

Sticking temperature investigations of glass/metal contacts – Determination of influencing parameters

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Sticking experiments between hot viscous glass and metallic substrates have been performed with a glass press apparatus on a laboratory scale, allowing a precise determination of the sticking temperatures, T_s , versus selected experimental parameters (nature of the substrate, composition of the glass). Complementary surface analyses have also been carried out to identify the surface and interface reaction products following the glass/metal contact. Experimental results have been compared to ternary phase diagrams, in order to test the reliability of thermodynamic calculations to predict the nature of the phases produced by the contact at high temperature. The sticking phenomenon is governed by a coupling between the rheological behaviour of the glass melt and the physicochemical reactivity of the contacting surfaces. Sticking occurs when the temperature at the interface remains sufficiently high, so that the glass viscosity remains low enough to enhance the real contact area and thus, to induce physicochemical interactions between substrate and glass. Sticking is attributed to the presence of an interfacial oxide layer which strongly adheres onto the glass. Chemical analysis of the sticking surfaces identifies a physicochemical driving force contributing to the sticking phenomenon. The predominant reaction consists in the reduction of the sodium oxide of the glass at the expense of the oxidation of the metallic elements of the substrate during pressing, in agreement with thermochemical calculations presented by the ternary phase diagrams. The strong chemical reactivity of the soda–lime–silica glass is thus attributed in particular to the highly reactive sodium oxide constituent.

Untersuchungen der Klebetemperatur an der Kontaktfläche Glas/Metall – Bestimmung der Einflußparameter

Versuche zum Kleben von heißem viskosem Glas an Metallsubstraten wurden unter Verwendung einer Glaspreßeinrichtung im Labormaßstab durchgeführt, die eine genaue Bestimmung der Klebetemperaturen, T_s , in Abhängigkeit von ausgewählten experimentellen Parametern (Art des Substrates, Glaszusammensetzung) erlaubte. Zusätzlich wurden Oberflächenanalysen zur Identifizierung der Ober- und Grenzflächen-Reaktionsprodukte vorgenommen, die als Folge des Glas/Metallkontaktes entstehen. Die Versuchsergebnisse wurden mit ternären Phasendiagrammen verglichen, um die Zuverlässigkeit thermodynamischer Berechnungen zu überprüfen und die Art der Phasen vorherzusagen, die durch den Kontakt bei hohen Temperaturen gebildet werden. Das Phänomen des Klebens wird bestimmt durch eine Überlagerung des rheologischen Verhaltens der Glasschmelze mit dem physikochemischen Reaktionsvermögen der einander berührenden Oberflächen. Das Kleben tritt auf, wenn die Temperatur an der Grenzfläche so hoch ist, daß die Glasviskosität niedrig genug ist, um den tatsächlichen Kontaktbereich zu vergrößern und dadurch die physikochemischen Wechselwirkungen zwischen Substrat und Glas hervorzurufen. Kleben wird zurückgeführt auf das Vorhandensein einer oxidischen Grenzschicht, die fest am Glas haftet. Eine chemische Analyse der zusammenklebenden Oberflächen weist auf physikochemische Kräfte hin, die zum Phänomen des Klebens beitragen. Die vorherrschende Reaktion besteht in der Reduktion von Natriumoxid des Glases auf Kosten der Oxidation metallischer Elemente des Substrates während des Pressens, wie thermochemische Berechnungen in Hand der ternären Phasendiagramme gezeigt haben. Das ausgeprägte Reaktionsvermögen von Kalk–Natronsilicatglas wird deshalb vor allem mit dem reaktionsfreudigen Bestandteil Natriumoxid in Verbindung gebracht.

1. Introduction

The contact behaviour of hot viscous glass towards tool materials is a critical factor in the production of glass containers. The industrial processing is demanding in terms of increase of production rates, lifetime of the moulds and quality of the products. The forming process has to ensure smooth glass surfaces and prevent micro-defects which impair the mechanical properties of the formed articles. During the process, containers are formed from hot viscous glass whose temperature

decreases from about 1100 to 600°C in a few seconds, depending on the weight of the final article. Consequently, the mould is subjected to extremely high thermal, corrosive and abrasive wear of its surface. Since worn mould surfaces dramatically affect the quality of the glass product, the mould has to be systematically polished during its lifetime and finally to be replaced. Moreover, a periodic lubrication of each mould has to be performed during the forming process, in order to reduce the dynamic friction during the loading step of the glass melt into the mould, to minimize the corrosion of the mould surface during its lifetime and to prevent

