Wetting and reactions in the lead borosilicate glass–precious metal systems

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Sessile drop experiments of lead borosilicate glass (liquid) on silver, gold and platinum were performed in air, vacuum and helium at 700° C. Wetting occurred in all cases. Strong adherence or bonding with the glass occurred for all three metals in air due to reactions with a thin oxide film present on the metal surfaces, and for silver in vacuum due to a redox reaction. Experiments in helium lead to poor adherence with all three metals.

1. Introduction
Studies of interfaces between glass and metal are important in developing an understanding of composite systems and devices employing both types of materials. Common approaches are the utilization of sessile drop experiments to determine wetting and spreading behaviour of liquid glasses on metals at elevated temperatures in controlled atmospheres. Subsequent cross-sectioning at room temperature and analysis with modern analytical tools for determination of composition changes and composition gradients provides information on reactions that occurred at the interfaces.

Such studies are reported here for lead borosilicate glasses on the precious metals silver, gold and platinum (Ag, Au and Pt). Atmospheres employed were air, vacuum and helium.

2. Experimental details
Contact angle measurements of lead borosilicate (PBS) glass (70 wt % PbO, 10 wt % SiO_2, 20 wt % B_2O_3) on silver, gold and platinum were conducted in several atmospheres. The precious metals used were 99.99% pure and were in the form of 1 cm × 1 cm × 0.025 cm substrates. The glass used was prepared from 99.98% pure oxides and was formed into small beads (approximately 0.5 mm diameter).

For air atmosphere conditions a Hevi duty Lindberg tube furnace, open at both ends was used. The rate of temperature increase was about 50° C min^{-1} and the accuracy of the temperature reading was ±5° C. For vacuum and inert atmosphere conditions, two contact angle furnaces were used. The first furnace (referred to as "graphite furnace") consisted of a graphite tube resistance heating element in a vacuum chamber. Inside this tube was an alumina "dee tube" on which the sample (glass drop on the metal substrate) was placed. The graphite tube was connected to water cooled copper electrodes using graphite holders. The vacuum chamber was connected to an oil diffusion pump (capable of providing about 10^{-5} Pa vacuum) with a liquid nitrogen cold trap and to an inert gas supply. The sessile drops were viewed through the fused silica windows of the vacuum chamber.

The second furnace (referred to as "alumina furnace") consisted of 1 inch diameter, 8 inch long, Kanthal resistant wire wound, high density alumina tube (open at both ends) inside a large vacuum chamber (about 10^{-5} Pa) which was connected to an oil diffusion pump and an inert gas supply. A sheet of tantalum was wound inside the alumina tube to reduce the partial pressure of oxygen. A leak value on the vacuum chamber allowed inert gases to be introduced into the furnace. The pressure in both of the furnaces was measured with a cold cathode ionization gauge. A liquid nitrogen cold trap was used to condense vapours from the diffusion pump. All experiments were carried out at 2.6 × 10^{-4} Pa at the test tem-

TABLE I Sessile drop measurements of lead borosilicate glass on silver, gold and platinum

Metal	Atmosphere	Temperature (°C)	Contact angle (degrees)	Adherence (qualitative)
Ag	Air	600	0	very strong
	Vacuum	700	2–12	good
	He	700	5–48	poor
Au	Air	700	18	strong
	Vacuum	700	7	poor
Pt	Air	700	2–3	strong
	Vacuum (no C)	700	58	poor
	Vacuum (with C)	700	73	poor

Vacuum at 2.6×10^{-4} Pa; helium atmosphere at about 1 atm.

perature. Under these conditions the equilibrium partial pressure of oxygen in the alumina furnace was about 10^{-7} Pa at 700° C and the equilibrium partial pressure of oxygen in the graphite furnace (calculated using the reaction $C + 1/2\,O_2 \rightleftharpoons CO$) was about 10^{-30} Pa. However, due to residual leaks, outgassing of the furnace walls and other non-equilibrium conditions, P_{O_2} was many orders of magnitude higher than these values. The graphite tube furnace was used to intentionally introduce carbon impurities into the system and study the effect of carbon adsorption on the surface energies of the precious metals by measuring the contact angles of glass drops on these metals.

The temperature in both of these furnaces was measured (accuracy $\pm 5°$ C) with two Pt–Pt10Rh thermocouples (after calibration) which were kept close to the sample (< 8 mm above the specimen).

