

## Influence of glass/mould interfaces on sticking

Jérôme Pech, Gregory Berthomé, Michel Jeymond and Nicolas Eustathopoulos

Laboratoire de Thermodynamique et de Physico-Chimie Métallurgiques, ENSEEG, Saint-Martin d'Hères (France)

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The sticking of glass on mould materials is a critical problem since it can lead to the interruption of glass container production. This study is a contribution to understanding the phenomena at the origin of sticking. The experiments involve loading and spreading glass gobs on flat metallic substrates. They are performed directly on a glassmaking machine, thus the thermal conditions of the processes are simulated as closely as possible. Special attention is paid to characterizing the metal and glass surfaces before and after contact using a surface profilometer, AFM, and SEM with an EDX spectrometer. The influence on sticking of mould temperature, surface roughness and surface chemistry (nonoxidized, pre-oxidized and lubricated) is investigated.

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### 1. Introduction

In the production of glass containers, mould materials are used in cyclical spinning and pressing processes [1]. Each one involves loading the mould preheated to a given temperature  $\vartheta_0$  with hot glass melt, spreading the glass over the mould surface and then cooling and removing the glass article. Repeated glass/mould contacts lead to glass sticking, i.e. to the impossibility of properly separating the glass article from the mould. Some or all of the article then remains stuck to the mould surface, thus requiring significant cooling of the mould well below  $\vartheta_0$  and in most cases the interruption of industrial production. Obviously, glass container industries have always looked for ways to limit glass sticking and supported research to find solutions. On the one hand, empirical studies have been carried out regarding the type of mould surfaces [2 and 3] while on the other, several systematic investigations have been performed to determine the influence of different parameters on glass sticking. These investigations were based on laboratory experiments that more or less accurately reproduce industrial conditions.

Kapnicky, Dowling and Dartnell [4 to 6] were the first to develop a simple experiment to study glass sticking by dropping hot glass beads on heated and tilted metallic surfaces. From this experiment, it was possible to determine the temperature of the surfaces at which the glass stuck. They investigated the effect of surface features such as surface temperature, roughness and chemistry on glass sticking. These authors always compared their results with each other leading to a classification of surface features in terms of sticking. However, they did not try to describe the microscopic phenomena involved in glass/mould sticking.

Trier et al. [7] carried out similar experiments, giving measurements of glass sliding coefficients as a function of

temperature for both polished and rough surfaces. They produced interesting ideas that helped to explain the impact of microscopic configurations at the glass/substrate interface on local heat transfer. These considerations suffer from the absence of microscopic characterizations of glass and mould surfaces formerly in contact. Moreover, even if sliding and sticking phenomena are related, they also present significant differences.

Less than ten years ago, Manns et al. [8] developed an original experiment to study glass sticking and investigate several metals, surface coatings and roughness. Their experiment consisted in plunging a metallic surface into a bath of hot glass melt many times. Each time, they measured the force needed to separate the metallic surface from the glass and found that this diverged when the temperature of the metal increased towards a well defined level characterizing sticking. Manns et al. explained this divergence by the establishment of a true interface between the glass and the substrate, which is a reasonable hypothesis. However some of their results are surprising, for instance they found no effect of roughness on the sticking temperature, a result which does not agree with the well-established experience of glassmaking practice. Manns et al. attributed this disagreement to thermal exchanges between the glass and the metallic surface on the scale of their experiments, which were radically different from those involved in industrial practice. As previously [7], Manns et al. did not characterize the substrate and glass surfaces formerly in contact.

More recently, Falipou et al. [9] suggested that sticking is due to reactions between the glass and mould. However, the present authors showed in a recent study that strong adhesion and sticking can occur even in the absence of reactions between the glass and the metal [10].

At this stage, it is necessary to define sticking properly, since in the past different definitions have been used. Tomsia

et al. [11] consider that sticking occurs when a glass, melted at high temperature on a substrate, adheres to it during cooling up to room temperature. Although this definition is reasonable for sticking related to enamels, the definition used in glass industry processes is adopted in the present study. If  $\vartheta_0$  is the mould temperature, as mentioned above, no sticking means that the glass article and the mould can be separated properly at a temperature greater than or lower but close (within a few decades of degrees) to  $\vartheta_0$ . As for sticking, it signifies that glass/mould separation requires considerable cooling of the system down to a temperature that is significantly lower than  $\vartheta_0$  by several hundreds of degrees.

The present study was conducted taking into account two considerations suggested by the analysis of previous attempts to explain sticking: a) since thermal exchanges play a crucial role in sticking, experiments that are as close as possible to industrial practice have to be performed, and b) since the key for understanding sticking is the microscopic configuration at the glass/substrate interface, an effort must be made to characterize systematically glass and substrate surfaces formerly in contact. We decided to work with a chromium steel as substrate, as this is largely representative of mould materials, and the well-used soda-lime glass.

This study is the continuation of previous investigations, carried out on laboratory scale with the same materials, concerning the wetting and adhesion of glass on steels [10]. The experiments were performed in isothermal conditions with small glass masses (typically 100 mg), at high temperature (from 960 to 1200 °C) and in helium atmosphere, so that the chemistry of the free substrate surface was kept constant during the experiments. The main conclusions of that work, which will be useful in discussing the results of the present study, are briefly the following: First, in agreement with the literature [12 and 13], the glass wets metallic surfaces (final contact angle,  $\theta_f$ , lower than 90° by 20° to 30°), even in the absence of reaction between the metal and the glass. Note that the pre-oxidation of metallic surfaces significantly improves wetting ( $\theta_f \ll 90^\circ$ ). Second, wetting associated with the low viscosity of glass at high temperature allowed all substrate surface defects to be penetrated by the glass, leading to the establishment of a true interface on nanometric scale. This was confirmed by the characterizations of substrate and glass surfaces formerly in contact. Third, under these true interface conditions, it was found that sticking occurred whatever the steel roughness and surface state (oxidized or not). Indeed cooling at a temperature  $\vartheta$  much lower, by several hundred degrees, than the vitreous transition temperature  $T_g$ , was necessary in each case to generate enough thermal stress to cause glass/substrate separation. Note that the pre-oxidation of the steel substrates increases the tendency to stick.

