301		1125	0.267	1188
	1250	0.561	2497		1220	0.265	1178
	1320	0.665	2959		1300	0.293	1304
	1450	0.817	3637		1450	0.342	1521
S-37-3	1000	0.339	1513	S-38-1	1000	0.177	787
	1070	0.428	1904		1050	0.177	787
	1225	0.501	2232		1225	0.216	961
	1300	0.512	2280		1325	0.257	1144
	1450	0.502	2237		1450	0.383	1702
S-39-3	1000	0.303	1341	S-40-1	1000	0.285	1269
	1130	0.36	1602		1150	0.394	1752
	1250	0.494	2198		1215	0.528	2352
	1370	0.681	3076		1275	0.535	2380
	1400	0.690	3075		1400	0.534	2378
	1450	0.686	3052		1450	0.532	2368
S-48-3	1000	0.081	362	S-50-1	1000	0.448	1996
	1140	0.293	1306		1150	0.516	2299
	1240	0.392	1745		1250	0.545	2421
	1390	0.579	2578		1400	0.552	2456
	1450	0.735	3273		1450	0.551	2454
S-52-1	1000	0.109	486	S-52-2	1000	0.193	861
	1140	0.146	652		1140	0.352	1570
	1200	0.223	992		1250	0.454	2025
	1300	0.579	2581		1350	0.509	2267
	1450	0.386	1722		1450	0.549	2445
S-60-1	1000	0.356	1585	E	1000	0.319	1419
	1080	0.578	2574		1150	0.38	1691
	1175	0.693	3084		1200	0.506	2224
	1300	0.686	3055		1300	0.532	2369
	1400	0.678	3021		1400	0.705	3139
	1450	0.674	3003		1450	0.714	3178
SP-4	1000	0.123	547	SP-5	1000	0.042	187
	1100	0.121	540		1100	0.123	552
	1225	0.188	834		1280	0.227	1008
	1325	0.296	1317		1345	0.281	1250
	1400	0.439	1956		1420	0.408	1818
	1450	0.450	2001		1450	0.427	1905
SP-6	1000	0.086	383				
	1130	0.115	512				
	1250	0.235	1048				
	1350	0.241	1073				
	1450	0.244	1086				

Data on the interactions of silicon carbide with indvidual oxides which may be constituents of the glass, are contradictory. The general concept is that silicon carbide would not interact with Al_2O_3, CaO, MgO, BaO, Y_2O_3, Na_2O, K_2O, Li_2O up to 1400 °C [8–11].

In silicate melts, metal cations may act as corroding agents. According to Kulikov [12], alkaline cations cannot interact with silicon carbide, because the Gibb's free energy is positive for the reactions. Yet there are many alkaline silicates–$Na_2Si_3O_7$, Na_2SiO_3, $Na_2Si_2O_5$. The oxidation process of silicon carbide is a chain reaction