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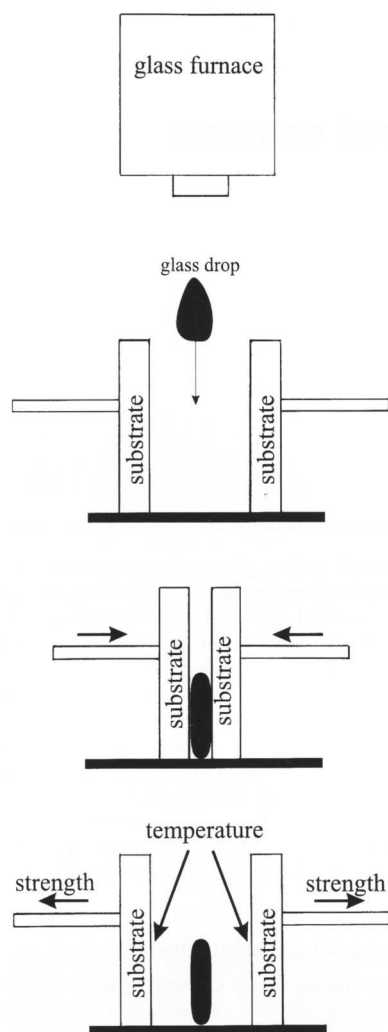


Figure 1. Schematic view of the glass press apparatus.

sticking and adhesion of the glass during the forming step. Indeed, a sticking phenomenon occurs between the hot viscous glass and the metallic substrate at a precise temperature named "sticking temperature", T_s .

As a matter of fact, the glass container industry is looking for mould materials exhibiting a relatively inert contact behaviour, with low friction and long lifetime. However, testing new materials in production is expensive, time-consuming and does not ensure that the parameters responsible for an improvement of the glass/mould behaviour are clearly identified. Rather than the multiplication of tested mould materials which do not have the potential to match design requirements, a powerful experimental approach consists in the development of standardized and reproducible laboratory tests allowing to qualify and quantify the effect of a given set of experimental parameters on the glass/mould behaviour. Such a procedure does not act as a substitute for industrial tests, but as a strong guideline for further industrial developments. Previous studies report laboratory tests dealing with the wetting behaviour of molten

glass on mould materials, without any unambiguous correlation between surface energy values and adherence [1 and 2]. Other authors have developed experiments to identify bulk material compositions and glass surface treatments leading to a noticeable increase of the sticking temperature, T_s [3]. Trier has studied the contact between hot glass and wet porous materials [4]. The effect of various glass compositions and metallic alloy materials on interfacial reactions and adherence has been studied on the basis of experiments carried out at low partial pressures of oxygen, thus leading to a rather complete description of the glass/metal reactivity [5 and 6]. Nevertheless, the experimental conditions remain very different from those characteristic of the industrial production of glass containers. Many studies have been focused on the role of the thermal transfer on the sticking phenomenon, with highlighting the influence of the glass temperature [7] and viscosity [8], the nature [9] and the temperature of the materials [10 and 11], together with the contact pressure [10] and pressing time [12]. More recently, a more systematic investigation of the glass/mould sticking has been performed with various types of mould materials, coatings, surface roughnesses and contact temperatures with a soda-lime-silica glass [13]. These authors clearly show that the sticking of glass melts onto solid surfaces is primarily governed by the rheological behaviour of the glass at high temperature, whereas the nature of the mould does not play a predominant role, except in the case of specific coatings containing boron nitride, which exhibit a shift towards higher sticking temperatures. Further investigations on mould materials leading to improvements in wear and oxidation resistance with high thermal stability are suggested.

On the basis of such considerations, the authors have carried out sticking experiments between hot viscous glass and metallic substrates to identify the effect of a given set of parameters (nature of the substrate, glass composition) on the sticking temperature. Experiments have been performed with a glass press on a laboratory scale, allowing a precise determination of the sticking temperatures, T_s . Complementary surface analyses have also been carried out to identify the surface and interface reaction products following the glass/metal contact. Experimental results have been compared to ternary phase diagrams, in order to test the reliability of thermodynamic calculations to predict the nature of the phases produced by the contact at high temperature.

