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The titanium-molten glass system: interactions and wetting

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Titanium interactions with three molten glasses based on sodium disilicate, with additions of TiO_2 or La_2O_3, are studied under very reducing conditions, and the kinetics of spreading and equilibrium contact angles are determined. Titanium enters the molten glass as Ti^{3+}, as shown by EPR spectrometry. Redox reactions occurring at solid–liquid interface and inside bulk glass are studied, and their influence on drop equilibrium is analysed.

1. Introduction

Glass-to-metal bonding has been extensively studied, particularly when noble metals such as copper, tungsten and iron are used as metal substrates [1–11]. On the other hand, very little [9–13] seems to have been done concerning the Ti–molten glass system. The main purpose of this paper is to clarify some aspects of the interfacial interactions taking place between titanium and glass at high temperatures and in very reducing atmospheres, either under dynamic or static conditions.

Experiments were carried out by the sessile drop method: a small molten glass drop is at equilibrium on a titanium surface when total free energy of the Ti–molten glass system is at a minimum [14]. Under the very restrictive hypothesis of no gravity, of undeformable solid and of absence of mass transport and chemical reactions, this condition may be expressed by Young's relationship

$$\sigma_{sv} = \sigma_{sl} + \sigma_{lv}\cos\theta \qquad (1)$$

between the solid surface tension σ_{sv}, the interfacial tension σ_{sl}, the liquid surface tension σ_{lv}, and the contact angle θ. When dealing with low-energy surfaces, where solid–liquid interactions are due to weak forces, Equation 1 predicts a lowering of θ (increasing wetting), as the liquid surface tension decreases and the solid surface tension increases.

Generally, such a prediction is not valid for high-energy surfaces, nor for reactive systems like molten glass–metal at high temperatures. It has, in fact, been observed that the addition of oxides, which increase surface tension of molten glasses, sometimes improves glass-to-metal adhesion [15], because of the decrease in interfacial tension caused by chemical reactions. Indeed, to reach a final good join of glass and metal, good wetting should occur as well as strong adhesion at the interface. This may only be obtained if chemical equilibrium has been reached [16] at the interface, and a continuous crystal structure has been set up from bulk metal to bulk glass. This effect may be achieved if metallic cations are present in the molten glass, which are reduced by base metal, with which they may alloy.

Titanium has a very low free energy of oxidation ($\Delta G^{0}_{1000^\circ C} = -162\,\text{kcal mol}^{-1}$), and is highly reactive with sodium disilicate and other silicate glasses: this has been experimentally verified and will be discussed in the next section.

2. Experimental procedure

We prepared glasses from silica, sodium carbonate, titanium dioxide and lanthanum oxide pure reagents. Weighed quantities, ball-milled for a long time, were melted in platinum crucibles at 1500° C for 12 h with intermediate stirring. As a support to the sessile drop, 99.7% pure titanium metal was

TABLE I

Glass	Composition (mol %)				Expansion coefficient, $\alpha \times 10^7$, 200 to 400° C	Reference for α
	Na_2O	SiO_2	TiO_2	La_2O_3		
1	33.33	66.67	–	–	142–176	[17]
2	17.5	62.5	20	–	89	[18]
3	17	78	–	5	90.9	[19]

used in the form of mirror-finished slides measuring 12 mm by 12 mm by 1 mm.

Chemical compositions of the glasses used in the tests are given in Table I. Ti and La glasses were chosen mainly because their expansion coefficient matches well that of Ti metal.

Sessile drop tests were carried out in a horizontal furnace where a graphite susceptor was heated by high-frequency. The system could work under an inert atmosphere or under a vacuum of 10^{-6} Torr [20]. Photographs were taken with a motor-driven camera using a very high-contrast film. We estimated the error in reading linear dimensions of the drop's image at about ± 2 μm, and at about ± 1° in contact angles.

On each run, a small quantity (0.10 to 0.15 g) of glass, premelted under a vacuum to eliminate dissolved gases, was put on the Ti slide in the furnace. After evacuation down to 10^{-6} Torr at about 400° C, a liquid nitrogen trap was inserted in the system, and the working cell was filled with pure He at 400 Torr. The temperature rise was always very rapid, reaching about 40 to 50 sec for a maximum temperature of 1400° C.

Figure 1 Base glass on Ti; test temperature $T = 1100°$ C.

Fig. 1 shows a cold glass drop on the Ti substrate after two h at 1100° C.