## 2. Experimental procedure

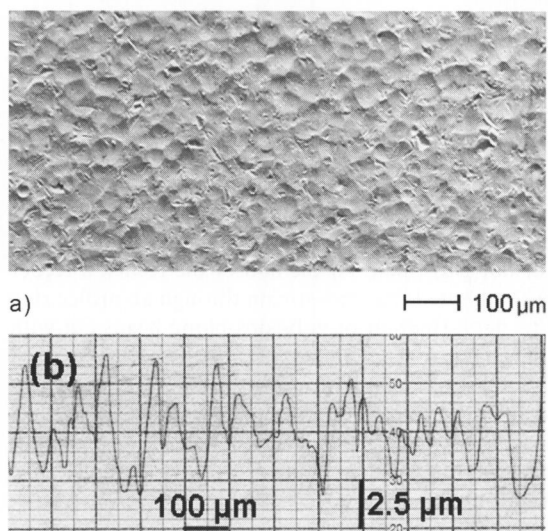
The glass used in this investigation is common soda-lime glass. Its composition (in wt%) is 13.4 Na<sub>2</sub>O, 10.9 CaO, 1.4 MgO, 1.6 Al<sub>2</sub>O<sub>3</sub> and balance SiO<sub>2</sub>. The glass mass, fixed at (100±2) g, was chosen to be representative of the usual masses of articles included in the 10 to 1000 g range. A widespread stainless steel was selected from among the different mould materials used in glass container production.

This steel is composed of (in wt.%) 16.86 Cr, 1.88 Ni, 0.43 Mn, 0.27 S, 0.20 Co and balance Fe. The steel samples are 200 mm in diameter and 10 m in thickness. All the experiments were carried out in air.

In order to be as close as possible to production conditions, an experimental layout consisting of two main parts was built specifically on a glassmaking machine. The first part was a common glass feeder delivering a continuous stream of hot glass melt. At the end of the feeder, a feeder mechanism pulsed the glass stream through an orifice ring leading to the formation of gobs or oblong beads cut with a shear mechanism. The temperature of the gobs was fixed at 1200 °C ± 2 K and monitored using an IR pyrometer focussed on the orifice ring output and calibrated with a fixed glass emissivity of 0.95. The second part consisted of a heating plate designed to support the steel samples. The orifice ring output and the steel sample surface were separated by about 1.6 m. A temperature regulation system, inserted inside the heating plate, controlled the temperature with an accuracy of ±2 K. Each disk sample, lying on the heating plate, was equipped with a K type thermocouple to control the temperature at the disk centre and 3.5 mm below the surface. This study does not aim to provide detailed information on the distribution of temperature through the glass/substrate interface as a function of time, but to obtain thermal data for appreciating the reproducibility of the experiments.

An experiment was conducted as follows: a) a steel sample surface was heated to the required temperature ( $\vartheta_0$ ), b) a gob was taken up and dropped onto the heated steel surface, c) the spreading of the gob was filmed using an analogical rapid camera (250 images s<sup>-1</sup>). The axis of the camera was set to follow the geometric parameters of the article correctly in time. Given the time required to transform films from analogical to numerical format, only a few of them were digitized for quantitative analysis. The substrate temperature close to the glass contact surface was collected simultaneously on a computer at regular small time steps of 0.1 s, d) once the final shape of the article was reached, the glass/steel system was left in place until thermal equilibrium was recovered, i.e. the experimental temperature of the steel sample approached, within a few degrees, its initial value,  $\vartheta_0$ . At that time, equal to about 5 min, the "solidified" glass article was carefully pushed with a metal rod. If the article was successfully removed from the steel surface, no glass article annealing was done to preserve its surface topography and chemistry. It should be noted that the article sometimes broke suddenly when it was removed or cooled to room temperature, thus the experiment was repeated again until it succeeded. If the article was not separated from the steel surface, the system was returned to 180° and quickly cooled down by quenching in air to force the article to separate from the substrate at a given detachment temperature ( $\vartheta_d$ ). Separation occurs under the effect of mismatched thermal contraction between the substrate and the "solidified" glass. For each experiment, the steel and glass surfaces formerly in contact were collected for further characterizations.

Various techniques were employed to determine the roughness and chemistry of the substrate and glass surfaces. A Talysurf surface profilometer as well as a high resolution interferometric profilometer were used to measure roughness over areas from a few to several mm<sup>2</sup> and atomic force



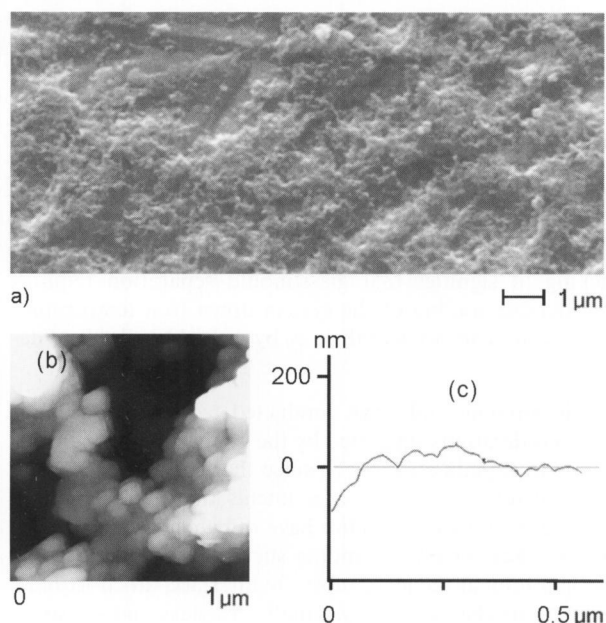
Figures 1a and b. SEM picture of a micro-blasted surface (figure a) and corresponding roughness profile (figure b).

microscopy (AFM) for characterizing surface evenness defects with areas of several μm<sup>2</sup>. In parallel, a scanning electron microscope (SEM) with an energy-dispersive X-ray (EDX) spectrometer was operated to obtain data on local chemistry.