$$Me_2O{*}\zeta SiO_2 \xrightarrow{SiC} Me_2O(\zeta - 1)$$

$$ {*}SiO_2 \xrightarrow{SiC} Me_2O(\zeta - 2){*}SiO_2 \quad (12)$$

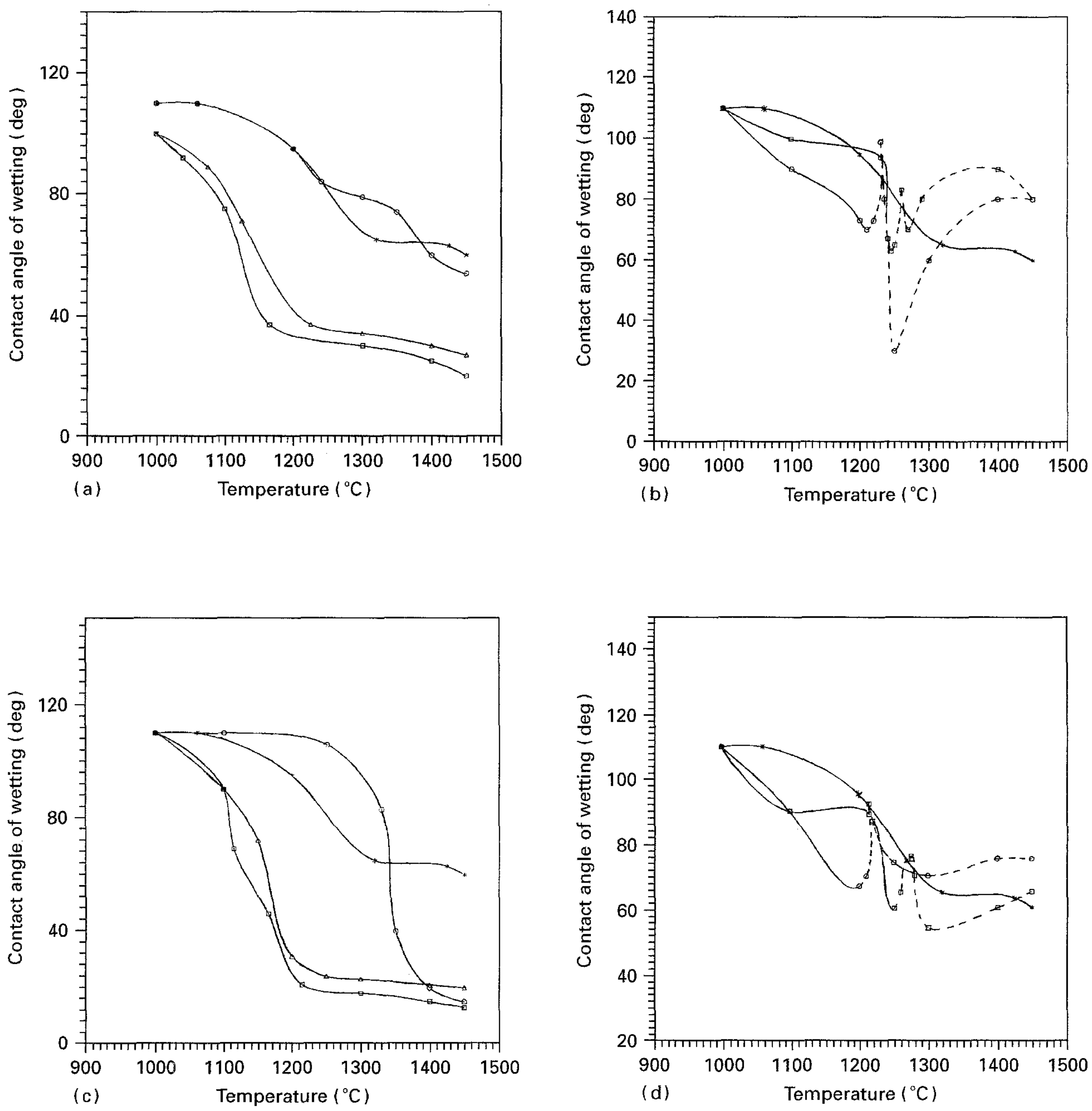


Figure 5 Temperature dependence of the contact equilibrium angle of wetting of silicon carbide monocrystal with (*) melt of glass S-25-2 with additives: (a) BaO, (○) 5%, (□) 10%, (△) 20%; (b) ZnO, (○) 10%, (□) 20%; (c) SrO, (○) 5%, (□) 10%, (△) 20%; (d) CoO, (○) 10%, (□) 20%.

in the direction of reducing alkaline oxide content, which may give rise to gaseous products. The presence of sodium and potassium cations in the melt should enhance the interaction with the silicon carbide.

The presence of alkalies in glass melts may promote bubbling, although bubbling has not yet been linked with the presence of alkalies. In principle, the role of alkalies may be played by boron oxide.

On the other hand, the reaction may only occur between SiC and SiO_2, but cations may shift the equilibrium to lower temperatures. In any event, at 1000 °C the value of the molar work of adhesion of glass S-25-2 is significantly lower than that of the S-25-2 + 10% BaO glass. At 1300 °C there is no difference in the values of the molar work of adhesion.

3.2. Wetting of silicon carbide monocrystals, treated by different reagents

Preliminary treatment of the substrate plays a considerable role. The aim of the treatment is the accurate cleaning of the surface of oil, removal of oxidized layers, adhered particles and other impurities, improvement of roughness and surface activity. Preliminary treatment of plates may change the wetting behaviour of the melts on the substrates. Chemical etching is used to clean the surface of oil and partial damage of surface in order to make it rough. The level of roughness depends upon the rate at which centres of etching occur and the etching velocity.

