The Wetting of Platinum and Its Alloys By Glass


Research Laboratories, Johnson Matthey & Co Limited

I—CONTACT ANGLE DETERMINATIONS BETWEEN GLASS AND PURE PLATINUM

Most of those industrial processes involving the bulk handling of molten glass would be facilitated if the platinum surfaces employed were more resistant to wetting. No reliable information on this subject has hitherto been published, and some recent work in the Johnson Matthey Research Laboratories has demonstrated the complexity of the high temperature relationships encountered. The way in which glass reacts with pure platinum is described in the first part of this paper. Subsequent parts will show how the equilibrium contact angle increases gradually with increasing rhodium content and more rapidly with the addition of small quantities of gold. The resistance to wetting of certain of the rhodium-gold-platinum alloys will then be correlated with their microstructure and physical properties.

Previous studies of the way in which molten glass reacts with platinum have in general been carried out within a rather academic context. With one exception (1) none of the investigators found it convenient to make observations on glasses of practical value in the industrially important temperature range, and little attention had been devoted to time-dependent effects such as the rate at which equilibrium contact angles were assumed.

Experimental studies in the Johnson Matthey Research Laboratories have been recently undertaken with the object of providing detailed information on the way in which borosilicate and soda glasses interact with platinum and its alloys at temperatures comparable to those encountered in industry. Accurate contact angle measurements have been made at temperatures up to 1500°C, a summary of the results obtained on pure platinum being described in this report.

The Hot Stage Microscope

The equipment illustrated in Fig. 1 and shown diagrammatically in Fig. 2 was designed so as to permit detailed microscopic examination to be made of the way in which small glass beads melt in contact with flat platinum surfaces. The rhodium-platinum tape heater, which was largely self-supporting, provided a rectangular hot zone 5 cm long, 2.5 cm wide and 1 cm high into which test
 specimens could be rapidly introduced. These test specimens were supported on two thin alumina tubes as shown in the diagram. The thermocouple wire, introduced through these tubular supports, was arranged so that the hot junction came into direct contact with the under surface of the platinum test specimen. The position of this hot junction, in relation to the glass bead, can be seen in Fig. 4.

Power was fed into the heater from a low voltage transformer through water-cooled current leads. Temperature control in the heater was monitored by a thermocouple welded to its midpoint which controlled a small resistance in series with primary circuit of the transformer. The heater was provided with additional support from below by an alumina knife edge, and surrounded by a nest of platinum radiation shields split so as to provide apertures for vertical and horizontal specimen
examination. The whole heater assembly was mounted in a water cooled casing machined from a solid Duralumin block. This casing, provided with quartz viewing ports, had demountable joints sealed by Neoprene "O" rings so that tests could be made in any desired atmosphere or in vacuum.

With a 1\(\frac{1}{4}\)-inch bore oil diffusion pump fitted to the enclosure, operating pressures of \(10^{-5}\) Torr could be maintained with the heater at 1400°C. The volume of the evacuated chamber was approximately two litres, leak rates after prolonged degassing being approximately 10 to 15 microns per hour.

To provide adequate working distance with reasonable magnification the vertical microscope was fitted with a \(\times 15\) reflecting objective. The horizontal microscope fitted with a conventional refracting objective had a total visual magnification of approximately twenty diameters.

The Glasses Studied

A widely used plate glass, and a borosilicate glass typical of the kind employed for glass fibre manufacture, were selected for this investigation. The former was Pilkington Universal Plate Glass, a soda-lime-silica glass, and the latter was a Pilkington "E" glass, a low alkali calcium-alumino-boro-silicate glass.

Contact Angle Determinations

The contact angle referred to in this paper is the angle included between the solid surface and the tangent to the liquid drop at the solid-liquid interface. Complete wetting occurs when the contact angle is zero. No wetting occurs if the contact angle is higher than 90°.

Small clean beads of glass were prepared by melting cracked fragments on a block of hard graphite in air. By melting rapidly and avoiding overheating, contamination was reduced to a minimum. Only those beads between 1 and 1.5 mm in diameter were used for these determinations, as experience had shown that within these limits bead size had little effect upon the measured contact angle.

The platinum test specimens, 1 cm square and approximately 0.5 mm thick, were cut from rolled sheet. The test surfaces were ground and polished by conventional metallographic techniques, the final finish being attained by polishing on a cloth with 1 micron diamond powder. After water washing, degreasing and drying with acetone the specimens were annealed at test temperature immediately prior to placing of the
Fig. 4 Typical "skirt" effect caused by retraction of the glass droplet on the platinum surface at 1400°C (×30)

Subsequent laboratory tests showed that pre-annealing had little effect upon the contact angles observed and one or two of the experimental points obtained with work hardened specimens are shown in Fig. 7.