The study parameters concerning spreading and sticking are the steel temperature ( $\vartheta_0$ ), varying in the range met in glass container production (450 to 600 °C), the initial surface state changing from polished to micro-blasted, and the initial surface chemistry differing from metallic to lubricated or pre-oxidized. The initial polished surfaces are of metallic appearance and present numerous defects due to the scratches from the polishing process, leading to an average roughness ( $R_a$ ) determined with the profilometer of  $0.05 \pm 0.01 \mu\text{m}$ . AFM investigations showed that the scratches look like open defects about  $0.5 \mu\text{m}$  deep and  $5 \mu\text{m}$  wide. Obviously during heating up to  $\vartheta_0$ , the initial metallic surface becomes covered with a thin oxide layer. For instance at  $\vartheta_0 = 450$  or  $600 \text{ }^\circ\text{C}$ , the oxide layer is quite homogeneous, a few ten and hundred nm thick and does not change – or only a little – the average roughness ( $R_a$ ), which is close to  $(0.05 \pm 0.01)$  and  $(0.08 \pm 0.01) \mu\text{m}$ , respectively.

Micro-blasted substrate surfaces are obtained by blasting hard steel balls of 50 to 100 μm in diameter at a pressure of 100 kPa over polished surfaces. Ball impinging induces the formation of fairly large and deep defects, about 50 μm in diameter and 5 μm in depth, respectively. The SEM picture of the micro-blasted surface in topographic mode shows that the defects are homogeneously distributed and look like craters (figure 1a). By following a line on the micro-blasted surface with the profilometer, the topography described is a succession of hills (borders of craters) and valleys (centers of craters) (figure 1b). The slight oxidation of micro-blasted surfaces during heating up to  $\vartheta_0$  does not change their average roughness, measured using the profilometer, which remains equal to  $(0.9 \pm 0.1) \mu\text{m}$ .

Lubrication is achieved by acetylene cracking directly onto polished surfaces as is done in production processes. Lubricated substrate surfaces are covered with a layer that



Figures 2a to c. SEM and AFM pictures of a lubricated surface (figures a and b) and corresponding AFM roughness profile (figure c).

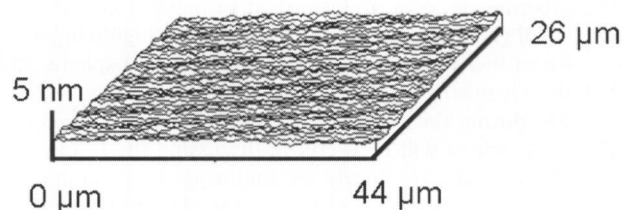


Figure 3. Reference glass surface by high resolution interferometric profilometry.

is fairly porous and non-homogenous particularly with regard to thickness, as seen on a SEM picture (figure 2a). EDX microanalysis reveals that the layer consists essentially of carbon. Due to its nonadherence to the substrate, parts of the layer are detached locally, so that it is possible to measure its thickness by AFM; this is in the range of 100 to 500 nm. Actually, the layer appears to consist of agglomerated particles (figure 2b). These particles are around 50 nm in diameter and separated by very small spaces, about 20 nm wide and deep (figure 2c). Heating the substrate to  $\vartheta_0$  does not modify the lubrication, since carbon appears to be stable in air in the temperature range of this study.

As the experiments were performed in air, the metallic surfaces of the steel samples were always oxidized during heating to  $\vartheta_0$  and finally covered with a thin oxide film. To appreciate the effect of a thicker oxide layer, a polished steel surface was initially pre-oxidized at 800 °C for 2 h in air. This treatment leads to the formation of a micron-thick layer of more or less homogeneous thickness. EDX microanalysis shows the formation of chromium oxides. The roughness determined using the profilometer is significantly increased to  $(0.21 \pm 0.02) \mu\text{m}$  compared with those of polished substrates, which are close to  $0.05 \mu\text{m}$ . Heating the

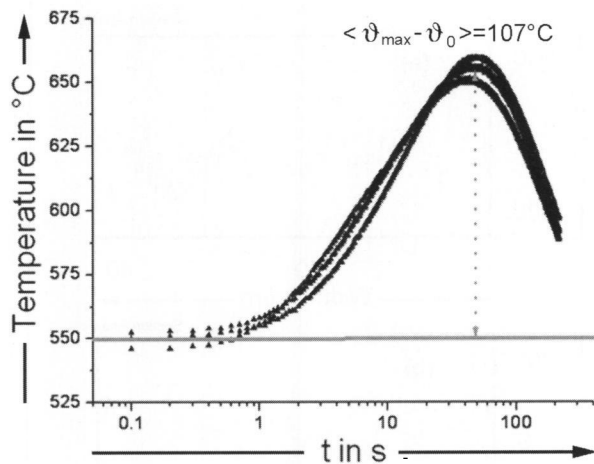


Figure 4. Variation in time of the thermocouple temperature obtained for three different experiments at  $\vartheta_0=550^\circ\text{C}$ .

Table 1. Interfacial temperatures  $\vartheta_i$  calculated for different  $\vartheta_0$  values of mould in the case of a polished surface and for  $T_g=1200^\circ\text{C}$ .  $A$  is a parameter calculated using literature data on thermal properties of steel used (Saarsthal GmbH, Germany) and glass [15], see section 6

$\vartheta_0$ in $^\circ\text{C}$	$\vartheta_{\max}$ in $^\circ\text{C}$	$A$	$\vartheta_i$ in $^\circ\text{C}$
400	540	2.68	617
450	571	2.82	646
500	629	2.94	678
550	655	3.05	710
600	692	3.33	739

pre-oxidized substrate to  $\vartheta_0$  does not alter the layer of oxide formed since  $\vartheta_0$  is lower than the pre-oxidation temperature.

Regarding the glass, the reference surface is a free “solidified” glass surface that has never been in contact physically with any other surface. As an example, we chose the upper surface of a glass article, which has a very low roughness value, in the range from 2 to 5 nm (figure 3).