2.1. Electron paramagnetic resonance (EPR) analysis

Ti^{3+} is paramagnetic while Ti^{4+} is not: it is thus possible to detect it by EPR spectrometry. Previous works on glasses containing TiO_2 and reduced by carbon or gamma radiations showed

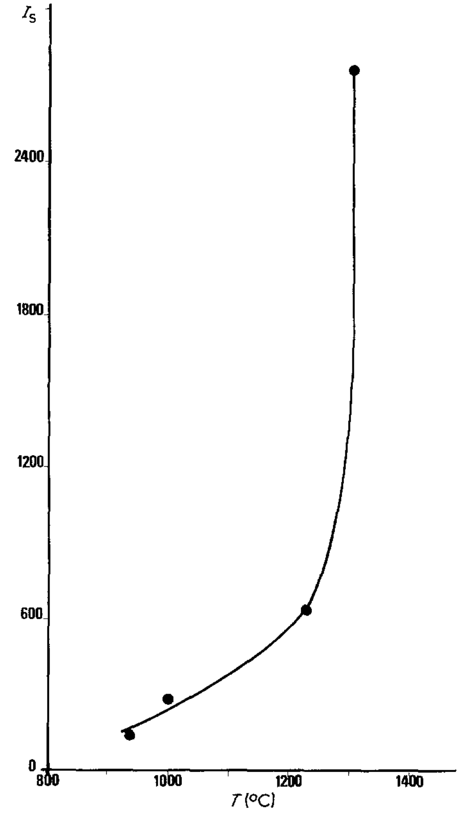

Figure 2 Dependence of EPR signal on test temperature for base glass (Signal intensity I_s is in arbitrary units).

the possibility of detecting the presence of Ti^{3+} at ambient temperature [21–22].

We recorded EPR spectra on drops of molten glass No. 1 on Ti which had been detached from the metal and then powdered. We found a fairly symmetric signal at ambient temperature, and an asymmetric one at 77 K. g values were 1.930 at 300 K, and 1.915 at 77 K. The signal was about 80 Gauss wide at 300 K, and 130 Gauss at 77 K. Figs. 2 and 3 give the dependence of signal intensity on test temperature (Fig. 2), and on the temperature at which EPR analysis was made, (Fig. 3) for glasses kept at two different temperatures.

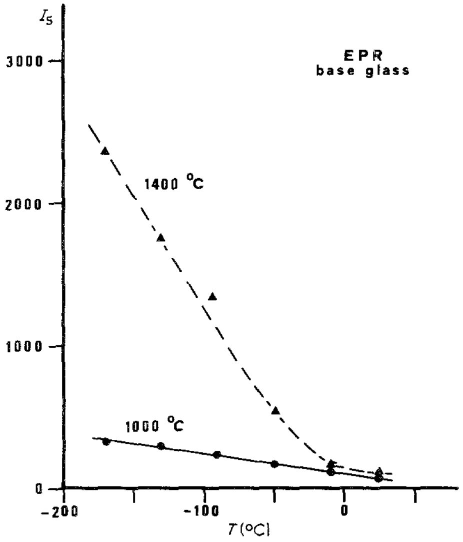

Figure 3 EPR analysis of two specimens of base glass treated at two temperatures.

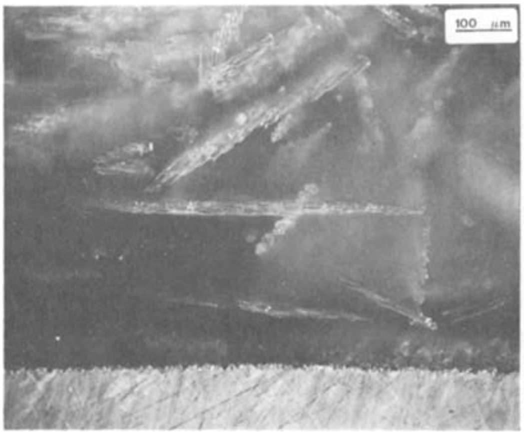

Figure 4 Crystals in 5% La–glass; polarized light; test temperature T = 1100° C.

2.2. Electron probe microanalysis

Representative specimens of all glasses were cut along a plane perpendicular to the metallic plaque, and then observed with optical and electronic microscopes. Specimens of base glass showed cracks at the interface but no precipitation along the solid–liquid boundary. Figs. 4 to 6 show the glass–metal interface in the cases of lanthanum glass (Figs. 4 and 5) and titanium glass (Fig. 6). The morphology is very different: precipitates are present, though in the case of La glass they are very fine at the interface and needle-like in the bulk glass. Electron probe microanalysis showed that they are mainly made up of mixed silicon–lanthanum oxide. In contrast, titanium oxide whiskers grow at the solid–liquid boundary with titanium oxide glass. A typical microanalysis is

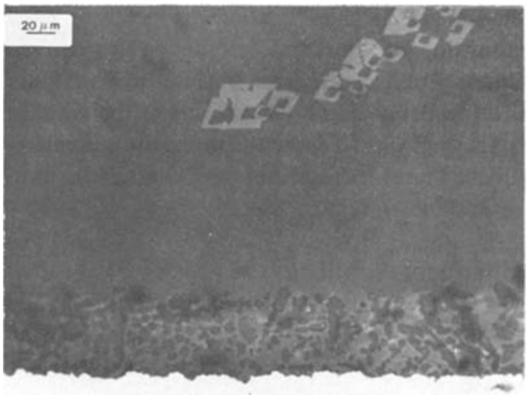

Figure 5 Precipitates in 5% La–glass at the interface and in the Glass; test temperature T = 1210° C.