The contact angles were measured using a telegoniometer (Rame-Hart Inc., NJ) which consisted of a Model 102-00-00 telescope with rotatable cross hairs moveable in x, y, z and θ directions, and a circular scale to measure the angles. The accuracy of measuring the angle with this instrument was $\pm 1°$C.

In the actual experimental runs, glass–metal samples were weighed before and after the experiment. Before heating to the test temperature the vacuum chamber was pumped to about 2.6×10^3 Pa (using a mechanical pump) and then pumped to about 1.3×10^{-4} Pa with a cold trapped diffusion pump. The substrate and the drop were heated to the test temperature (about $15°$ C min^{-1} up to 400° C and about $20°$ C min^{-1} after that to the test temperature of 600, 700° C) and held until equilibrium was attained, i.e. no further change in the contact angle for 30 min. The assembly was then furnace cooled.

The surface of the substrates at the edges of the drop were examined using optical microscopy. Some of the specimens were subjected to bending in order to separate the glass from the metal or fracture the glass (depending on the strength of bonding) to obtain qualitative data about glass–metal adherence.

3. Results and discussion
3.1. Lead borosilicate glass and precious metals
The results of the sessile drop experiments using PBS glass on silver, gold and platinum with several ambient atmospheric conditions are tabulated in Table I.

3.1.1. Silver
In an air atmosphere a small glass drop spread into a uniform circle (contact angle = 0°). Spreading started at 500° C and continued rapidly. When the experiment was repeated with a larger amount of glass, the glass spread over the edges to the bottom side of the substrate. In both cases, crystallization was observed at the periphery. The optical micrograph in Fig. 1 shows the top view of the glass–silver transition region which is diffused; careful examination indicates presence of crystals. Fig. 2 shows the crystals at a higher magnification. Spreading of glass occurred along the grain boundaries as well. At the glass–metal interface the grain boundaries of the metal are prominently visible, indicating a stronger attack at the grain boundaries.

A finite contact angle (2 to 12°) was obtained for the glass drop on silver in vacuum in the alumina furnace at 700° C for 0.5 h. The drop attained equilibrium very quickly, e.g. a contact angle quickly decreased to about 2° and then increased to about 5°. The optical micrograph in
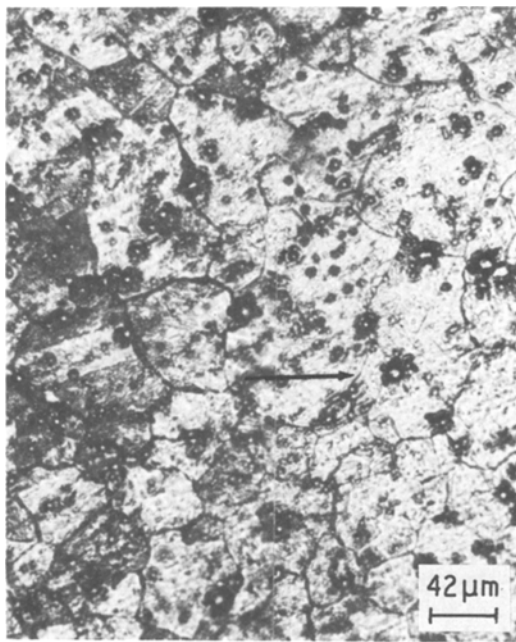
Figure 1 Optical micrograph top view of edge of lead borosilicate glass drop on silver substrate in air at 600° C. Direction of glass spreading shown by arrow.

Fig. 3 shows the edge of the drop on silver as viewed from the top. Movement of the liquid (glass) along the grain boundary is no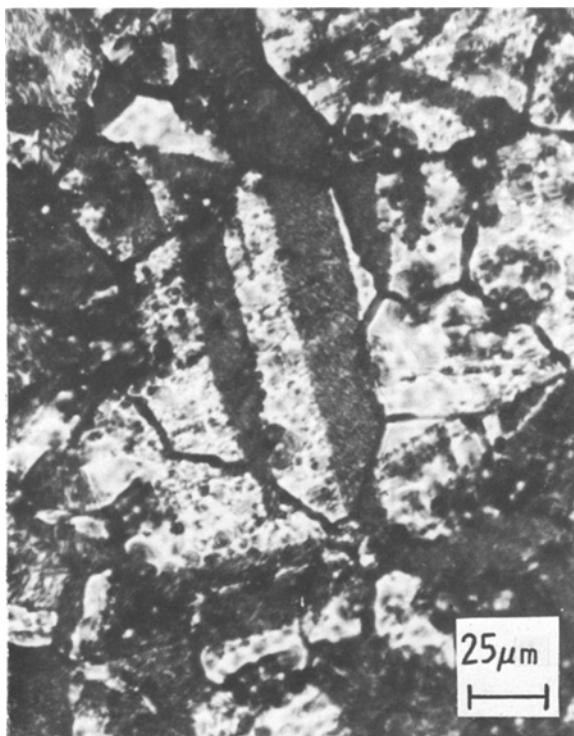ticeable. Grain boundaries below the glass layer are clearly visible. The edge of the glass drop is irregular but there is no indication of crystallization. A redox reaction is indicated by the occurrence of a weight loss of about 8 wt % of the glass.