2. Experimental

2.1 Glass press apparatus

Figure 1 presents a schematic view of the glass press apparatus constituted by two main parts. The upper one is a glass furnace allowing to produce continuously small glass drops at 1150°C, with a typical mass of 5 g, thanks to a cutting mechanism. The lower part consists in the press allowing to squeeze statically the glass drop be

tween two interchangeable flat substrates whose temperature can be monitored between 20 and 900°C. The temperature of the flat substrates is measured using a thermocouple located inside the substrate, 1 mm below the surface in contact with the glass drop. Each flat substrate is equipped with a force transducer allowing the measurement of the strength due to the contact between the glass drop and the two substrates. The experimental procedure consists in recording continuously the values of the force versus the number of pressing cycles (one cycle corresponds to the contact between one glass drop with the substrates). Thus, the determination of a sticking temperature is achieved on the basis of the following procedure as depicted in figure 2. The temperature of the substrates is progressively increased during the succession of pressings. A positive pressing force is detected for each cycle during the pressing step, and is cancelled at the end of the cycle when no sticking is observed. A sudden negative force, at the time of the opening step, associated with a noticeable increase of the substrate temperature, corresponds to the sticking phenomenon. This procedure allows a rough determination of the sticking temperatures. Indeed, sticking is observed after many pressing cycles during which the substrate temperature is progressively increased. The exact value of T_s may be affected by the progressive wear and corrosion of the substrates during the pressing cycles preceding the sticking phenomenon. Thus, a more precise determination of T_s is achieved by performing a second set of pressing cycles, with new virgin substrates of the same material heated with the same temperature slope, but starting at a temperature just below the rough value determined by the first set. The second set of experiments is systematically reproduced three times to test the reproducibility of the sticking temperature measurement. Results are depicted with the sticking temperature and standard deviation values for each experiment.

2.2 Nature of the tested mould materials and glasses

Since it is often claimed that ideal mould material should be resistant to oxidation, two different model substrates have been tested: pure iron (Armco) and a titanium-aluminium alloy, called TA6V. Their compositions are reported in table 1. These materials are characterized by a significant difference in the thermodynamical stability of their oxides. In the temperature range 20 to 1000°C, titanium(aluminium) oxides are the most stable and their formation leads to the passivation of the surface, preventing the bulk oxidation of the alloy. Iron oxides are less stable (as depicted in table 2 giving the Gibbs energy of formation of the different oxides at 0, 700 and 1000°C) and do not protect the bulk material from oxidation. In order to compare the sticking temperatures connected to these model substrates with the values related to a mould material commonly used by glass container manufacturers, a ductile cast iron substrate with spheroid graphite inclusions has also

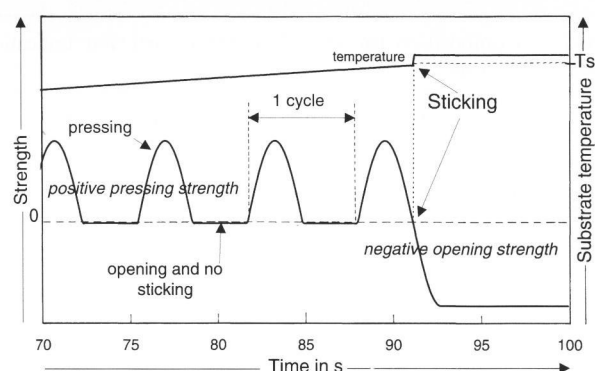


Figure 2. Typical experimental evolution of the strength of the flat substrate versus time. A positive force during one cycle corresponds to a pressing cycle without sticking. A negative force corresponds to the sticking phenomenon, associated with a temperature increase of the flat substrate due to thermal transfer from the hot glass to the substrate.

been tested. Its composition is described in table 1. All the substrates have been polished with a roughness coefficient $R_a < 0.2 \mu\text{m}$. These three kinds of substrates have undergone pressing experiments with a conventional molten glass (glass no. 1), whose composition and characteristic temperatures are given in table 3. The two model substrates have also undergone pressing experiments with a soda-enriched glass (glass no. 2), with an increase of 2 wt% of the Na_2O constituent, as compared to the glass composition no. 1. The higher soda content leads to a noticeable change in the characteristic temperatures, as depicted in table 3.

2.3 Analysis of contacting surfaces and interfaces

Parallel to the sticking experiments, the surfaces of the contacting materials have been investigated by complementary surface analysis tools: optical microscopy (OPT), scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (SEM/EDX) and X-ray photoelectron spectroscopy (XPS, performed with the $\text{MgK}\alpha$ X-ray) for the determination of the extreme surface composition. XPS results depicted in the present paper have been obtained after sputtering of the extreme surface contamination layers. It should be mentioned that for $T \geq T_s$, the pressed glass drop is sticking on the substrates. However, after cooling to room temperature at the end of the experiments, either the glass remains sticking or it can be easily separated from the substrate, probably due to thermal contraction differences between the two contacting materials. These two possibilities are of great interest from an analytical point of view: the glass/metal substrate allows a cross-sectional view of the interface, whereas the surfaces of the separated materials can be independently analyzed by the mentioned techniques.