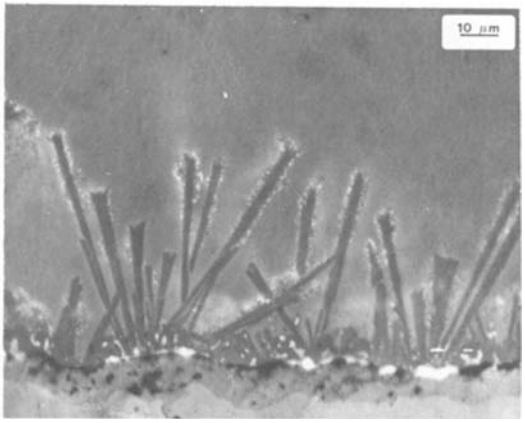

Figure 6 Whiskers at the interface in 20% Ti–Glass; test temperature T = 1200° C.

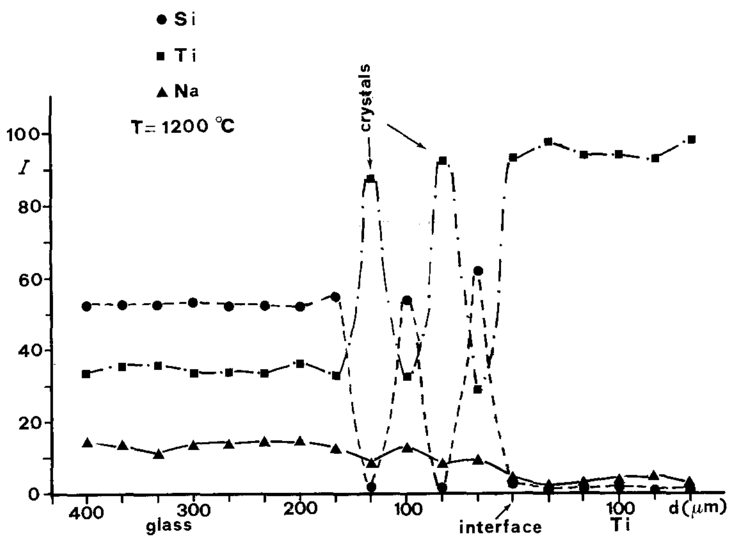

Figure 7 Intensity of EDAX lines for Ti, Na and Si in 20% Ti–Glass treated at 1200° C.

given in Fig. 7. Intensities of EDAX* peaks are given for Na, Si and Ti cations, respectively. The composition of whiskers corresponds to peaks on titanium profile, and seems to show that titanium oxide (probably Ti_2O_3) is present in the whisker crystals. Figs. 8–10 show the same crystals emerging from the drop base, and the Ti and Si distributions in them.

3. Chemical equilibria

From the point of view of chemical equilibria, the system, sodium disilicate on titanium in the presence of graphite, is very complex and difficult to analyse. Nevertheless, following Denbigh's method to find the number of independent reactions [23], we can state that the following species may be present: Ti, TiO, Ti_2O_3, TiO_2, $Na_2Si_2O_5$, SiO_2, Na, Si, C, CO, CO_2, O_2. There are five atomic species, Ti, O, Na, Si and C, so that we may write five mass-balances;

$$\Delta Ti + 2\Delta Ti_2O_3 + \Delta TiO + \Delta TiO_2 = 0$$

$$2\Delta glass + \Delta Na + 2\Delta Na_2O = 0$$

$$2\Delta glass + \Delta Si + \Delta SiO_2 = 0$$

$$2\Delta O + 3\Delta Ti_2O_3 + 2\Delta TiO_2 + 5\Delta glass + \Delta CO + 2\Delta CO_2 + \Delta TiO + \Delta SiO_2 + \Delta Na_2O = 0$$

$$\Delta C + \Delta CO + \Delta CO_2 = 0$$

As we have 13 possible species and five relationships, it follows that eight independent reactions

Figure 8 Precipitates near the base of a 20% Ti–Glass drop; test temperature $T = 1410°$ C.

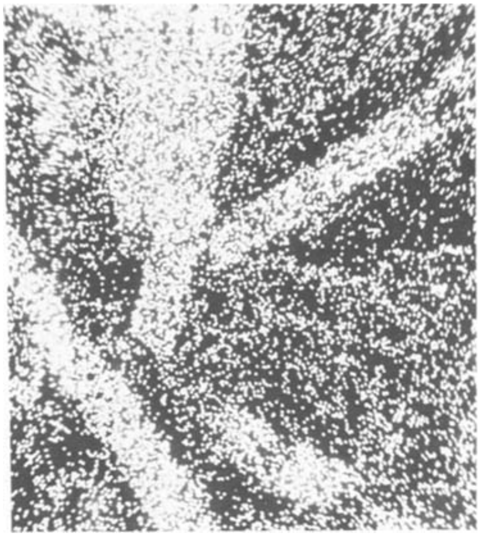

Figure 9 Ti–map of the same area as in Fig. 8.