In the presence of gettered helium the equilibrium contact angle was in the range of that obtained under vacuum conditions (5 to 48°). The edge of the glass drop in these cases has a sharp boundary with no spreading of the glass along grain boundaries. The weight loss was negligible, about 0.1 wt % of the glass.

Very strong adherence of the drop to the substrate was obtained for air atmosphere conditions. In vacuum conditions, the adherence was good. On bending the substrate, the glass was broken into slivers. In gettered helium atmospheres, adherence was poor. The whole drop came off the substrate and the interfaces were clean.

An equilibrium contact angle is obtained when a balance of the horizontal components of surface tensions (or surface energies) is reached as described by Young's equation (Equation 1).

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta. \qquad (1)$$

The sharp edge of the glass drop and its poor adherence to silver in the presence of helium indicates a metastable chemical equilibrium and a lack of reaction between the glass and the silver,
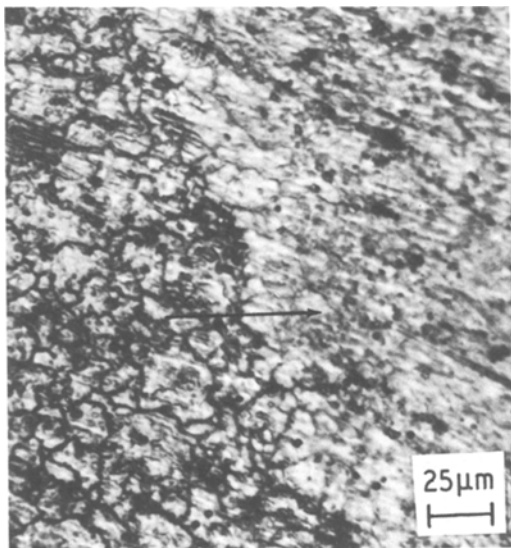

Figure 2 Crystallites formed at the periphery shown in Fig. 1.

Figure 3 Optical micrograph top view of edge of lead borosilicate glass drop on silver substrate in vacuum at 700° C. Direction of glass flow shown by arrow.

resulting in van der Waal's bonding. It is known that the surface tension of silver (γ_{sv}) measured in a pure helium atmosphere is the intrinsic surface tension as helium is insoluble in silver, does not chemisorb and will not be physically adsorbed at high temperatures [1]. A surface energy of about 1160 erg cm^{-2} at 932° C is reported for a helium atmosphere, but deviations can occur because of absorbed and adsorbed impurities. Due to additional complications of the high vapour presence of silver, some erratic values have been reported for vacuum conditions. Surface energy of silver is very sensitive to the presence of oxygen and is about 1000 ergs cm^{-2} * at an oxygen partial pressure of 0.01 Pa and becomes considerably less as the partial pressure of oxygen increases [2].

Silver in air chemisorbs oxygen forming an oxide film which reduces γ_{sv} and hence should increase the contact angle. However, the glass drop spreads in air, with the occurrence of good adherence. This spreading is due to a reaction occurring at the interface involving the substrate as an active participant whose free energy of reaction per unit area and unit time contributes to a reduction of interfacial energy (γ_{sl}) [3]. Increased wetting or a decrease of a contact angle has also been attributed to interfacial reactions by other investigators [4, 5]. The reaction leads to the formation of a compound which was not identifiable by X-

*1 erg = 10^{-7} J.

ray diffraction; the crystallites formed at the periphery of the drop are considered to be a silver silicate from EDAX (energy dispersive X-ray analysis) and electron microprobe studies. This reaction contributes to the driving force for wetting causing it to exceed γ_{lv} and thus results in spreading. Also, saturation of the interfacial zone with silver oxide results in a sharing of the oxygens with a continuity of electronic structure across the interface (chemical bonding) which causes a reduction in the interfacial energy and strong adherence.