Silicon carbide is believed to be a chemically inert substance. It does not react with HCl, but treatment in HCl changes the SiC surface. Silicon carbide slowly

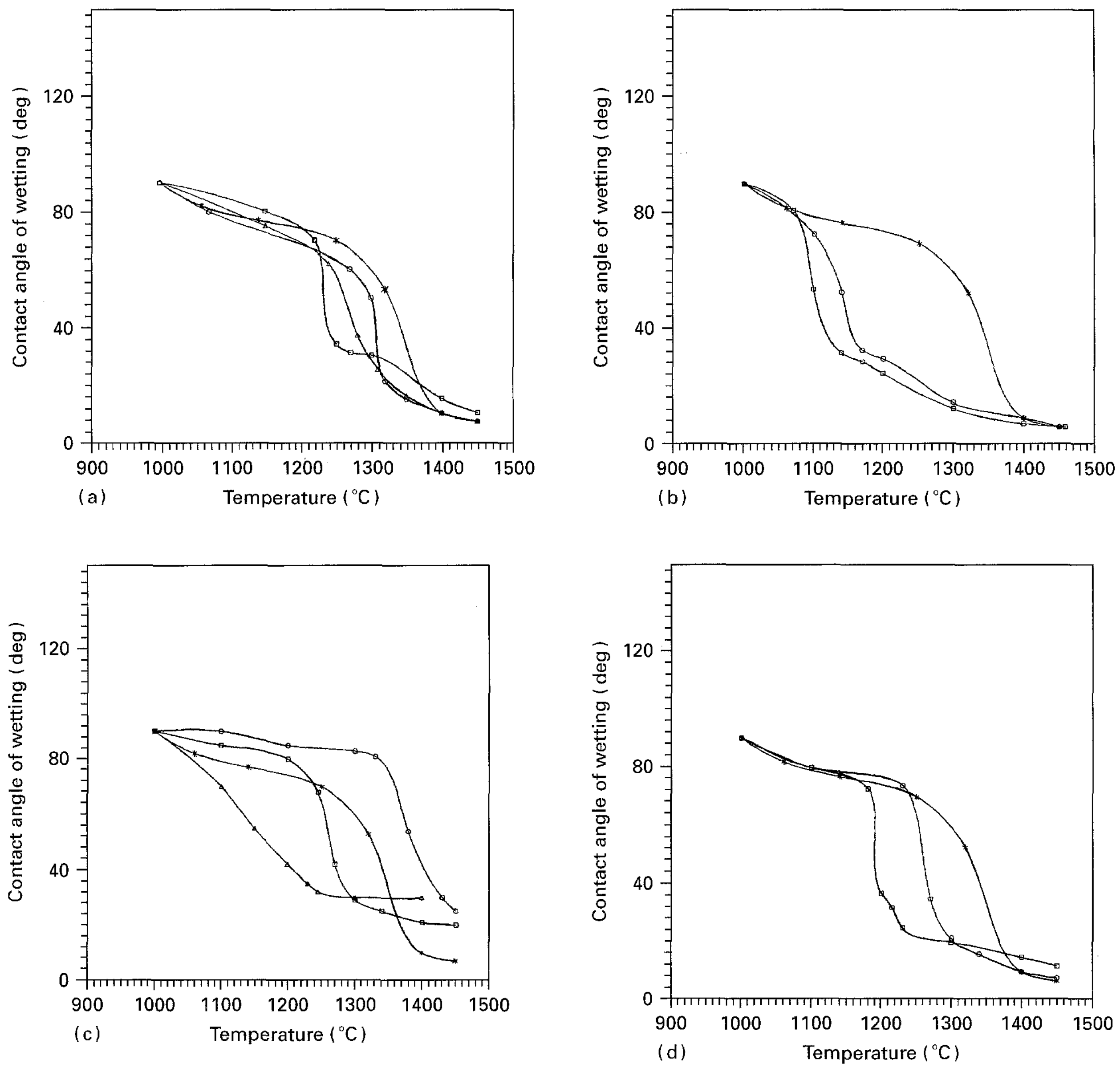


Figure 6 Temperature dependence of the contact equilibrium angle of wetting of silicon carbide monocrystal with (*) melt of glass S-37-1 with additives: (a) BaO, (○) 5%, (□) 10%, (△) 20%; (b) ZnO, (○) 10%, (□) 20%; (c) SrO, (○) 5%, (□) 10%, (△) 20%; (d) CoO, (○) 10%, (□) 20%.

disolves in H_3PO_4 and NaOH. Data concerning interactions of SiC with solute salts are contradictory.