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*Energy dispersive analysis of X-rays.

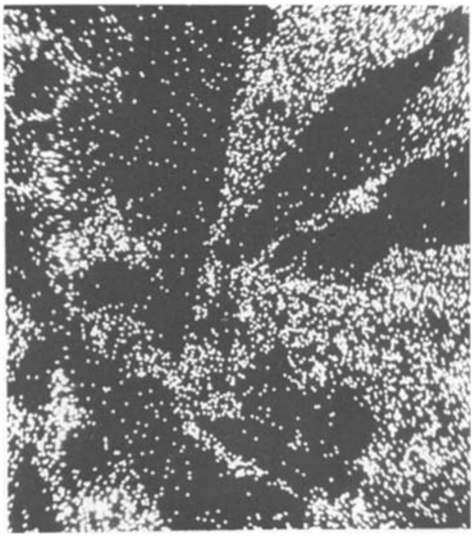

Figure 10 Si–map of the same area as in Fig. 8.

TABLE II

Reaction		$\Delta G^{\mathrm{O}}_{1300\ \mathrm{K}}$ (kcal mol^{-1}) [24]
$Ti + O_2 \rightleftarrows TiO_2$	(1)	−163.9
$2Ti + \frac{3}{2} O_2 \rightleftarrows Ti_2O_3$	(2)	−278
$Ti + \frac{1}{2} O_2 \rightleftarrows TiO$	(3)	−94.6
$2Na + \frac{1}{2} O_2 \rightleftarrows Na_2O$	(4)	−52.1
$Si + O_2 \rightleftarrows SiO_2$	(5)	−162.2
$Na_2O + 2SiO_2 \rightleftarrows Na_2Si_2O_5$	(6)	−59.3
$2C + O_2 \rightleftarrows 2CO$	(7)	−108.5
$2CO + O_2 \rightleftarrows 2CO_2$	(8)	−80.5

may be written which fully describe the system (Table II).

When glass is absent, Reactions 7 and 8 are by far the most important, as they determine the oxidizing conditions in the system. In reaction 8: $K_P = P^2_{CO_2}/(P^2_{CO}P_{O_2})$: hence oxygen partial pressure is determined by the P_{CO}/P_{CO_2} ratio. To avoid titanium oxidation (Reaction 1), the oxygen partial pressure must be kept below a definite value. Assuming Ti and TiO_2 to be at unit activity from the free energy of formation of TiO_2, we get the limiting P_{O_2} values which, according to reaction 8, give the P_{CO}/P_{CO_2} ratio at different temperatures (e.g. $P_{O_2} = 3.31 \times 10^{-26}$ atm and $P_{CO}/P_{CO_2} = 3.48 \times 10^6$ at 1100° C). Analogous to Reactions 2 and 8 (Table II) we obtain a value of P_{CO}/P_{CO_2} which is about 10^8. Under our conditions, we can markedly increase the P_{CO}/P_{CO_2} ratio, determined by the presence of graphite, by condensation of CO_2 in a liquid nitrogen trap. In doing so, a considerable shift to the right of Reaction 8 is obtained, i.e. a lowering of P_{O_2} partial pressure (it should be noted that, at 77 K, $P_{CO_2} = 10^{-11}$ atm and $P_{CO} = 0.7$ atm). Indeed after blank treatment (without glass) titanium slides appear to be very shiny without any visible trace of oxidized layers.

When entering such a highly reducing system, molten glass induces new equilibria which fix final wetting and adhesion conditions. Redox equilibria in molten glasses have been extensively studied both in the presence and absence of solid metals [8, 16, 25–28]. Sodium oxide and silicon oxide dissociate at high temperatures and make available an internal source of oxygen which nevertheless, is still kept at very low pressure by the buffer action of the graphite susceptor. Titanium exerts its reducing effect against dissolved oxides, and enters their molten mass in its trivalent form, as clearly shown by the above-mentioned EPR analysis.