Table 1. Composition (in wt% if no other particular indication inset) of the model metallic and cast iron substrates used for sticking experiments

	C	Mn	Si	S	P	Cr	Ni	Mo	V	Ti	Cu	Fe	Al
Ta6V alloy	—	—	—	—	—	—	—	—	4	90	—	—	6
iron (Armco)	0.01	0.1	—	80 ppm	0.01	—	—	—	—	—	0.03	99.85	—
cast iron	3.58	0.019	2.818	0.004	0.022	0.041	0.051	0.005	0.173	0.014	0.017	93.256	—

Table 2. Gibbs energy of formation (in kJ/0.5 mol O₂) of iron, titanium and aluminium oxides at 20, 700 and 1000°C in ambient air

	Gibbs energy at		
	20°C	700°C	1000°C
FeO	-241	-199	-180
Fe ₃ O ₄	-275	-190	-153
Fe ₂ O ₃	-207	-112	-70
TiO ₂	-429	-370	-344
Al ₂ O ₃	-509	-448	-421

3. Results

3.1 Sticking behaviour of the model substrates with the conventional glass no. 1

Table 4 includes the sticking temperatures, T_s , and the standard deviation values related to the two model substrates pressed with the conventional glass no. 1. The sticking phenomenon is observed at 728°C with the TA6V alloy and 772°C with the iron substrate. Optical

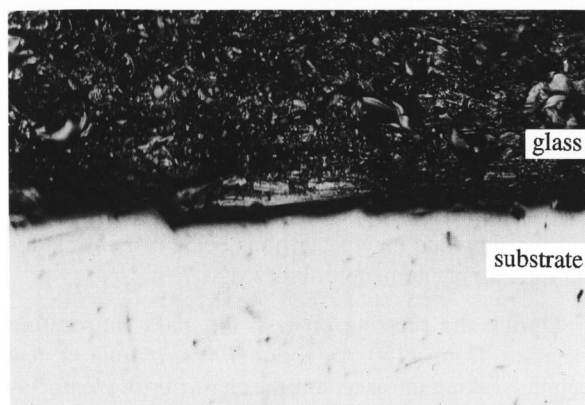
cross-sectional views of the glass/model substrate interfaces depicted in figures 3a and b show that the interface is particularly plane and regular in the case of TA6V and more irregular in the case of iron. Indeed, surface roughness measurement indicates no modification of the R coefficient in the case of the TA6V substrate ($R < 0.2$) and a slight increase of the R coefficient in the case of the iron substrate ($R = 0.3$). XPS investigations (figures 4a and b) performed on both substrate surfaces after sticking do not exhibit any trace of silicon nor calcium, but traces of sodium are detected (NaKLL binding energy = 260 eV). XPS analysis of the corresponding glass surfaces (spectra not reproduced here) shows in each case the presence of the constitutive elements of the substrate materials (iron, titanium and aluminium) in an oxidized state. This indicates that the glass surface is partially covered by a thin oxide layer probably responsible for the sticking phenomenon. The major constituents of the glass (silicon, calcium and sodium) are also detected in an oxidized state. From the intensity of the silicon and sodium signals and sensitivity factors of both elements, the sodium/silicon atomic ratios related to the glass surfaces sticking on the TA6V ($\text{Na/Si} = 0.06$) and iron ($\text{Na/Si} = 0.11$) substrates, are compared in table 5 to the atomic ratio of a stretched

Table 3. Composition (in wt%) and characteristic temperatures (in °C) of the two kinds of soda–lime–silica glasses used for the sticking experiments

glass no.	composition in wt%						refining temperature in °C at $\eta = 10^1$ Pa s	parison temperature in °C at $\eta = 10^2$ Pa s	Littleton temperature in °C at $\eta = 10^{6.6}$ Pa s	transformation temperature in °C at $\eta = 10^{12.4}$ Pa s
	SiO ₂	Na ₂ O	CaO	Al ₂ O ₃	MgO	minor constituents				
1	72.1	13.1	10.9	1.5	1.2	1.2	1443	1192	735	552
2	71.7	15.0	8.8	1.3	2.8	0.4	1437	1175	718	536