Adherence between glass and metal was good in the case of sessile drop measurements conducted at 700° C in a vacuum with a partial pressure of oxygen of about 10^{-7} Pa which is less than the dissociation pressure for silver oxide. Adherence was better at the edges than at the centre. The colour of the glass had slightly changed to milky white, due to a colloidal dispersion, but no crystals were observed as in the case with air firing. These factors indicate the existence of a redox reaction between silver and lead oxide in the glass without a change in the oxygen/silicon ratio. The possible reaction taking place under the conditions of the experiment is

$$2Ag_{(substrate)} + PbO_{(glass)} = Ag_2O_{(interface)} + Pb_{(g)}. \qquad (2)$$
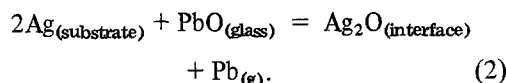
This type of reaction is similar to the ones indicated by Brennan and Pask [6] in studies on sodium disilicate glass-base metal systems. The free energy for the reaction, ΔG is given by

$$\Delta G = \Delta G° + RT \ln \frac{a_{Ag_2O_{(int)}} P_{Pb}}{a_{PbO_{(glass)}}} \qquad (3)$$

$\Delta G°$, the standard free energy for the reaction, is positive since the oxidation potential of the substrate (Ag) is lower than that of lead, which would be the cation to be reduced. (Standard oxidation potentials at 25° C are, Ag → Ag$^+$ − 0.800 V, Pb → Pb^2 + 0.126 V).

The reaction, therefore, will be feasible if the equilibrium constant for the reaction at the interface (Equations 2 and 3) is sufficiently < 1 to result in a negative ΔG. Reaction could be achieved when $a_{(Ag_2O)}$, activity of Ag$_2$O, is low and lead formed as vapour is immediately removed from the reaction site. At 700° C, the $a_{Ag_2O_{(int)}}$ is low because of the low P_{O_2}, and the vapour pressure of
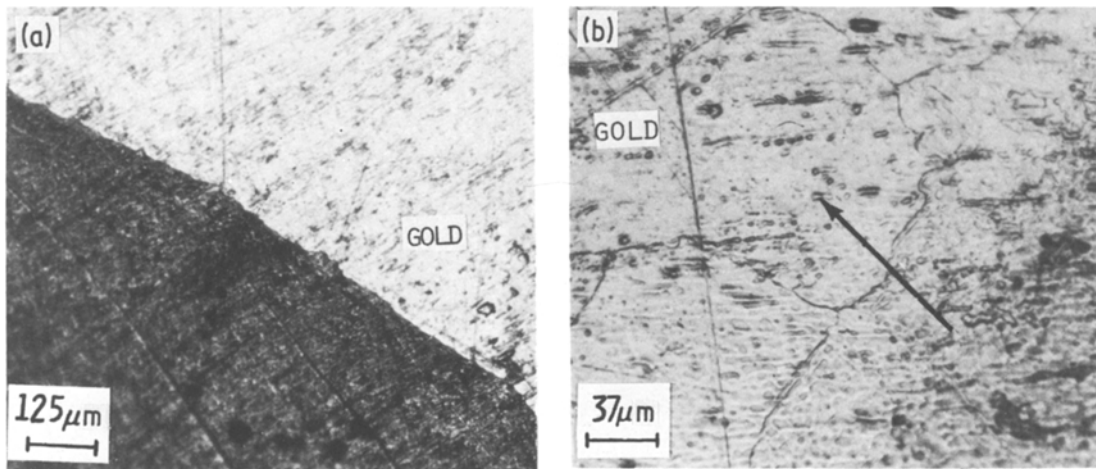
Figure 4 Optical micrograph top view of edge of lead borosilicate glass on gold at 700° C in (a) vacuum and (b) air.