In the case of glass N3, one mass balance and two species, La and La_2O_3, are added to the system, so that a new independent reaction can be chosen, for example:

$$2Ti + La_2O_3 \rightleftarrows Ti_2O_3 + 2La \Delta G^{\mathrm{O}}_{1000\,^\circ\mathrm{C}}$$

$$\Delta G^{\mathrm{O}}_{1000\,^\circ\mathrm{C}} = 81.2 \text{ kcal mol}^{-1}$$

At equilibrium, the change in free energy is zero, but as the standard free energy change is positive and large, the extent of the above reaction should be neglegible. Nevertheless, when molten glass touches the metal, equilibrium has not yet been set up, so we can write:

$$\Delta G_T = \Delta G^{\mathrm{O}}_T + RT \ln\left(\frac{a^2_{La}a_{Ti_2O_3}}{a^2_{Ti}a_{La_2O_3}}\right).$$

La_2O_3 activity in glass is greater than zero and initially the La and Ti_2O_3 activities in glass tend to zero. If $\ln\,[a^2_{La}a_{Ti_2O_3}/a_{La_2O_3}] < -30$, i.e. if $K_a \simeq 10^{-13}$, this term becomes predominant and shifts ΔG_T towards negative values.

As a consequence of the above discussions, the following principal sites where reactions occur may be set out:

(a) Liquid–vapour interface: Here sodium and, in lesser amounts, silicon evolution takes place as a result of Reactions 4 and 5 (Table II).

(b) Solid–liquid interface: Reaction 2 (Table II) mainly occurs. Titanium enters the molten mass mainly as Ti^{3+} and dissolves in it. In the case of

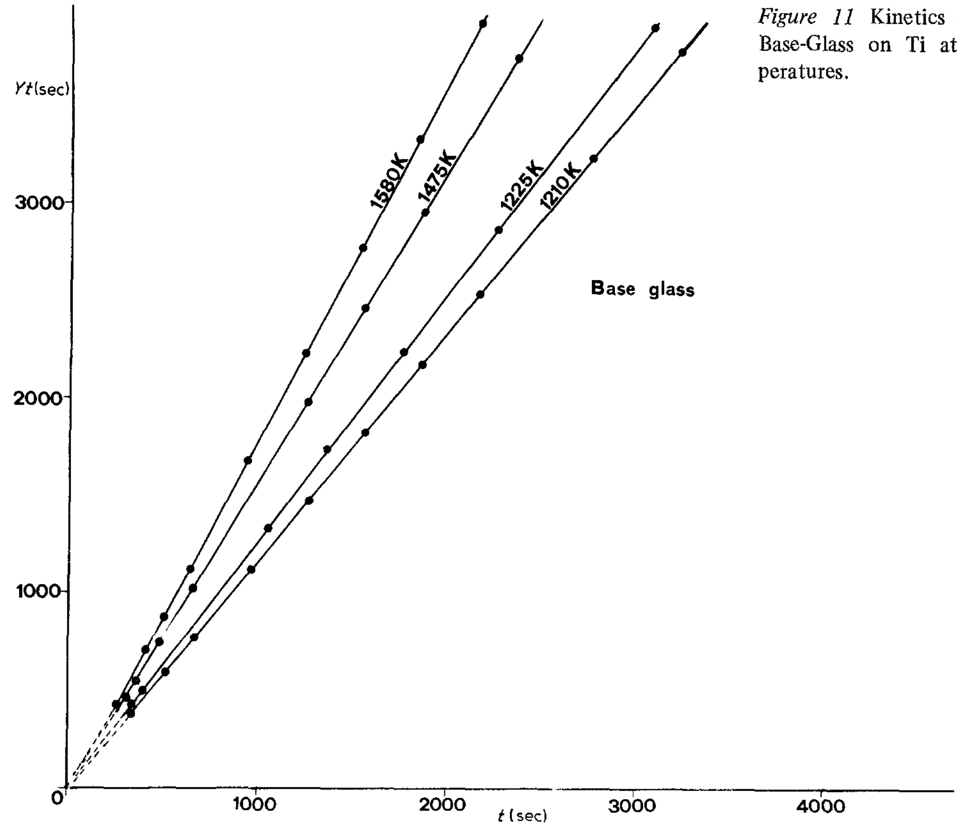

Figure 11 Kinetics of spreading of Base-Glass on Ti at different temperatures.

Ti–glass, the solubility product of Ti_2O_3 is reached near the interface, and the oxide grows. The formation of whiskers shows that the reaction at first takes place at the interface, where suitable nucleation sites exist, and then growth occurs through a process involving transport in the liquid mass and crystallization onto the denser crystallographic plane of the crystals.

As the solubility of La_2O_3 is fairly low (with $La_2O_3 > 10\%$, a white precipitate always forms, even in an oxygen atmosphere) in the case of La–glass the presence of Ti^{3+} ions causes a silicon–lanthanum oxide to precipitate, as shown by microanalysis. Furthermore, SiO_2 may be reduced by Ti following, for example, the reaction

$$3\,SiO_2 + 9\,Ti \rightarrow 2\,Ti_2O_3 + Ti_5Si_3$$

whose ΔG^O_{298} is of the order of -100 kcal. The intermetallic compound forms an eutectic with Ti at 1330° C. In fact, at higher temperatures, a molten metallic mass, containing about 15 to 20 at.% Si, has sometimes been observed outside the border of the glass drop.