Table 4. Experimental sticking temperatures and standard deviations related to the different substrates and two kinds of glasses

	glass no. 1		glass no. 2	
	sticking temperature in °C	standard deviation in K	sticking temperature in °C	standard deviation in K
TA6V alloy	728	3	695	4
iron	772	2	750	3
cast iron	801	6	not measured	—



a)



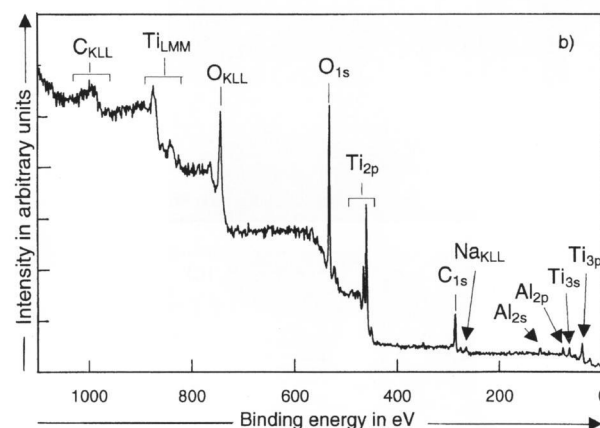
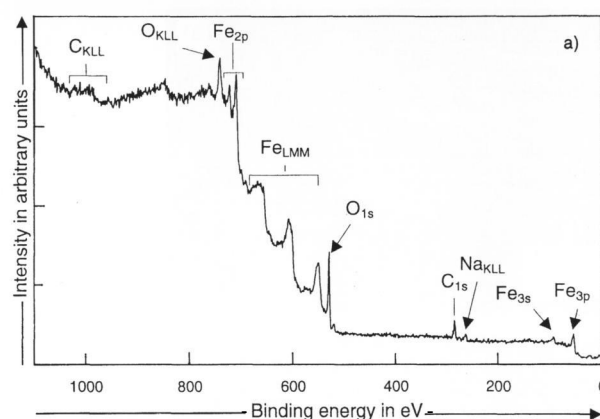
b)

Figures 3a and b. Optical direct-light micrographs of the glass no. 1/iron (figure a) and glass no. 1/TA6V (figure b) interfaces.

glass sample ($\text{Na}/\text{Si} = 0.31$) deduced from XPS analysis, and to the atomic ratio calculated from the bulk composition of the glass ($\text{Na}/\text{Si} = 0.35$), the two last ratios being in the same range. XPS experiments performed both on the glass and metallic substrates after pressing without any sticking (by stopping the temperature increase at $T < T_s$ during the experiments) do not detect any trace of the glass constituents on the metallic substrate and vice versa. This indicates that the chemical surface modifications observed at $T = T_s$ can be attributed to the sticking phenomenon. In particular, whatever the nature of the substrate material, there obviously is a noticeable decrease of the sodium concentration on the glass surface after sticking, the sodium being transferred onto the substrate surface, as depicted in figures 4a and b.

3.2 Effect of the glass composition on the sticking temperature of the model substrates

Table 4 includes the sticking temperatures of the two model substrates pressed onto the soda-enriched glass no. 2. Results are 695 and 750°C, respectively, for the TA6V and iron substrates. Thus, a systematic decrease in T_s of 33 (TA6V) and 22 K (iron) is observed as compared to the conventional glass no. 1.



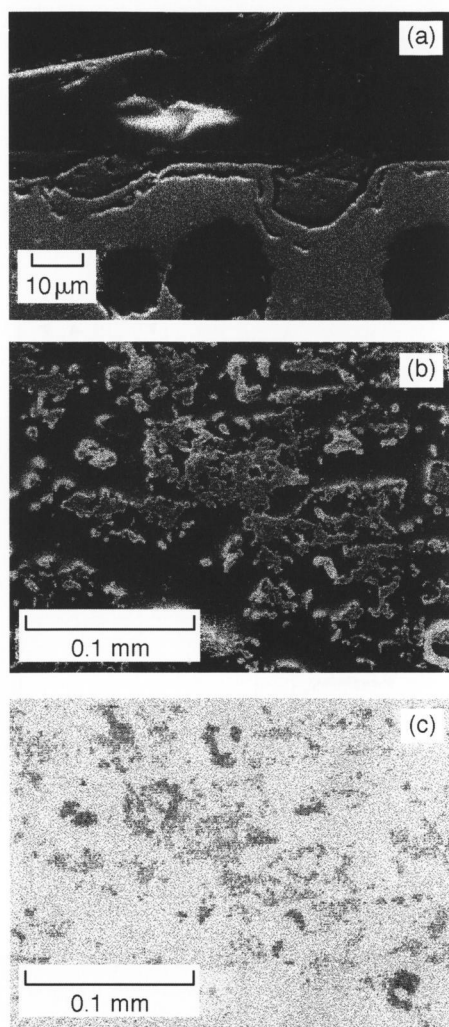
Figures 4a and b. XPS spectra of the metallic substrates after sticking of glass no. 1 with iron substrate (figure a) and TA6V substrate (figure b).