lead is 0.13 Pa which is quite high compared to the total ambient pressure of 2.6×10^{-4} Pa in the furnace. This insures that the lead formed could be easily removed to maintain P_{Pb} at the interface low enough for the redox reaction to continue. Ag_2O resulting from this reaction can be dissolved by the glass and the metal, giving a chemical continuity of silver oxide in the interfacial zone and hence good adherence. It will be easier for Pb(g) formed at the interface to escape from the edges of the drop than from the centre; hence, there is a greater driving force at the edges for the reaction to take place. Further evidence for the occurrence of a reaction at the low ambient pressure was a weight loss of about 8% of the glass and emergence of bubbles from the liquid sessile drop and formation of deposits on the colder parts of the furnace, including the viewing ports. Auger analysis of these deposits on the fused SiO_2 window verified the presence of lead. The irregular edges of the drop seen in Fig. 3 further support the presence of a reaction between the glass and the substrate metal. The grain boundaries appear to be attacked more strongly as would be expected. In this case, the contribution of ΔG/unit area/time of the reaction caused reduction of the contact angle to about 2° but was not sufficient to cause spreading.

In the presence of gettered helium at 1 atm, the adherence was poor; the whole drop could be readily removed from the surface of the metal without leaving any traces. With the high ambient atmosphere pressure the formation of lead as a vapour phase which is necessary for the redox reaction was prevented. This conclusion is supported by a weight loss of only 0.1% of the glass during the experiment. Under these conditions ΔG was positive and hence no redox reaction could take place. This effect was reflected in the absence of adherence due to the absence of Ag_2O at the interface, and the presence of a high contact angle (48°). This contact angle could be used to calculate the driving force for wetting $(\gamma_{sv} - \gamma_{sl})$ which is equivalent to $\gamma_{lv} \cos \theta$. Assuming γ_{lv} for the glass to be 180 ergs cm^{-2} [7], $\gamma_{sv} - \gamma_{sl}$ becomes 120 ergs cm^{-2}. In the absence of a reaction, γ_{sl} in helium becomes 1040 ergs cm^{-2} since γ_{sv} for silver is 1160 ergs cm^{-2} [1]. In vacuum, $(\gamma_{sv} - \gamma_{sl})$ becomes 179 erg cm^{-2} while the redox reaction is in progress. In air, $(\gamma_{sv} - \gamma_{sl})$ exceeds 180 ergs cm^{-2} as indicated by the spreading due to the decrease of γ_{sl} by the free energy of the reaction to form the observed crystals.

3.1.2. Gold

The LBS glass drop on gold has an acute contact angle in both an air atmosphere (18°) and vacuum in the alumina furnace (7°) at 700° C. However, the adherence obtained in vacuum conditions was poor, even though the contact angle was lower than in the air atmosphere. On bending the substrate, the whole drop came off the metal without leaving a trace. In air firing, good adherence was observed. When the substate was bent, the glass drop was broken into slivers still adhering to the substrate. On strong scratching with a sharp instrument, the centre of the drop could be eroded. Adherence was stronger at the edges than the centre.
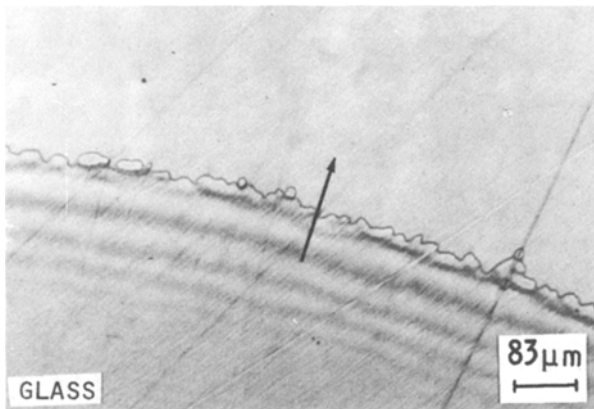
The peripheries of the drops as observed in the optical microscope are shown in Fig. 4. In the presence of oxygen, the edges of the drop are irregular and indicate preferred movement along the grain boundaries. However, in vacuum the edge of the drop is regular and no spreading of the liquid is observed.

The absence of spreading and poor adherence obtained in vacuum conditions indicate the absence of any reaction between the glass and the gold substrate. In the presence of oxygen, better adherence is due to solution of the gold oxide layer on the gold by the glass at the interface producing a gold oxide saturated interfacial zone which results in electronic continuity between the glass and the metal, i.e. chemical bonding. Thus, stronger adherence results. The difference in adherence between the centre and the edges is due (i) to the better access that the interface at the edge has to oxygen and (ii) to the possibility of the edge of the glass dissolving more surface oxide as it moves along the surface toward its equilibrium angle. Since the contact angle then remains constant, the edge of the drop is saturated with gold oxide.