### 3. Results

Repeated experiments performed in the same conditions, for instance at  $\vartheta_0=550^\circ\text{C}$  with polished substrates, led to correctly overlapped  $\vartheta_t$  curves, underlining the correct reproducibility of the experiments (figure 4).

Whatever the study parameter, substrate temperature ( $\vartheta_0$ ), substrate roughness ( $R_a$ ) or surface chemistry (lubricated or pre-oxidized), the temperature measured inside the substrate presents the same variations in time. Initially, the temperature rises for about 50 s, reaching a maximum value ( $\vartheta_{\max}$ ) and then gradually decreases back to its initial value ( $\vartheta_0$ ) in about 5 min. The difference in temperature between  $\vartheta_0$  and  $\vartheta_{\max}$  is around  $100^\circ\text{C}$  (table 1) and changes slightly from one study parameter to another. For instance, at the same  $\vartheta_0$  value,  $\vartheta_{\max}$  diminishes slightly (by a few degrees) from a polished to a micro-blasted surface and from a metallic to a lubricated or pre-oxidized surface.

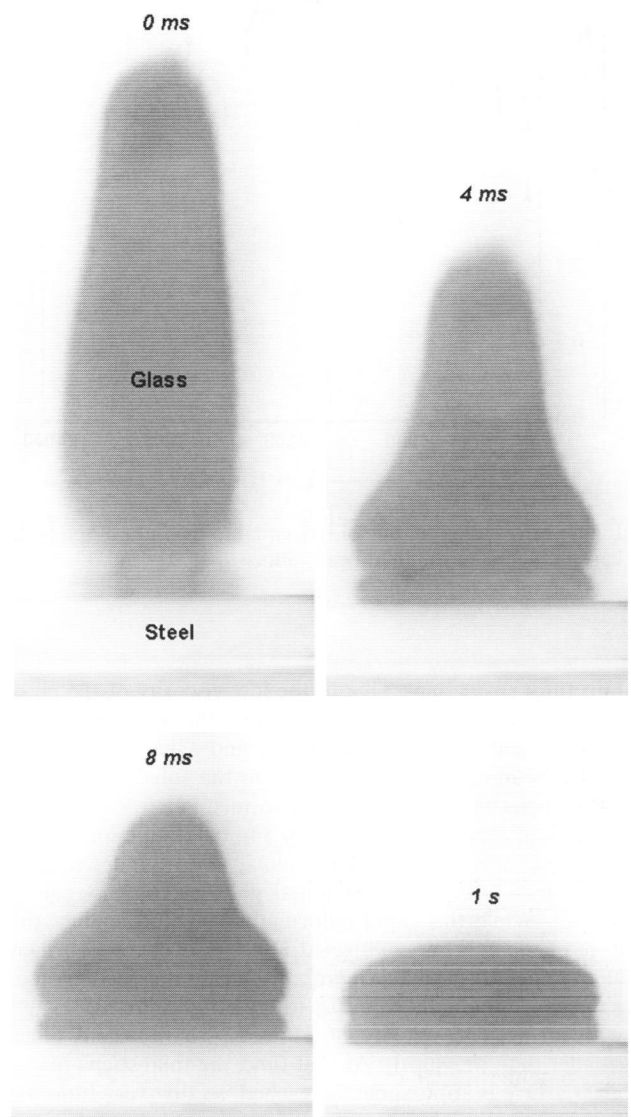


Figure 5. Selected pictures of glass bead spreading showing sudden deformation at impact for  $t=4$  and  $8$  ms, respectively, followed by slower deformation of the upper part of the bead up to  $1$  s. The time  $t=0$  s is considered just before impact and  $\vartheta_0=550^\circ\text{C}$ .

Articles look like flat crepes characterized by their mean radius ( $R$ ) and their thickness ( $e$ ), which are nearly constant from one experiment to another:  $(38\pm 2)$  and  $(11\pm 2)$  mm, respectively. The final shape and the geometric dimensions of the articles are thus quite independent of any study parameter.

In examining the films taken with the ultra-rapid camera, it should be noted that glass spreading always occurs in the same way. Figure 5 presents the main pictures of the general glass bead deformation during spreading. This deformation can be quantified through the variation in time of the gob radius,  $R_t$ , which is measured directly on the digitized pictures. Figure 6 shows the ratio  $r(t) = \frac{R_t}{R_f}$  of  $R_t$  by the final article radius  $R_f$  determined at room temperature, in the case of an experiment performed with a polished substrate heated to  $\vartheta_0=550^\circ\text{C}$ . Spreading can be broken

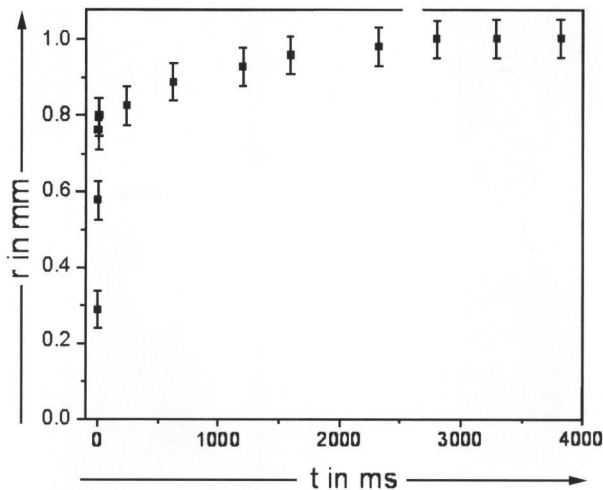
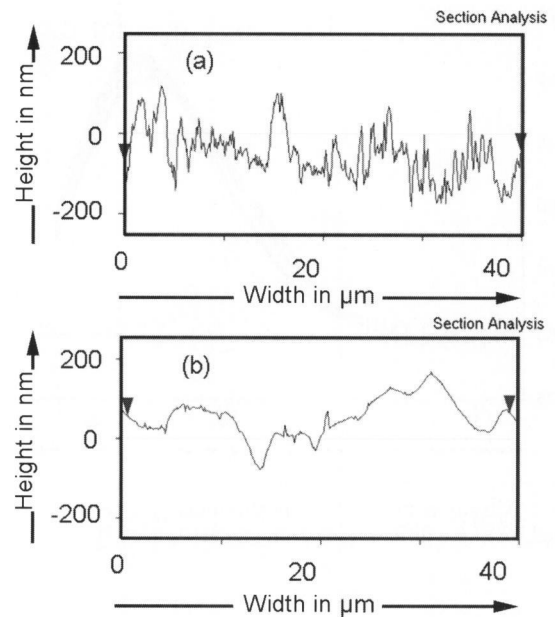