In our research, plates of silicon carbide monocrystals were etched in HCl, H_3PO_4, NaOH (boiling solute and boiling melt), $ZrOCl_2$, $CaCl_2$, $AlCl_3$ and $Mg(NO_3)_2$. These agents may also dissolve the silicon dioxide film on the surface of SiC, or change the SiC surface.

The etching of substrates and varnishing of the intermediate primer layer are commonly used in coating practice. The base layer usually provides better adhesion, while the surface layer gives stability to environmental conditions. The intermediate layers may enhance or deteriorate adhesion, depending upon the nature and depth. Thin films of substances with a less-covalent structure than SiC, may change the wetting behaviour of silicate melts on SiC. For this purpose the silicon carbide monocrystal plates were treated in a 20% sol of silica and its mixture with H_3PO_4 and in solutions of ethylsilicate with $ZrOCl_2$, $CaCl_2$, $AlCl_3$, $Mg(NO_3)_2$.

Preliminary treatment of SiC in salts, acids and alkalies increases the contact angle of wetting in the temperature range 1000–1300 °C (Fig. 7). Treatment in HCl, $ZrOCl_2$, NaOH and $AlCl_3$ decreases wetting in all temperature intervals; for example, after treatment in HCl the contact angle of wetting increases from 8° to 42°. Treatment in solutions of $Mg(NO_3)_2$ and $CaCl_2$ slightly improve wetting in the temperature range 1300–1450 °C.

The treatment of SiC in a melt of NaOH and H_3PO_4 plays no role in the wetting behaviour in the temperature range 1300–1450 °C and decreases wetting at lower temperatures.

Silicon carbide is inert to HCl, but the wetting behaviour of SiC after treatment in HCl deteriorates. One of the possible explanations is that the etching of SiC in acids, alkalies and salts, removes the surface

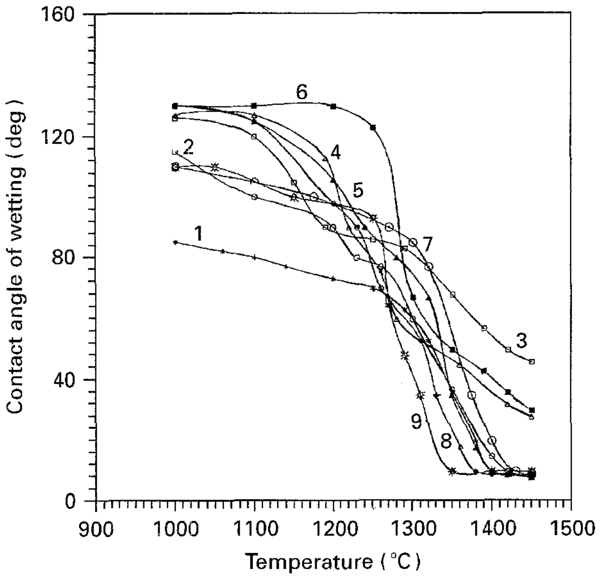


Figure 7 Temperature dependence of the contact equilibrium angle of wetting with melt of glass S-37-1 of silicon carbide monocrystal (1), treated in (2) H_3PO_4, (3) HCl, (4) NaOH, (5) boiling NaOH, (6) $ZrOCl_2$, (7) $AlCl_3$, (8) $CaCl_2$, (9) $Mg(NO_3)_2$.