The higher contact angle in air (18°) as compared with the contact angle in vacuum (7°) can be explained on the basis of Young's equation (Equation 1). The γ_{LV} of the glass can be assumed to be constant (about 180 ergs cm^{-2}). A change in the surface energy of gold due to oxygen adsorption has been observed by Udin [1]. In helium, γ_{SV} is about 1370 ± 65 ergs cm^{-2} at 1040° C, and in air it is about 1210 ± 60 ergs cm^{-2}. If we assume the same values at 700° C, the corresponding values of γ_{SL} can then be calculated for air and vacuum conditions. In air γ_{SL} becomes 1039 ergs cm^{-2} and in vacuum, 1191 ergs cm^{-2}. The driving force for

wetting is 171 and 179 ergs cm^{-2}, respectively. The reduction of 152 ergs cm^{-2} in γ_{SL} in air should cause a decrease in the contant angle, but the smaller driving force for wetting was responsible for the larger angle. However, the value of 171 ergs cm^{-2} is the extrinsic driving force; if the intrinsic value for γ_{sv} of 1370 were present, then the intrinsic driving force for wetting would become 331 ergs cm^{-2}.

3.1.3. Platinum

The glass drop on platinum has a contact angle of 2 to 3° and remains clear under air atmospheric conditions at 700° C. On bending the substrate the glass is broken into slivers indicating strong adherence of the glass to the substrate. The periphery of the drop as seen in Fig. 5 is irregular.

The contact angle of the drop at 700° C under vacuum conditions (2.6×10^{-4} Pa) with carbon contamination is 73° and without carbon contamination, 58°. The glass drop attained a dark colour due to the reduction of PbO to metallic lead in the graphite tube furnace which was caused by a sufficient reduction in the partial pressure of oxygen due to reaction of the ambient gas with the graphite tube. The adherence is poor in both cases and the whole drop breaks away from the substrate on bending. The boundary between the edge of the drop and the substrate is regular with no penetration of glass along the grain boundaries.

The low contact angle and strong adherence of glass observed in air are due to the saturation of the interfacial zone by metal oxide. Strong evidence for adsorption of oxygen on platinum surfaces [8, 9] has been reported. Due to the solution of the surface oxide of platinum in glass the inter-

facial energy is greatly reduced resulting in the low contact angle (2 to 3°); with γ_{lv} of 180 ergs cm^{-2} the driving force for wetting is about 179.5 ergs cm^{-2}. However, in vaccum the partial pressure of oxygen is less than 10^{-7} Pa resulting in the high contact angle (58°) of glass on platinum which is caused by a driving force for wetting of about 95 ergs cm^{-2}. Further, the adherence is very poor because of the absence of dissolution of surface oxide or any interfacial redox reaction which would have resulted in a reduction of interfacial energy and a chemically continuous interface.

The glass–Pt γ_{sl} in carbon-free vacuum can be calculated using Young's equation with γ_{SV} of about 2000 ergs cm^{-2}* and γ_{LV} of about 180 ergs cm^{-2} at 700° C. For a contact angle of 58°, γ_{SL} is calculated to be about 1905 ergs cm^{-2}. In the air atmosphere both γ_{SV} and γ_{SL} change. Due to the adsorption of oxygen, γ_{SV} decreases and if this was the only change, it would cause the contact angle θ, to increase. Presence of water vapour in the atmosphere would also have similar effects. However, the additional reduction of the interfacial energy γ_{SL} caused by the solution of metal oxide results in an increase of the driving force for wetting to reduce the contact angle.

In vacuum, in the presence of a graphite tube, carbon impurities are introduced. The contact angle of glass on platinum then is 73° at 700° C. Surface studies have indicated carbon adsorption on a platinum surface [11, 12]. Due to this adsorption the surface energy of platinum (γ_{SV}) is reduced. Also, since the partial pressure of oxygen is very low, no change of the interfacial energy is expected as evidenced by poor adherence and a very regular periphery of the drop. The net effect would hence be a contact angle higher than the angle obtained for vacuum conditions without carbon impurities. A similar increase in contact angle due to carbon adsorption has been observed in the borate glass–platinum system [13]. It is possible to calculate the reduction in γ_{SV} due to adsorption of carbon impurities responsible for the increase of the contact angle from 58 to 73°. Using the values of γ_{SL} = 1905 ergs cm^{-2} obtained from contact angle measurements in vacuum without carbon contamination and an unchanged γ_{LV}, the reduction of γ_{SV} is calculated to be about 43 ergs cm^{-2}. Any reduction in γ_{LV} that may have occurred in the graphite furnace would result in a higher calculated reduction of γ_{SV}. This compares

*Many different values have been reported close to this value [10].

with the value of 50 ergs cm^{-2} obtained by Holmquist and Pask [13] in studying the carbon contamination of borate glass–platinum system.