The metal specimen with its associated glass bead was positioned on the specimen supports of the hot stage microscope and moved into the hot zone of the furnace which was independently controlled at the desired test temperature. The contact angle between the "sessile" glass droplet and its supporting metal surface was measured as soon as possible after the latter had arrived at furnace temperature, and was subsequently monitored at constant temperature until the droplet had assumed stability. Equilibrium in the case of a glass such as the "E" glass was not attained until the specimen had been held at temperature for several hours, and this sluggishness was attributed initially to high viscosity.

Effect of Time

The changes of contact angle that occurred with time when the "E" glass was supported on pure platinum in air at constant temperature are plotted in Fig. 3. At 1030°C the initially high contact angle of 88° decreased rapidly and arrived asymptotically at an equilibrium value of 20° after about thirty minutes. The gradual advance of the glass bead over the platinum surface resulting from this progressive decrease of contact angle with time can readily be appreciated.

At 1400°C, however, the contact angle, initially low, increased rapidly with time and arrived at a peak value after eight minutes. This increase of contact angle involved a corresponding retraction of the glass bead. In its earlier stages this dewetting process usually resulted in the formation of a skirt round the droplet similar to that shown in Fig. 4. Further retraction generally caused the skirt to break away, leaving a ring of "debris" such as that shown in Fig. 5.

These changes in contact angle are not due to changes in temperature, as determinations were only commenced after the specimens had arrived at test temperatures. The relatively slow changes of contact angle with time plotted in Fig. 3 can be interpreted in terms of the equilibrium contact angle curves as discussed in the next section.

The dewetted area left behind after retraction had a higher reflectivity than its surroundings. Fig. 6 shows the characteristic appearance of a dewetted specimen which had been cooled to room temperature before photographing.

Effect of Temperature

Curves showing the effect of temperature on the equilibrium contact angles of the "E" glass and Universal plate glass on pure
platinum surfaces in air are plotted in Fig. 7. Most of the points on the curves represent the mean value of two determinations made on separate beads of glass which were heated rapidly to test temperature and held there until apparently stable conditions had been attained. The shape of these curves explains to some extent why dewetting occurs. If, for example, a specimen of "E" glass is heated rapidly to 1400°C from room temperature it must pass through the temperature region 1000 to 1200°C where the equilibrium contact angle is low and the platinum is readily wetted. The droplet spreads, therefore, and in some way conditions the platinum surface. At 1400°C, however, the contact angle is very much higher and the droplet is forced to retract. The rate of this retraction is limited to some extent by the viscosity of the glass and by its reluctance to abandon a platinum surface with which it has become closely related. This intimate relationship probably explains the skirt formation and its final breakdown.

While dewetting occurs at constant temperature the conditions which make dewetting possible undoubtedly arise during the rapid, transient heating period.

The dotted lines plotted in Fig. 7 represent the only test results we were able to find in the literature which were in any way comparable to our own. Although Cherniak and Naidus (1) studied a borosilicate and soda glass they assumed that their test specimens had assumed stable equilibrium after only thirty minutes at temperature and also used an indirect method of contact angle determination. This probably explains the apparently higher contact angles observed. Their graphs certainly provide no indication of a reversed curvature at higher temperatures.

**Thermal Hysteresis**

The finding that the shiny areas left behind after retraction had properties different from those of the surrounding material suggested that fairly pronounced interaction and bonding occurred between heated platinum and glass and that the equilibrium finally attained reflected to some extent the prior thermal history of the sessile drop. In order to pursue this line of thought, glass beads were heated directly to temperatures
of 1400 to 1500°C and held there until thermal stability had been arrived at. The contact angle was then monitored as the temperature was slowly decreased or maintained constant at an intermediate level.

The results of one such experimental study are plotted in Fig. 8. The glass droplet was allowed to assume equilibrium at 1400°C in the usual way, after which the temperature was lowered by decrements of 50°C, sufficient time being allowed at each temperature level for the glass to assume its new equilibrium contact angle. The new equilibrium curve was almost invariant with temperature, no tendency for the glass droplet to retract being observed even when the temperature was lowered to 980°C.

This behaviour was interpreted as an indication that the first, increasing temperature contact angle curve did not represent conditions of true equilibrium. This conclusion was confirmed when a specimen was heated to 1125°C and held at this temperature for sixteen hours. The contact angle gradually increased with time until, as shown by the dotted line on Fig. 8, a position of higher equilibrium had been arrived at. The changes in contact angle observed when a platinum specimen with a bead of "E" glass was slowly heated from 1000°C to 1500°C are shown in the same diagram. The temperature level was increased by 50°C increments and held constant for three hours at each level to ensure the attainment of stable equilibrium. No significant change in contact angle was observed with increasing temperature, and the curve was almost coincident with that obtained by slow cooling from 1400°C.

As the starting-point of this heating curve already lay near the upper cooling curve the agreement between these two sets of results might, it was felt, have been largely fortuitous. Further test specimens were therefore rapidly heated to 1050 and 1125°C and held at these temperatures until stability had been attained. They were then slowly cooled, as shown. During this slow cooling it was expected that the contact angle would tend to increase in the direction of the upper equilibrium curve.