Hence, we could say that diffusion of Si in the Ti metal is faster than viscous flow of molten glass on the Ti surface, so that the solid surface where the drop spreads has an instantaneous composition different from the original one.

4. Wettability

Wettability tests were made on the three types of glasses at different temperatures (between 900 and 1450° C) in Helium atmospheres.

4.1. Kinetics of spreading

We made tests by the sessile drop method using the glasses already described and taking photographs at regular intervals, at constant temperatures, until static equilibrium was reached. Base-drop diameters were then measured as function of time. From experimental data, a hyperbolic law relevant to spreading was derived:

$$Y = \frac{K}{t} + a \qquad (15)$$

where $Y = d_t/d_0$, d_0 standing for the diameter when $\theta = 90°$, and $a = d_\infty/d_0$, d_∞ standing for the diameter at equilibrium ($t \rightarrow \infty$).

In Figs. 11, 12, 13, we set out the experimental data for different glasses together with the inter-

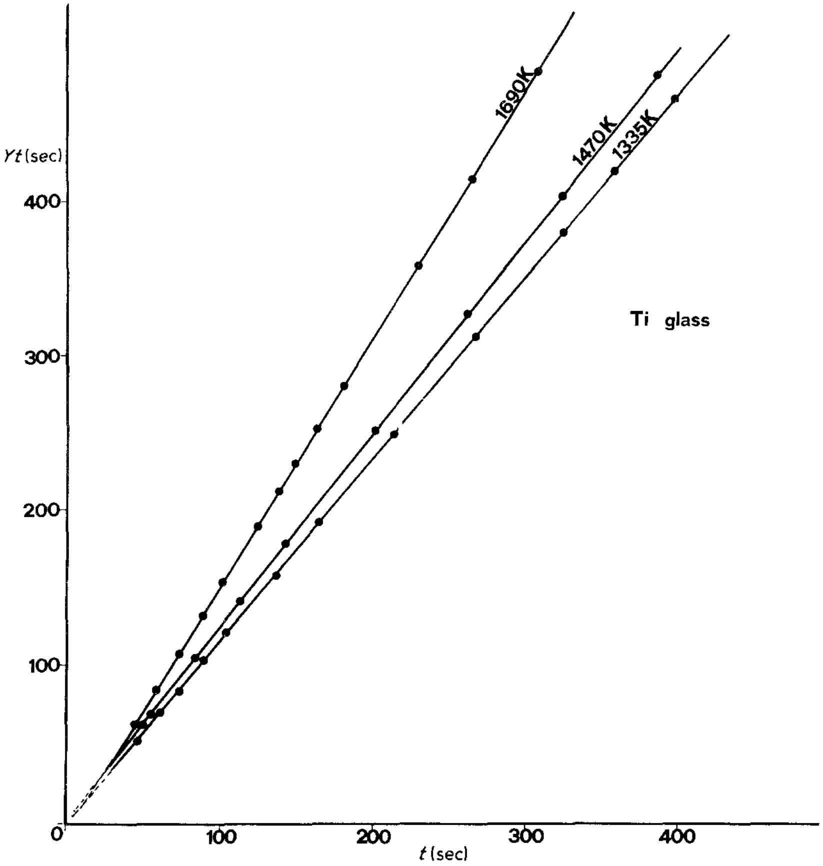

Figure 12 Kinetics of spreading of Ti–Glass on Ti.

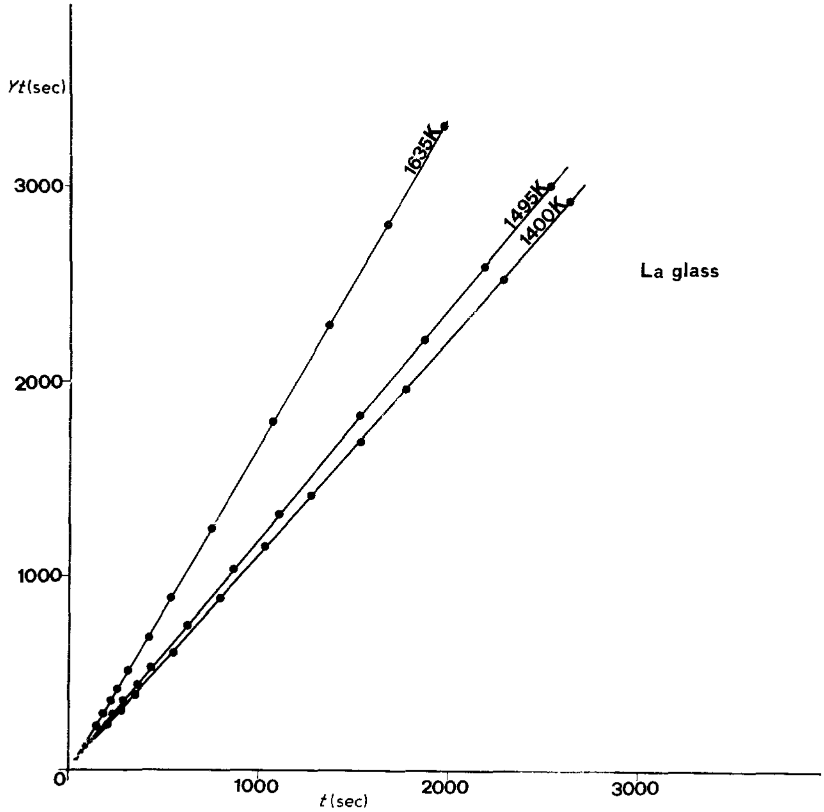

Figure 13 Kinetics of spreading of La-Glass on Ti.