Table 5. Atomic Na/Si ratios deduced from XPS, related to the virgin glass no. 1, the sticking glass no. 1 on TA6V substrate and the sticking glass no. 1 on the iron substrate. XPS has been performed in each case after sputtering of the superficial contamination layers. The Na/Si atomic ratio deduced from the bulk composition of the glass is 0.35.

	atomic ratio Na/Si
virgin glass	0.31
glass sticking on TA6V	0.06
glass sticking on iron	0.11
glass sticking on cast iron	0.07

3.3 Sticking behaviour of the cast iron substrate with the conventional glass no. 1

The cast iron material exhibits the highest value of the sticking temperature (801°C), in comparison to the model substrates (see table 4). The glass/cast iron interface is observed by SEM in cross-sectional view (figure 5a). A porous interfacial layer, approximately 1 μm thick, separates the glass and the cast iron, some graphite spheroids being embedded in it. After separation of the glass from the cast iron substrate, a hetero-



Figures 5a to c. SEM/EDX investigations of the glass no. 1/cast iron system, a) cross-sectional view (SEM micrograph), b) surface view (SEM micrograph), c) surface iron distribution (EDX analysis).

geneous transfer layer is observed on the glass surface (figure 5b). An EDX map identifies the iron surface distribution in figure 5c, corresponding to the SEM image depicted in figure 5b. An XPS investigation of the glass surface has been performed after sputtering of the extreme surface contamination layers. In agreement with the EDX analysis, iron in an oxidized state is detected. As in the case of the two model substrates, the Na/Si ratio (0.07) related to the sticking glass surface is lower than the value related to the bulk composition, indicating a noticeable sodium loss on the glass surface, following the sticking phenomenon (table 5).

4. Discussion

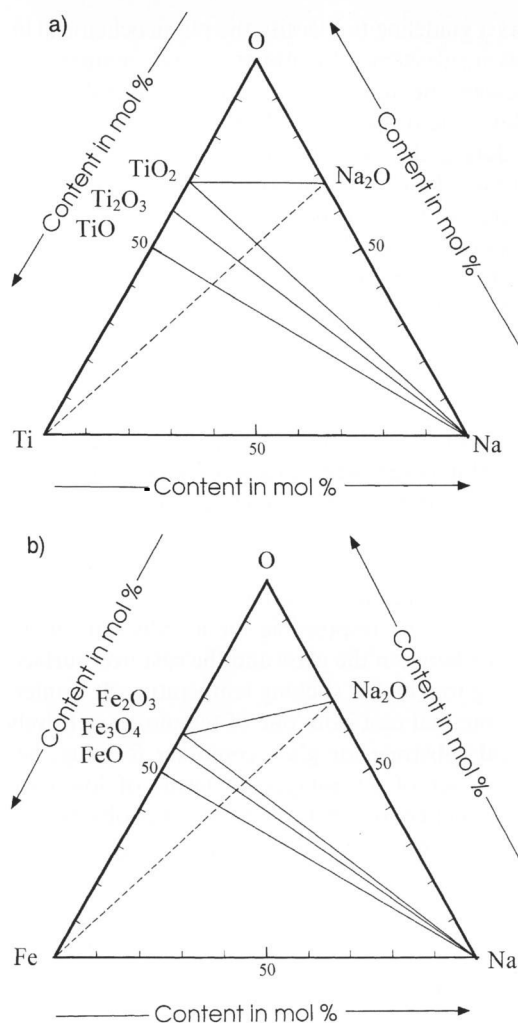
The following will emphasize the conditions which have to be checked to observe the sticking phenomenon. Dur-

ing pressing, the kinetics of the heat transfer from the glass to the substrate depends in particular on the real contact area and the thermal conductivity of the substrate. For a given substrate with a known thermal conductivity and surface roughness, the contact area is maximal if the viscosity of the glass is low enough. In this case, physicochemical reactions between the glass and the substrate may occur, thus being responsible for the sticking phenomenon observed at T_s .