Figure 6. Variation in time of  $r(t)$ , equal to the ratio of the bead base radius  $R_b$  to the final bead radius  $R_f$  at  $\vartheta_0=550^\circ\text{C}$ .

into three main steps. Due to the low viscosity of the glass at high temperatures and the fall from the orifice ring output, the gob has an oblong shape and a high velocity of about  $5.6\text{ m s}^{-1}$  when impinging on the substrate surface. At impact, the gob is suddenly deformed in a few ms (figure 5), and  $r$  increases sharply from 0.3 to 0.8 (figure 6). During this first step, the spreading velocity is around  $5\text{ m s}^{-1}$ , which is very close to the initial gob velocity just before impact. While this rapid deformation involves mainly the base of the gob, the unaffected upper part of the gob then slowly spreads until 1 s (figure 5). During this second step,  $r$  increases gradually from 0.8 to 0.95 (figure 6), associated with an average velocity of  $5\text{ mm s}^{-1}$ , a thousand times smaller than previously. At that time, the final shape of the glass article is approximately reached, so that very little deformation takes place from  $r=0.95$  to 1 until the end of the experiment in about 5 min (figure 6).

All glass articles present some ripples on the glass surface formerly in contact with the substrate. The ripples, which are localized in the periphery, represent more or less 30% of the total glass surface in contact and they look like waves having a millimetric wavelength and a micrometric amplitude. Ripples are well known in the glass industry and several authors have already described in detail the process leading to wave generation founding their explanations on the rippling process involved in metal casting [14 to 16]. It is well established that the temperature of the bulk glass plays a crucial role, a low temperature favouring rippling. In our experiments ripple formation occurs for  $t > 12\text{ ms}$ , i.e. during a period in which the bulk glass temperature depends on the thermal exchanges at the glass/substrate interface. In the framework of the present study, the ripple features are used as a qualitative but pertinent indicator of these thermal exchanges. Regarding the results, the ripple features change with the mould surface state. For the same temperature,  $\vartheta_0 = 600^\circ\text{C}$ , the ripples are strongly accentuated in the case of a pre-oxidized surface, whereas they are less numerous and less pronounced when the surface was initially lubricated and they tend to disappear in the case of a micro-blasted surface. This clearly means that the thermal exchanges are less intensive at the interface for lubricated

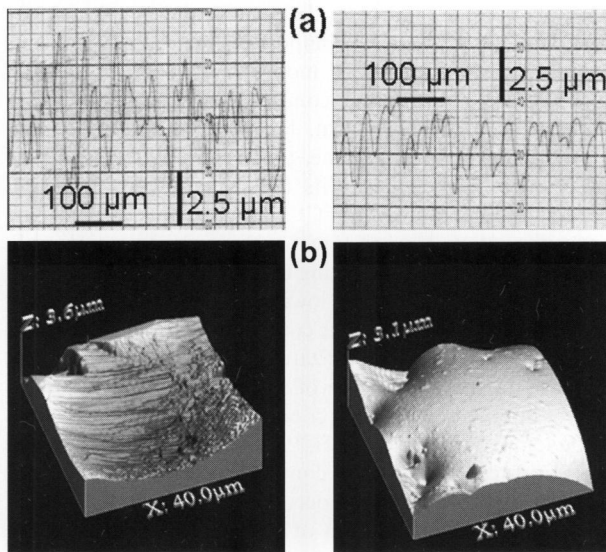


Figures 7a and b. AFM roughness profiles of the polished steel surface measured on the area between scratches (figure a) and the corresponding glass surface (figure b);  $\vartheta_0 = 550^\circ\text{C}$ .

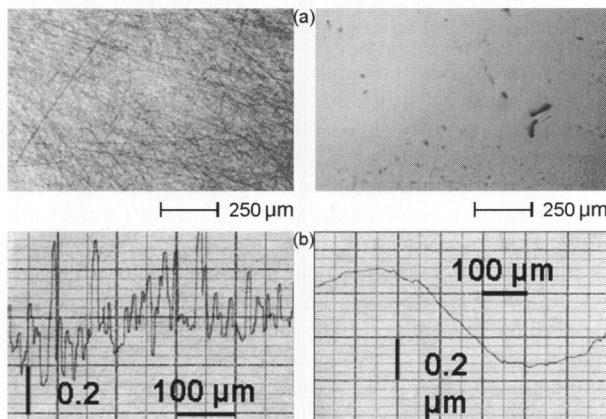
or micro-blasted surfaces, leading to a higher glass bulk temperature than for a pre-oxidized surface.

Nonsticking of glass means that the article was easily detached from the substrate with an interfacial rupture at macroscopic scale. For polished substrates, nonsticking occurred for  $\vartheta_0=400, 450, 500$  and  $550^\circ\text{C}$  with glass detachment observed during cooling back to  $\vartheta_0$ . For micro-blasted, lubricated or pre-oxidized substrates, nonsticking took place for  $\vartheta_0$  close to  $600^\circ\text{C}$  with glass detachment observed at  $\vartheta_d=540^\circ\text{C} \pm 10\text{ K}$  during quenching in air. Among all our results, just one case corresponds to sticking, namely the case of a polished substrate heated to  $\vartheta_0=600^\circ\text{C}$ . In this case, the peripheral part of the article was detached and broke down into several pieces during quenching in air, while the central part of the glass article remained stuck to the substrate.