polated line (correlation coefficients were found to be always greater than 0.9999). The rate of spreading was

$$\dot{Y} = -\frac{K}{t^2}$$

or

$$\dot{Y} = -\frac{I}{K}(Y-a)^2$$

which implies apparent second-order kinetics.

In previous work dealing with molten polymers on oxides surfaces [29], we found an exponential law: $Y = a - Be^{-ct}$ which gave the following kinetic law (1st order):

$$\dot{Y} = -c(Y-a)$$

It is indeed interesting to note that, in the latter case, no reactions occurred at the interface, as we used organic molecules on high-energy surfaces at fairly low temperatures (150 to 250° C). On the contrary, in the present investigation, extensive reactions occur at the solid–liquid boundary, so that capillary forces do not play a predominant role, and the free energy of reaction turns out to be the most important parameter in determining the rate of spreading.

4.2. Equilibrium wetting

At equilibrium all glasses show a temperature-dependent contact angle on titanium metal (Fig. 14). If we compare the magnitude of contact

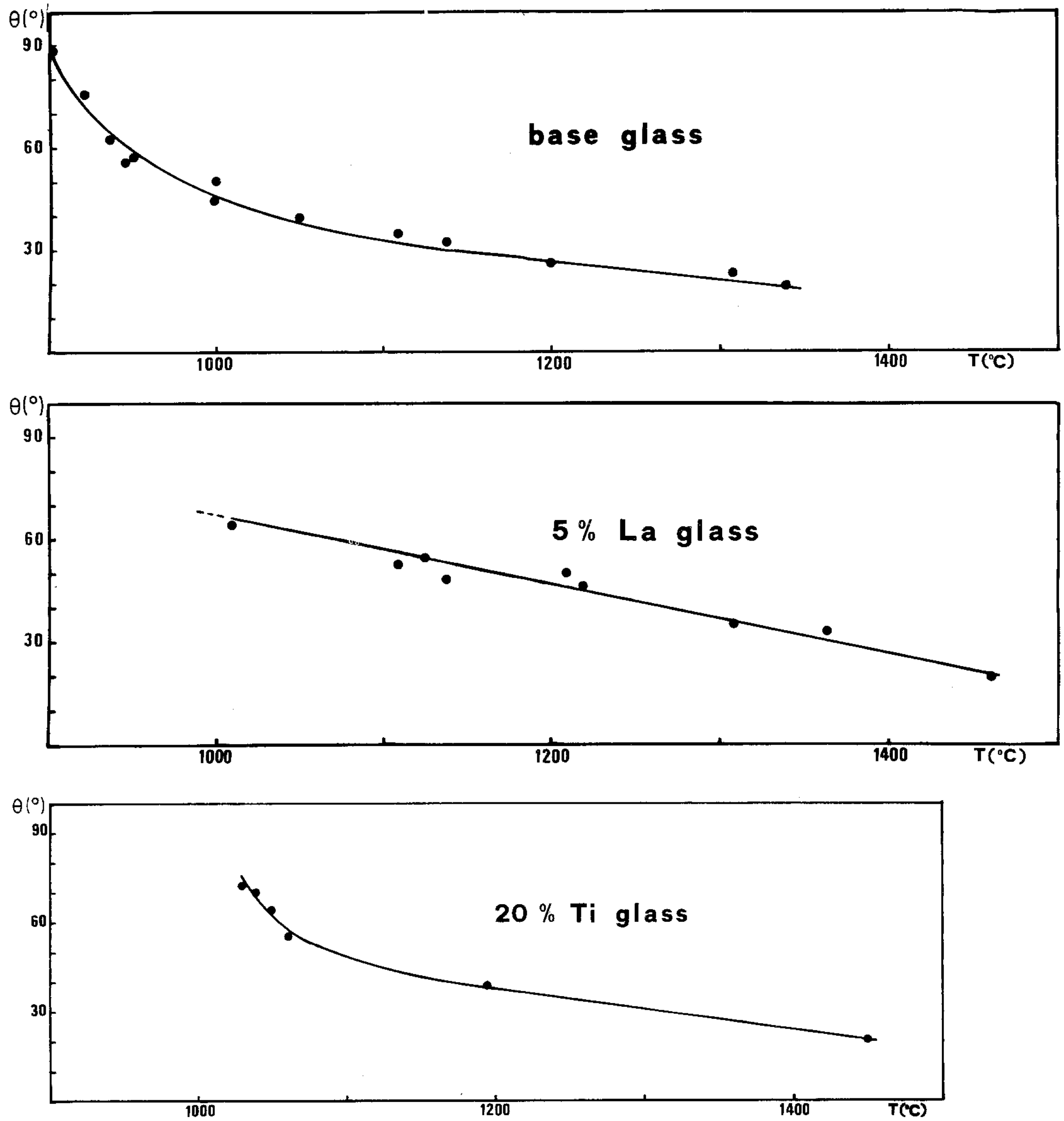

Figure 14 Polytherms of equilibrium contact angles.

angles at each temperature as a function of silica content in glass, we always find a minimum value corresponding to base–glass composition. Addition of Titania or Lanthana increases contact angles at low temperatures; at high temperatures, contact angles become nearly equal for all three types of glasses, up to a value between 15° and 25°. This fact may be explained as follows.

At low temperatures, capillary effects still play an important role in determining final drop shapes. There are differences in surface tension of the three types of glasses: preliminary results obtained by us in our laboratory show that Lanthanum oxide increases surface tension of base glass; e.g. at 1000° C, 5% La_2O_3 addition increases surface tension by about 25%. Moreover, wetting of a metal by molten glass can be increased by also increasing the content of non-bridging oxygen anions in glass. It is postulated [3] that TiO_2 increases negativity of the anionic group and decreases positivity of the cationic group, thus increasing wetting. But under our conditions, Ti^{4+} is not stable and, in our best knowledge, no data on network position of Ti^{3+} ions are available. However, La^{3+} and Ti^{3+} ions are likely to behave as Al^{3+} ions, that is, they reduce negativity of the anionic group and cause contact angles to increase as compared with base glass. At higher temperatures, reactions occur strongly at the interface so that reductions in free energy due to reactions determine final drop shapes at equilibrium. Our contact angle values relevant to sodium disilicate compare favourably with the value reported elsewhere (26° at 1200° C) [12].