During the pressing process, the glass temperature decreases from 1150 to about 700°C within a few seconds. Taking into account the characteristic temperatures of the conventional glass no. 1 and the values of the experimental sticking temperatures, the sticking phenomenon occurs with a difference of 40 K between the TA6V and the iron substrates, thus, corresponding to a sticking viscosity range $\lg \eta = 6.0$ to 6.8 (η in Pa s). In the case of the soda-enriched glass no. 2, the sticking temperature difference (55 K) and the corresponding sticking viscosity range ($\lg \eta = 5.9$ to 6.7) are quite similar. Indeed, the sticking temperatures 772°C (glass no. 1) and 750°C (glass no. 2) related to the pure iron substrate correspond to sticking viscosities of $\lg \eta = 6.0$ (glass no. 1) and $\lg \eta = 5.9$ (glass no. 2). Since the viscosity of the soda-enriched glass is smaller than the viscosity of the conventional glass at a given temperature, a systematic decrease of the sticking temperature occurs with glass no. 2, thus leading to the sticking phenomenon in the same viscosity range for the two glasses. Consequently, the present sets of experiments clearly indicate that the sticking temperature range of glass/metal contacts (with comparable surface roughnesses) is predominantly controlled by the viscosity of the glass melt at the glass/substrate interface, as already mentioned by other authors [3 and 12]. The viscosity at the interface is determined by the temperatures of the mould and the glass. If the glass viscosity is sufficiently low, the real area of contact is maximal, thus allowing physicochemical interactions to be effective to induce the sticking phenomenon.

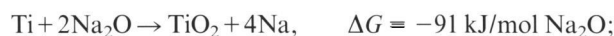
From these results, it becomes interesting to highlight the systematic differences of sticking temperatures observed between the TA6V and the iron substrates whatever the nature of the glass is. Indeed, such differences are significant, taking into account the standard deviation values (less than 5 K) of the measurements. As explained above, as long as the viscosity is low enough to ensure a close contact between the glass and the substrate, physicochemical reactions occur at the interface and are responsible for the sticking phenomenon. The nature of these physicochemical reactions may be elucidated by coupling the chemical analyses depicted in sections 3.1 to 3.3 with thermodynamic calculations. Whatever the substrate, the interface is constituted by an oxidized layer resulting from the oxidation of the metallic substrate due to the combination of high temperature and oxidizing conditions. This oxidized layer strongly adheres to the glass after sticking. The XPS results are

of interest showing that the sticking glass surfaces have a low sodium content, compared to the bulk composition, and the substrates have some traces of sodium without any silicon nor calcium. This suggests a high reactivity of the sodium oxide which may be the origin of some interfacial chemical reactions responsible for the affinity of the contacting surfaces during pressing. The reactivity of sodium has been already pointed out by Winther and Schaeffer [14], who observed an increase in sticking temperature achieved by a gas-induced dealcalization of a soda-lime-silica glass. The glass reactivity due to sodium oxide can be discussed on the basis of thermochemical calculations allowing to quantify the relative stability of oxide compounds. For systems containing three or more elements, thermochemical calculations based on the simple enthalpy rule are not sufficient to determine the most probable reactions, since a great number of reactions are in competition. One way to completely describe a system containing more than two elements is to use isothermal sections of ternary phase diagrams. This approach has been performed to predict interfacial reactions in ion implantation [15] and ion mixing [16] of metals in ceramics and for tribochemical reactions during friction [17 and 18]. Reactions with M (= titanium or iron) and Na₂O are presented in the two ternary diagrams (M-Na-O) shown in figures 6a and b. The ternary diagram (Al-Na-O) is not presented since aluminium has a similar thermochemical affinity as titanium, this last element being the major constituent of the TA6V alloy. The diagrams were computed using Gibbs free energy data valid at 700°C. However, the validity of the diagrams has been checked up to 1100°C, so that they can be used for the thermochemical description in the whole temperature range related to the present experiments. In these diagrams, the tie lines were obtained by writing balanced equations for the reactants and products and determining the side that has the lower free energy. Calculations have been performed using the data published in [19]. The stable products can be seen at the vertices of each of the triangles through which the reaction line passes. The dashed line indicates the nature of the two reactants (metal and Na₂O). It can be seen, for example, that both iron and titanium react with Na₂O to form respectively the iron oxide Fe₂O₃ and the titanium oxide TiO₂, and metallic sodium. In contrast, such calculations performed with the same metallic species and SiO₂ (not reproduced here) indicate a similar thermochemical stability of the oxides. Thus, from a thermodynamic point of view, sodium oxide is the less stable glass constituent oxide. Moreover, it is less stable than the iron, titanium and aluminium oxides at temperatures below 1100°C. The reactivity between the metallic base and soda of the glass during the sticking phenomenon at high temperature seems to be confirmed by the XPS results shown in figures 3a and b and table 1. From this consideration, the small but reproducible difference of sticking temperatures observed between the TA6V alloy and the iron substrate whatever the nature of the glass, may be explained in terms of thermo-