Using calculations similar to the ones used by Holmquist [14], it is further possible to approximate the amount of carbon responsible for the reduction of γ_{SV}. From the oxidation reaction of carbon, the activity of carbon can be estimated.

$$C_{ads} + 1/2\ O_2(g) \rightleftharpoons CO(g)$$
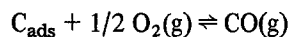
$$K_{eq} = \frac{P_{CO}}{P_{O_2}^{1/2} a_C}$$

where the partial pressure of oxygen and CO have replaced their activities, as at low pressures these gases could be assumed to be ideal gases. Assuming the equilibrium constant for bulk carbon oxidation to CO to be applicable, at 1000 K

$$K_{eq} = 10^{10.459}\ [15]$$

$$P_{O_2} \sim (0.2)(3 \times 10^{-6})\ torr = 1.0 \times 10^{-7}\ Pa$$

$$P_{CO} \sim 2(1.0 \times 10^{-7})\ Pa$$

$$a_C = 10.$$

Now, using the Gibbs adsorption equation [11]

$$d\gamma = \Gamma RT\ d \ln(a_c)$$

where $d\gamma$ is the change in surface energy, Γ is the adsorption density, R is the universal gas constant and T is the absolute temperature (1000 K).

$d\gamma$, calculated from sessile drop measurements, = 43 ergs cm^{-2} and the amount of carbon responsible for this lowering of γ_{SV} (Pt) is calculated to be $\Gamma = 1.016 \times 10^{13}$ atoms cm^{-2}. For comparison, the (1 1 1) surface of platinum has about 1.5×10^{15} atoms cm^{-2}.

To summarize the results on platinum, absence of oxygen led to an increased contact angle caused primarily by an increased γ_{SL} due to the absence of any interfacial reaction. The presence of carbon impurities further increased the contact angle due primarily to the reduction of γ_{SV} of platinum. The effect of carbon impurities and the absence of oxygen can thus be separately understood by these sessile drop measurements conducted in vacuum with and without the presence of carbon impurities. A reduction of about 42 ergs cm^{-2} occurred in the surface energy of platinum due to carbon adsorption.

4. Summary and conclusions
Wetting studies of PBS glass on silver, gold and

platinum were conducted in controlled atmospheres. The glass spread on silver in the presence of oxygen and good adherence developed. The driving force for spreading was provided by the reduction of interfacial energy caused by the reaction between silver oxide formed on the surface and a component in the glass (SiO_2). A low contact angle (2 to 12°) was observed for vacuum conditions. The good adherence obtained in this case was explained on the basis of a redox reaction between PbO in the glass and silver as indicated by a loss of lead from the glass.

With gold, good adherence observed in the presence of oxygen was due to the dissolution of the surface oxide layer in glass at the interface (contact angle 18°). In vacuum conditions the adherence was very poor, even though the contact angle was lower (7°) due to metastable chemical equilibrium as a result of absence of a reaction.

Presence of oxygen contributed to a low contact angle (2 to 3°) and good adherence between platinum and glass. In vacuum conditions carbon adsorption on platinum caused the contact angle to increase from 58 to 73°. The decrease in surface energy (γ_{SV}) of platinum due to carbon adsorption was calculated to be about 43 ergs cm^{-2}. Also, in vacuum adherence was poor and no reaction occurred, as with gold.

In all cases development of adherence was attributed to the saturation of the interfacial zone with the oxide of the substrate metal due to a reaction at the interface, i.e. solution of a surface oxide by the glass (for silver, gold and platinum) or a redox reaction between the metal and an oxide component in the glass (for silver). Although the surface oxide does not grow in thickness, the amount is sufficient to saturate the glass at the interface since the solubility limits of the precious metal oxides in glass are very low; also, interfacial saturation is sufficiently maintained since diffusion gradients are small because of the low oxide concentrations.

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