A recent study of titanium and titanium oxides wettability appeared [13] in which a value of $\theta = 74°$ at 1000° C is reported for sodium disilicate on titanium in a vacuum of 10^{-5} Torr which is claimed to leave a clean metallic surface. This value is close to the value $\theta = 80°$ obtained earlier [19] under similar conditions. By comparison, our value is $\theta = 48°$: this great difference stems from different experimental conditions.

First of all, titanium must be oxidized under a vacuum of 10^{-6} Torr, where thermodynamic conditions are favourable. However, kinetics factors play a retarding role: under a pressure of 1.9×10^{-5} Torr, a rate of $3.6\,\mu g\,cm^{-2}\,min^{-1}$ at 1000° C was found [30], which means a growth rate of about $100\,Å\,min^{-1}$. At lower oxygen pressures, the rate is much slower so that oxide may not be visible. The presence of oxidized layers outside molten drops leads to an increase in contact angles. Moreover, it was demonstrated [5] that hydrocarbons coming from oil diffusion pumps may adsorb on metals and give rise to carbon monolayers which dramatically increase contact angle up to temperatures of 900 to 1000° C.

5. Concluding remarks

At high temperatures and under highly reducing conditions, molten silicate glasses interact with titanium metal through redox reactions, leaving oxide precipitates at the interface, which alter the original capillary equilibrium. Moreover, the aspect of such precipitates strongly affects mechanical properties of a glass–metal couple at ambient temperature.

Titanium is very reactive against molten glasses; it enters them as Ti^{3+} under reducing conditions, and allows metallic cations of glasses to be reduced and to enter the metal base itself. Silicon diffuses easily into the metal base so that, at temperatures higher than 1350 to 1400° C, after a certain holding time, a molten Ti–Si alloy containing 15 to 20% of silicon appears near the border of an advancing drop.

Drops spread on titanium according to a law which depends on both the physico-chemical characteristics of glass and metal, and the extent of free energy change caused by reactions at the interface. In fact the rate at which our glasses spread on titanium implies apparent second-order kinetics, and at equilibrium reach contact angle values which decrease as temperature increases and, at the highest temperature, tend towards roughly a common value.

From a technological point of view, the strength of the adhesive bond between the glasses and titanium under these experimental conditions has not yet been tested. From a qualitative analysis of detachment of solidified glass drops from Ti metal, the adhesion between sodium disilicate to Ti appears to be very poor. In the case of Ti glass adhesion is critically dependent on the extent of reactions at the interface (i.e. on holding time); and it is fairly good in the case of La–glass, probably because Lanthanum gives rise, at the interface, to very fine precipitates which thus assure a continuous structural transition from bulk metal to glass.

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