Figures 6a and b. Ternary phase diagrams calculated for the systems Ti-Na-O (figure a) and Fe-Na-O (figure b) at 700°C. The diagrams are valid for temperatures up to 1100°C.

dynamic driving force as follows. The ternary diagrams in figures 6a and b indicate that iron and titanium react with Na₂O according to the reactions:



Taking into account the value of the Gibbs free energy of the two reactions, titanium is more reactive with sodium oxide than iron. This seems to be consistent with the lower values of the sticking temperatures observed with the TA6V alloy, as compared to the iron substrate. Moreover, the Na/Si ratio (table 5) related to the glass surface sticking on the TA6V is smaller than the ratio related to the iron substrate, indicating that the surface of the glass has been more impoverished in sodium in the case of a contact with the titanium alloy than with iron. Even if XPS quantitative results may be cautiously used, experimental results appear to be in good agreement with thermochemical data, which can be con-

sidered as a guideline to identify the physicochemical interactions in glass/metal contacts at high temperature. In particular, the use of low oxidizable metallic substrates for mould materials does not always prevent sticking during the forming process: indeed, such materials are resistant to oxidation thanks to a passivation layer inhibiting the diffusion of oxygen into the bulk, but this so-called protective layer may be continuously removed in severe wear conditions at high temperature. Thus, it is continuously restored, due to a high thermochemical reactivity, as in the case of the alloy constituents titanium or aluminium, since the corresponding oxides are thermodynamically very stable.

As mentioned in sections 3.1 to 3.3, the cast iron substrate exhibits the highest value of sticking temperature. Such a result may be explained taking into account the presence of graphite spheroids being oxidized into gaseous CO₂ during the high-temperature contact with the glass melt. This interfacial production of gaseous compounds may be responsible for a reduction of the close contact between the glass and the cast iron surface, thus, leading to a higher sticking temperature. It is interesting to note that cast iron, one of the most extensively used mould substrate for glass container forming, has a favourable set of advantages, in terms of low cost, suitable thermal conductivity and, as it was observed in the present experiments, relative high sticking temperature.

5. Conclusion

On the basis of experiments performed by using a laboratory glass press apparatus, the effect of the nature of various substrate materials and glass compositions on the sticking temperature of glass/metal contacts at high temperature has been elucidated. The sticking phenomenon is governed by a coupling between the rheological behaviour of the glass melt, and the physicochemical reactivity of the contacting surfaces. Sticking occurs when the temperature at the interface remains sufficiently high, so that the glass viscosity remains low enough to enhance the real contact area. This induces physicochemical interactions between the substrate and the glass. The sticking phenomenon is attributed to the presence of an interfacial oxide layer which strongly adheres onto the glass. Chemical analysis of the sticking surfaces identifies a physicochemical driving force which may contribute to the sticking phenomenon, as soon as the close contact is achieved between the substrate and the glass. The predominant reaction consists in the reduction of the sodium oxide of the glass at the expense of oxidation of the metallic elements of the substrate during pressing. Obviously, metallic sodium is instantaneously re-oxidized with oxygen from the ambient environment, which is consistent with XPS results identifying sodium oxide on the substrate surfaces. These experimental observations are in agreement with thermochemical calculations performed using ternary diagrams,

indicating the relative low thermodynamical stability of Na₂O as compared to most of other oxides at high temperature. From these considerations, the research on materials with high sticking temperatures may be oriented to identify mould surface compositions preventing chemical reactions with soda, or to modify the glass composition in order to lower the chemical reactivity of the glass due to Na₂O. Such conditions are achieved with the extensively used cast iron material, characterized by a relative high sticking temperature. It is probably due to the formation of a thin gaseous layer produced from the oxidation of the graphite spheroids, thus inhibiting the close glass/metal contact. Moreover, it was shown that the use of ternary phase diagrams proposes a powerful method for describing and perhaps predicting the reactivity and the phase formation related to glass/substrate contacts at high temperature.

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