Characterizations of glass and substrate surfaces formerly in contact in case of nonsticking were performed systematically. They show that, except in the case of the pre-oxidized substrate, glass detachment occurred with an interfacial rupture not only at the macroscopic scale but also at the microscopic one. No reaction product was found by SEM at the interface in any case. To appreciate the penetration of glass into substrate defects, local characterizations by AFM were performed. Initially polished substrates heated up to  $550^\circ\text{C}$  present numerous scratches about  $(0.5 \pm 0.1)\ \mu\text{m}$  deep and  $(5.0 \pm 0.5)\ \mu\text{m}$  wide, whereas the scratches moulded by the glass on the glass surface are around  $(0.25 \pm 0.05)\ \mu\text{m}$  high and  $(8 \pm 3)\ \mu\text{m}$  wide. As for the areas between the scratches, the roughness of the substrate measured by AFM is about 35 nm, while it is about 20 nm on the glass surface (figures 7a and b). All these results lead to the conclusion that for  $\vartheta_0 \leq 550^\circ\text{C}$  the glass does not penetrate all the steel surface defects, i.e. the interface is “composite”, partly metal/glass and metal/air. In the following, the term “composite” interface will be used by oppo-



Figures 8a and b. AFM roughness profiles of steel (left) and glass (right) contact surfaces (figure a), and a steel valley (left) and corresponding glass surface (right) (figure b); micro-blasted substrate and  $\vartheta_0=600^\circ\text{C}$ .

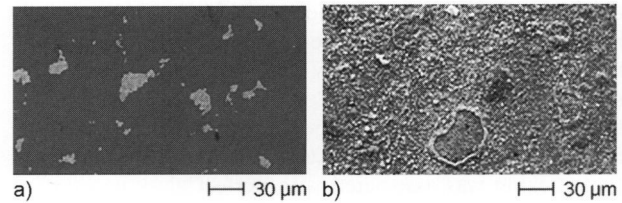


Figures 9a and b. Optical microscopy pictures of steel (left) and glass (right) surfaces (figure a), and roughness profiles of the above two surfaces (figure b); lubricated substrate and  $\vartheta_0=600^\circ\text{C}$ .

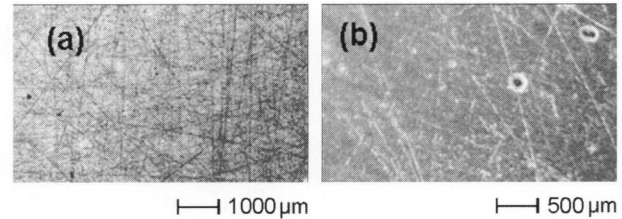
sition to a true interface, when the glass penetrates all substrate surface defects.

In the case of micro-blasting, the profilometer roughness of the glass surface previously in contact with the micro-blasted substrate is about  $(0.40\pm 0.05)\mu\text{m}$ , which is two times lower than the substrate roughness due to micro-blasting. Hence the glass only partly espouses the steel surface due to micro-blasting. Like the substrate surface, the glass surface in that case is also a succession of peaks and hollows, but the peaks are smoother and correspond to partial moulding of the steel hollows. The glass roughness, measured with AFM at the summit of the peaks, is close to the reference glass roughness, i.e. a few nm. This result corroborates the assumption of partial moulding illustrated on figures 8a and b and leads to the conclusion that the glass/micro-blasted interface is of “composite” type.

In the case of lubrication, the glass surface is not affected by contact with the substrate. As determined by



Figures 10a and b. SEM pictures of contact surfaces showing oxides pulled out on steel (figure a) and oxides stuck on glass (figure b); pre-oxidized substrate and  $\vartheta_0=600^\circ\text{C}$ .



Figures 11a and b. Optical microscopy pictures of the initial polished surface (figure a) and the glass/substrate interface through the stuck glass (figure b);  $\vartheta_0=600^\circ\text{C}$ .

AFM, the roughness is a few nm, as in the reference case, which clearly indicates the absence of significant physical contact between the glass and lubricated substrate (figure 9a). On the macroscopic scale, the glass surface presents undulations due to variations in lubrication layer thickness along the interface. Indeed, profilometer investigations show that the surface deformation is a few hundred nm for a distance along the surface of several hundred  $\mu\text{m}$  (figure 9b). After the experiment the lubrication layer disappeared under the contact surface with the glass and the metallic surface was revealed (figure 9a). The very partial contact between the glass and the lubricated surface, probably limited at some points, means that the interface is also of “composite” type.

In the case of the pre-oxidized substrate, the roughness of the glass and substrate surfaces formerly in contact are nearly the same, i.e.  $(0.08\pm 0.02)\mu\text{m}$ . The glass/pre-oxidized interface is then a true interface, since the glass espouses the substrate surface defects. Nevertheless the apparent interfacial rupture observed on the macroscopic scale is invalidated by SEM-EDX investigations. Indeed patches of metallic oxides, which have remained stuck to the glass surface, are clearly revealed on the SEM pictures (figure 10a). These regularly distributed patches correspond mainly to chromium oxide,  $\text{Cr}_2\text{O}_3$ , as identified by EDX microanalysis. The SEM characterizations of the corresponding substrate surface show distinctly that the initial oxide layer, rich in chromium oxide, has been pulled up at homogeneously distributed locations (figure 10b). Unlike previous results concerning nonsticking, glass separation from the pre-oxidized substrate occurs along a path lying within a brittle, chromium-rich oxide layer.

As in the case of sticking, the stuck central part of the glass article was transparent, enabling direct observation of the interface through the matter by optical microscopy. The substrate surface at the interface and around the stuck central part are similar in coloration and texture, i.e. no reaction product was formed at the glass/substrate interface (figures 11a and b). Close to the border of the central part,

the oxide layer that had developed during heating was fully removed by the glass, leading to a metallic appearance of the substrate. Unfortunately, because of sticking, this sample does not enable the contact surfaces to be characterized further. However, previous experiments performed in the laboratory and mentioned in the introduction showed that sticking was associated with perfect glass penetration of all surface defects, i.e. a true interface was established at any point of the contact area [10].