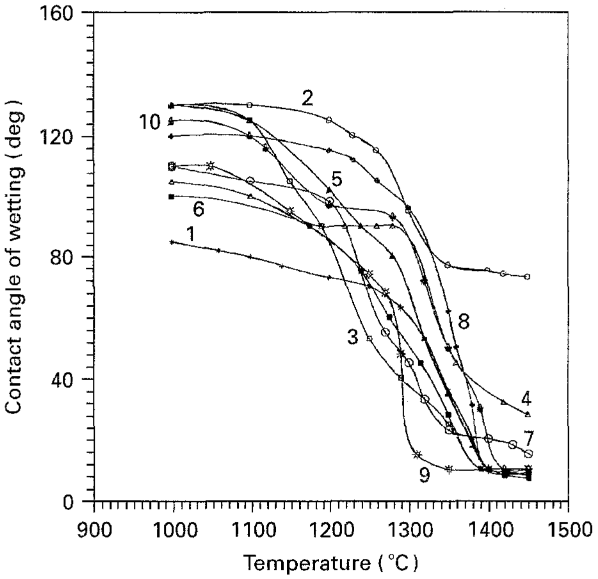


Figure 8 Temperature dependence of the contact equilibrium angle of wetting with melt of glass S-37-1 of silicon carbide monocrystals (1), with intermediate layers of (2) SiO_2 sol, (3) $SiO_2 + H_3PO_4$, (4) SiO_2 sol + $ZrOCl_2$, (5) $Et_4SiO_4 + H_3PO_4$, (6) $Et_4SiO_4 + AlCl_3$, (7) $Et_4SiO_4 + CaCl_2$, (8) $Et_4SiO_4 + Mg(NO_3)_2$, (9) Et_4SiO_4 + $ZrOCl_2$, (10) hydrolysed Et_4SiO_4.

film of silicon dioxide. In the case of HCl, $ZrOCl_2$, NaOH (solute) and $AlCl_3$, the treatment dissolutes the SiO_2 film and passivates the surface, thus the oxidation of silicon carbide, leading to new SiO_2 film formation which would enhance wetting, does not take place. Etching in solutions of $Mg(NO_3)_2$ and $CaCl_2$ also dissolves the SiO_2 film, but does not passivate the SiC surface.

Any intermediate layers (Fig. 8) decrease wetting in the range 1000–1250 °C. The base layers of SiO_2 sol, SiO_2 sol + $ZrOCl_2$, hydrolysed Et_4SiO_4 and Et_4SiO_4 + $Mg(NO_3)_2$ deteriorate wetting in all temperature intervals. Solutions of $H_3PO_4 + SiO_2$ sol, Et_4SiO_4 + $ZrOCl_2$ and $Et_4SiO_4 + CaCl_2$ improve wetting in the range 1250–1450 °C.

In the case of a base layer of $Et_4SiO_4 + ZrOCl_2$, the "shift" of temperature which leads to full wetting, is 100 °C. The phenomenon may be explained by the existence of more ionic bonds on the surface of silicon carbide. The existence of silicon dioxide film produced from SiO_2 sol and hydrolysed Et_4SiO_4, passivates the surface. (We suppose that the texture of the newly appeared SiO_2 film differs from the texture of the SiO_2 film which appears on the SiC surface due to oxidation.)

3.3. Wetting behaviour of silicon carbide polycrystals

The geometry of the solid surface affects the value of the contact equilibrium angle of wetting in a case of limited wetting. "Microhills" and "microcavities" lead to an increase of the real surface of the material in comparison to an ideal smooth surface. Eremenko [7] proposed that the contact angle of wetting on a rough surface, θ_0 is

$$\cos\theta_0 = k\cos\theta_0 \qquad (13)$$

where θ_0 is the contact equilibrium angle of wetting of the same liquid on an ideal rough surface, k is the coefficient of roughness – the ratio of the real surface to its projection on a horizontal plane.

The role of microtopography in the wetting phenomena is unclear. From one point of view, in the case of considerable toughness when $k < 1/\cos\theta$ and $\theta < 90°$, i.e. limited wetting, there may be change from limited wetting to full wetting. From another point of view, sometimes the opposite picture may emerge (change to no wetting). Eremenko considers that the latter result may occur when roughness is oriented parallel to the direction in which the drop spreads out [7].

The investigated silicon carbide materials are coarse-grained (Table II), porous and consist of a mixture of α- and β-modifications of SiC and small admixtures of SiO_2 and Si, Fe_2O_3. The wetting of porous plates of silicon carbide, as a rule, takes place at lower temperatures (Fig. 9a,b). Films of silicon dioxide may also enhance this phenomenon. More frequently, a drop of glass melt began to bubble on a porous plate (compared with a monocrystal).

The "bubbling" may be caused by gases in the pores, but may also be the result of a reaction, giving gaseous products, that is promoted by the more active and imperfect surface. "Pyrex" glass and S-52-2 bubbles on plates from coarse-grained material and sometimes on plates from less-coarse-grained material. The greatest work of adhesion is found in glass S-37-1.

No analytical dependencies can be proposed on the basis of which it would be possible to predict whether better wetting may occur on one type of SiC or another. It is necessary to take into account such factors as form and dimensions of grains, form and dimensions of pores, modifications, admixtures, etc.