No such increase was, in fact, observed, and when after several hours at temperature
the glass started to devitrify, the tests were discontinued. The reluctance of the glass to develop an increased contact angle may have been due to its high viscosity or to the tendency to crystallise which is always present below the liquidus at 1160°C (2). As the estimated accuracy of contact angle determination was only ± 2° any slight increases of contact angle that occurred before devitrification might, of course, have been undetected.

Discussion

The interesting wetting behaviour described in the previous section is characterised by its lack of reversibility and the results cannot therefore be interpreted if the conventional view of an equilibrium contact angle is adhered to. Of the upper and lower contact angle curves shown in Fig. 8, for example, which represents the equilibrium condition most accurately?

Irreversibility implies some type of permanent change in either the glass or the platinum. At an early stage in this research platinum contamination of the glasses was suspected and then confirmed by spectrographic examination. The glass was supported on platinum and completely surrounded by a platinum alloy heater. The surface of the molten glass beads could be examined in great detail through the microscopes of the instrument, and at temperatures below 1100°C thin films of what appeared to be metallic crystals were frequently observed. These crystals disappeared at higher temperatures in a way that suggested solution in the glass.

Subsequent work showed, however, that the presence of platinum in the glass had little effect upon the wetting angle attained. Attention was concentrated, therefore, upon the nature of a platinum surface upon which glass has been melted. Fig. 9 illustrates the nature of such a dewetted surface. The grain boundaries have developed as a result of thermal etching, and the line of debris left behind by the retreating glass can be clearly discerned. Although it was natural to suspect that such a surface was in fact still covered with a thin film of glass, no direct evidence for this has yet been detected. The surface of the platinum has, however, been passivated in some way as it strongly resists further thermal etching.

When a fresh glass bead was placed upon a surface similar to that shown in Fig. 9 and melted at 1125°C it immediately assumed an equilibrium wetting angle appropriate to the upper curve in Fig. 8. The simple test demonstrated that the difference between the upper and lower equilibrium curves was simply due to an irreversible change in the platinum surface. It also showed that viscosity effects were not important at 1125°C.

It is possible that when molten glass has been in contact with a platinum surface for some length of time the chemisorbed layer of oxygen originally present at the interface might be displaced. Such a platinum surface would then, according to a hypo-
thesis advanced by Pask (3), react with the silicon atoms in the glass less strongly. The surface energy of the interface would increase and this would reflect itself in an increased contact angle.

Such a hypothesis does not completely explain the low change of contact angle with temperature, nor does it account for the apparently fixed and permanent character of the conditioned platinum surface unless this were protected by an undetectable, impermeable glass layer. The results of some wetting tests now being undertaken at very low partial pressures of oxygen might help to resolve some of these apparent anomalies.

From the viewpoint of the technologist in the glass industry the implications of the present experimental results are perfectly clear. Pure platinum is generally employed as a batch melting crucible. The interior of such a crucible, being constantly in contact with molten glass, should remain passivated. Although the glass will change the equilibrium contact angle would correspond roughly to the upper curves in Fig. 9 and should therefore change little with temperature.

Summary and Conclusions

Contact angle determinations made in air on a specially designed hot stage microscope have demonstrated the complexity of the high temperature relationships between pure platinum and molten glass. The first test results seemed to indicate that the equilibrium contact angle, after decreasing rapidly above 900°C, arrived at a minimum close to 1100°C and then increased with rising temperature. This effect, however, appears to be caused by irreversible changes in the characteristics of the platinum surface. Fresh glass added to platinum that has been previously conditioned in contact with glass at high temperature very rapidly assumes an equilibrium contact angle which is almost invariant with temperature. Glass melted in contact with platinum which has not received this "conditioning" treatment first assumes a lower contact angle and then tends to approach the equilibrium value at a rate which depends on the temperature level. The two types of apparently stable contact angle seem to reflect differences between platinum surfaces with and without adsorbed layers of oxygen and these results suggest profitable lines for further investigation.

Acknowledgments

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References

2 Private communication from Mr R. C. Jewell

Anodic Protection for Sulphuric Acid Tank Car

The technique of anodic protection as a means of preventing corrosion has been described in this journal (Platinum Metals Rev., 1960, 4, 17 and 86; 1963, 7, 94) and a number of successful applications of the method have been reported in the literature. An unusually interesting example of this simple and inexpensive method has now been reported by the Anotrol Division of Continental Oil Co, who have for some time made available suitable equipment for this purpose.

For over a year one of these units has been in operation on a stainless steel tank truck used to transport 93 and 99 per cent sulphuric acid. The equipment includes a potential controller, a reference electrode, and a platinum cathode, current being derived from the normal battery in the truck. The protective film on the stainless steel is maintained by a pulse of 25 to 30 amp for one or two seconds every ten minutes. The installation reduced iron pick-up in the acid carried from around 10 to 15 p.p.m. down to 2.5 p.p.m. for the 99 per cent and 1.6 p.p.m. for the 93 per cent acid.