#### 4. Discussion

As the results show, about 80 % of the final shape of the glass article is already reached in about  $\tau=12$  ms. The time for the main glass deformation to occur is so short that the thermal exchanges between the bulk glass and the bulk substrate are almost nil. The order of magnitude of the glass thickness,  $L \approx \sqrt{D\tau}$ , affected by the thermal exchanges can be estimated from glass diffusivity,  $D$ , which is  $1.6 \text{ mm}^2 \text{ s}^{-1}$  [17], leading to  $L \approx 0.1$  mm. Regarding the substrate,  $L$  is about 0.6 mm within the same very short time. In both cases,  $L$  is much smaller than the glass or the substrate thickness,  $\approx 10$  mm. The main glass mass is then deformed during  $\tau$  with a quasi-constant bulk temperature, unlike the glass in direct contact with the mould. On impact the glass has a measured velocity of  $5.6 \text{ m s}^{-1}$ . After impact, the measured average velocity of the glass over 12 ms is  $5 \text{ m s}^{-1}$ , i.e. approximately the same. Thus the energy available for visco-elastic deformation of the glass is the incident kinetic energy. In the time  $\tau$ , the glass deforms until all kinetic energy is dissipated by viscous friction without significant viscosity variations, since the bulk temperature remains constant. These issues explain why the main factor determining the final shape of the glass article is the initial bulk temperature of the glass and not the other study parameters.

While the substrate temperature has little or no influence on the final shape of the glass article, it has a strong influence on all the other phenomena, especially on sticking and rippling. Indeed, this temperature together with the initial glass temperature, determines the temperature at the interface,  $\vartheta_i$ . As the above calculation of  $L$  at  $t=\tau$  suggests, this temperature  $\vartheta_i$  is established rapidly, namely at a time much less than  $t_{\text{max}}$ . This interfacial temperature was calculated (see section 6) for polished surfaces by neglecting the contact thermal resistance at the interface and assuming that the conditions of heat exchange at the glass/substrate interface are adiabatic [18]. In the frame of this calculation, the temperature in the contact zone jumps immediately on contact to the value  $\vartheta_i$ . The values of  $\vartheta_i$ , calculated from the thermal properties of the glass and steel involved (see section 6), are given in table 1.

The results obtained in [10] showed that glass wets deoxidized steels (final contact angle close to  $70^\circ$ ) and that this wetting is improved when the metallic surface is pre-oxidized, i.e. when glass wets metallic oxide. For polished surfaces heated up from 450 to 600 °C in air, the initial contact between the glass and the substrate is always a contact between glass and metallic oxides. Therefore the glass will tend to wet the surface well and to penetrate all the substrate surface defects, even if the glass wholly dissolves the oxide layer. However the topographical characterizations of glass and steel surfaces formerly in contact show that the penetra-

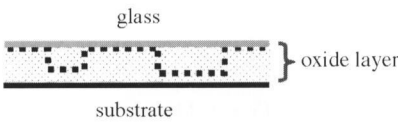
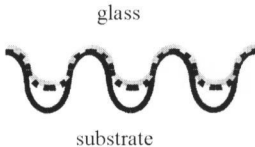
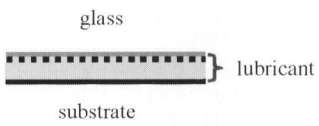
tion of substrate surface defects is always partial for  $\vartheta_0 \leq 550$  °C, leading to a “composite” interface. This means that the glass is unable to mould the defects in spite of favourable thermodynamic conditions. The only possibility is therefore to consider that, locally at the interface and within the experimental time, the viscosity of glass is not low enough, which limits its deformability. At the glass softening temperature,  $735$  °C<sup>1)</sup>, the glass can be deformed under the action of weak forces such as its own weight [17]. For  $\vartheta_0 \leq 550$  °C, it is interesting to compare  $\vartheta_i$  to  $735$  °C and to notice that  $\vartheta_i$  is always lower than this glass softening temperature (table 1). This is consistent with the conclusion drawn by surface characterizations, i.e. that the interfaces obtained in these cases are of “composite” type. For this type of interface, even slight cooling under the vitreous transition temperature,  $T_g \approx 560$  °C<sup>1)</sup>, is sufficient to separate the glass from the substrate. In contrast, at  $\vartheta_0=600$  °C and for a polished surface, sticking occurs. As shown in [10], this is due to the total penetration of all substrate defects by the glass. This is possible because the interface temperature in this case is high enough to permit glass deformation. It is interesting to note that with  $\vartheta_0=600$  °C,  $\vartheta_i$  is equal to  $739$  °C, so greater than the softening temperature (table 1). Obviously the quantitative agreement observed is fortuitous because with the  $\vartheta_i$  calculation it is possible only to extract tendencies and not to draw quantitative conclusions.

For a substrate temperature of 600 °C, the glass sticks on a polished substrate and does not stick on a micro-blasted surface. As the glass/substrate contact is of the same type in both cases and since the metallic surfaces are wetted by the glass, the absence of sticking in the case of micro-blasting can not be of thermodynamic origin. Characterization of the micro-blasted substrate surface showed that a) blasting defects are homogeneously distributed over the surface and that b) their depths are at least two magnitudes higher than those of polishing defects:  $5 \mu\text{m}$  against  $0.05 \mu\text{m}$  and less, respectively. In other words, for the same substrate temperature and same experiment time, the glass has to penetrate a hundred times more to lead to perfect moulding of the substrate surface in the case of micro-blasting. Characterizations of glass and substrate surfaces formerly in contact clearly show that the moulding of micro-blasted defects is only partial. The resulting “composite” interface helps in detaching the article, which is testified by the slight cooling down of the system: about 10 K under  $T_g$ . The absence of sticking is therefore of kinetic origin. The glass does not appear to have the necessary time to penetrate the valleys present in micro-blasted defects (table 2).