Glass melts with good wetting infiltrate through the pores inside the material to a depth of 200–300 μm

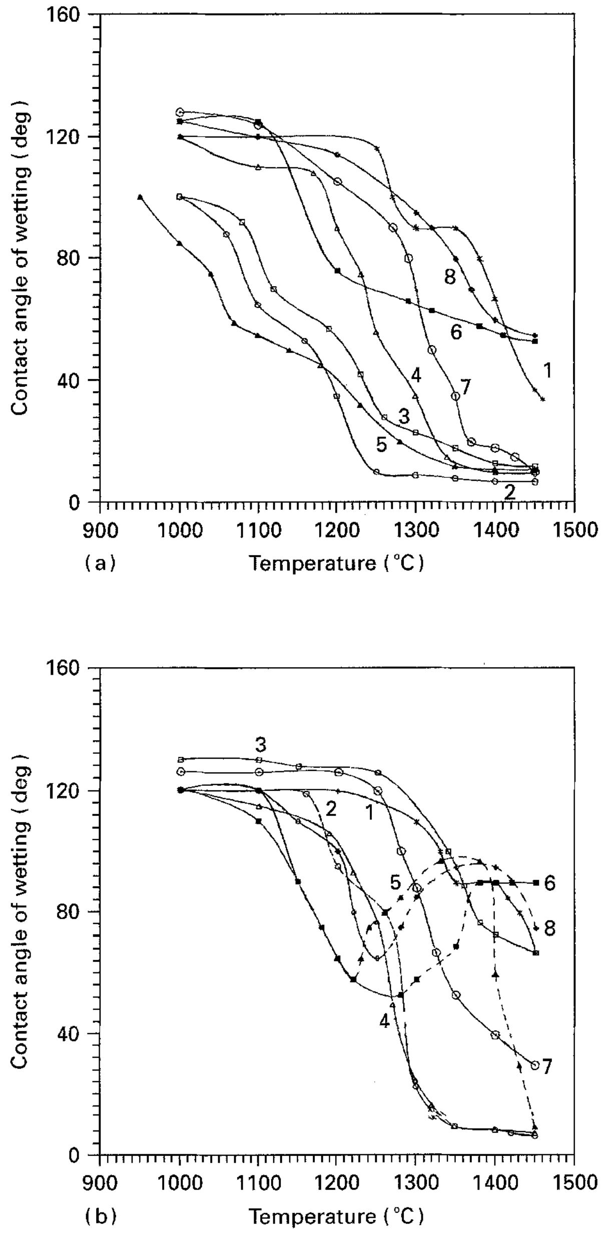


Figure 9 Temperature dependence of the contact equilibrium angle of wetting of silicon carbide polycrystalline substrates with melts of silicate glasses: (a) coarse-grained substrate; (b) fine-grained substrate. (1) S-25-2, (2) S-37-1, (3) S-37-2, (4) S-39-3, (5) S-52-2, (6) SP-4, (7) SP-5, (8) Pyrex.

(e.g. S-37-1). In the case of limited wetting (S-40-1) the glass melt infiltrates to a depth up to 50 μm and some regions of materials remain unfilled.

The equation

$$\rho g h = 2\sigma \cos\theta \qquad (14)$$

may allow the determination of the depth of penetration of the melt in the material in the case of limited wetting (where ρ is density, h the depth of penetration, σ the surface tension). However this equation does not take into account the oxidation of SiC with the glass melt, the change of melt composition due to oxidation of SiC, etc.

4. Conclusions

1. Silicate glasses demonstrate various wetting behaviour of silicon carbide monocrystals, varying from no wetting (contact equilibrium angle of wetting ($\theta > 90°$) to limited wetting ($0 < \theta < 10°$) and full wetting ($\theta < 10°$).
2. Wetting of silicon carbide by melts of silicate glasses is of a chemical nature.
3. Sometimes glass melts begin to "bubble" on the surface of silicon carbide monocrystal. During the wetting of SiC polycrystals, "bubbling" more frequently takes place.
4. Preliminary treatment of silicon carbide monocrystals changes the wetting behaviour of melts. Etching in different reagents may passivate or activate the wetting process. Varnishing the silicon carbide substrate with primer layers may enhance or deteriorate wetting of SiC by silicate glass melts.

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