For a substrate temperature of 600 °C, the glass sticks on a polished surface and not on a lubricated surface. Lubrication involves covering the polished substrate with a layer of carbon, but this material is not wetted by the glass ( $\theta_f \gg 90^\circ$ ) [10]. When the glass/lubricated substrate contact is established, capillary pressure acts as a barrier to glass penetration into the micro-holes along the interface. These micro-holes look like pores with a depth of about 20 nm and a maximum radius of 10 nm. The order of magnitude of the capillary pressure ( $P_c$ ) applied on the glass at the open surface of these pores can be calculated from  $P_c \approx \frac{2\sigma \cos \theta_f}{r}$ , where  $\sigma$  is the surface tension of the glass ( $\approx$

<sup>1)</sup> Given by the manufacturer for the soda-lime glass considered.

Table 2. The different modes of interface separation found in the present study for three different surface states; the dotted line indicates the path of the glass/substrate separation during cooling

surface state	type of interface	origin of nonsticking		intensity of rippling
pre-oxidized, $\vartheta_0 \approx 600$ °C	“real”	mechanic $\Rightarrow$		strong
micro-blasted, $\vartheta_0 = 600$ °C	“composite”	kinetic $\Rightarrow$		weak
lubricated, $\vartheta_0 = 600$ °C	“composite”	thermodynamic $\Rightarrow$		faint

0.35 J m<sup>-2</sup> [17]),  $\theta_f$  is the final contact angle of the glass/carbon system ( $\approx 135^\circ$  [10]) and  $r$  is the radius of the capillary defect ( $\approx 10$  nm). The calculated  $P_c$ , close to 50 MPa, is much higher than the pressure due to the weight of the glass ( $\approx 250$  Pa) and the pressure linked to the velocity of the gob at impact ( $\approx 30$  kPa). This explains the very limited contact between the glass and the lubricated surface, as shown by the characterizations of surfaces formerly in contact (figures 9a and b). The absence of glass penetration in the substrate micro-defects results in weak adhesion at the interface, which is corroborated by the fact that the article is easily detached at the slight cooling down of about 10 K under  $T_g$ . Clearly the origin of nonsticking in this case is thermodynamic (table 2). It should be noted that, after the experiment, the carbon layer is still present on the free lubricated steel surface, whereas it has disappeared under the area of contact with the article. The reason for this observation is not clear. What is sure is that the disappearance of the carbon layer has to take place after the article has spread and the glass next to the interface has “solidified”, otherwise the glass would penetrate into the metallic surface defects. It may be due to the reaction of carbon with oxygen retained at the “composite” interface, but it may also be linked to the reduction of metal oxides or glass oxides by the carbon. These reactions may occur as long as the temperature at the interface is high (close to 700 °C, table 1), i.e. for several tens of seconds.

For the same substrate temperature of 600 °C, the glass sticks on a polished surface and not on a pre-oxidized surface. In both cases the nature of the contact between the glass and the surfaces is the same, since the substrate surfaces are covered by an oxide layer that is wetted by glass [10]. As the characterizations have shown, the growth of oxides during the pre-oxidation stage is not regular and the surface roughness increases from 0.05  $\mu\text{m}$  (polished surface) to 0.20  $\mu\text{m}$  (pre-oxidized surface). This increase in roughness by a factor 4 does not explain the absence of sticking following the mechanism already described in the case of an initial micro-blasted surface, since after the experiment the glass and substrate roughness values are the same. The main

difference between the polished and pre-oxidized surfaces is therefore the thickness of the oxide layer. In the case of pre-oxidation, the thickness, which is on average close to 1  $\mu\text{m}$ , can reach several tens of  $\mu\text{m}$  locally due to the lack of homogeneity of the oxide layer. As the system cools down, the brittleness of the oxide layer, which in places is several tens of  $\mu\text{m}$  high, results in easy rupture. Parts of the oxide layer then remain stuck on the glass surface. The characterizations of glass and pre-oxidized surfaces formerly in contact clearly showed that this mechanism was sufficiently recurrent to be at the origin of the observed nonsticking, which this time is of mechanical origin (table 2).

## 5. Conclusions

With polished surfaces heated to 600 °C, sticking occurs due to the establishment of a true glass/substrate interface on the atomic scale. At the same temperature, nonsticking was obtained by three different modifications of the initial surface state: a) by greatly increasing the surface roughness, leading to a “composite” interface (partly metal/glass and metal/air) due to kinetic limitations. The same “composite” interface resulting in nonsticking can be obtained with a lower roughness substrate by reducing the temperature, b) by lubricating the surface leading to a “composite” interface because of thermodynamic reasons, i.e. nonwetting, c) by pre-oxidizing the surface, leading to a true interface, but separation occurs this time by a rupture path through the thick brittle oxide layer.

## 6. Appendix

The maximum temperature reached at the interface,  $\vartheta_i$ , is calculated by considering that, in the first moment of contact, the heat flows through the interface between the glass and the substrate, assumed to be semi-infinite bodies with initial temperatures  $T_g$  and  $\vartheta_0$ , respectively, are equal [18]. This adiabatic assumption gives the following expression for the interfacial tem-



perature:  $\vartheta_i = \frac{T_g + A \vartheta_0}{1 + A}$  with  $A = \sqrt{\frac{\rho_s C_s \lambda_s}{\rho_g C_g \lambda_g}}$ , where  $\rho$ ,  $C$ ,  $\lambda$  are respectively the density, the heat capacity and the thermal conductivity of the glass (g) and substrate (s) at their initial temperature, see table 1.

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This research was supported by the French Ministry of Economy, Finances and Industry under the program 004906079. We thank also Drs L. Bedel, L. Federzoni and E. Rigal of CEA Grenoble for helpful discussions.

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Contact:

N. Eustathopoulos  
 Laboratoire de Thermodynamique et de  
 Physico-Chimie Métallurgiques, ENSEEG  
 1130 rue de la Piscine  
 38402 Saint Martin D'Hères  
 France  
 E-mail: nikos@ltpcm.inpg.fr