The Wetting of Platinum by Molten Glass

A REVIEW OF RECENT INVESTIGATIONS

In the handling of molten glass in platinum or platinum alloy vessels, wetting of the metal by the glass is a factor of importance. During the past few years studies have been made in the United States, Germany and Russia on this subject from different points of view, but it is evident that there is a direct relationship between the affinity for oxygen and the wettability of the surface.

Platinum and its alloys are almost the only metals that will withstand long exposure in contact with molten glass without a protective atmosphere or coating. In an increasing range of glass-making and manipulating processes the inadequate physical and mechanical properties of siliceous refactories have encouraged the employment of platinum as a constructional material. In some of these uses wetting of the platinum metal by molten glass is a disadvantage; when optical glass is poured from large crucibles into moulds there may be a substantial gain in yield if the glass can be made to flow completely out of the crucible, while in the manufacture of continuous filament glass fibre wetting of the orifice face of the bushing sometimes interferes with filament formation. Interest has therefore been stimulated in the conditions that govern the interfacial relationship between the platinum metals and molten glass.

Only a limited amount of work has yet been done, and the viewpoint of the investigators has differed considerably, but it is possible to see a common factor in the available information—the significance of the surrounding atmosphere, and particularly the presence of oxygen, in differentiating the surface behaviour of the metals.

In the United States a series of papers has been published describing work carried out in the University of California, under the direction of Dr J. A. Pask (1, 2, 3), in which an experimental exploration of the fundamental mechanism of the interfacial reactions is described. Some of these papers discuss the behaviour of platinum, palladium and gold in contact with molten silicate glass at various temperatures and pressure, and in different atmospheres. The degree of wettability was determined in each case by measuring the contact angle, that is the included angle between the solid surface and a tangent to the liquid drop at the liquid-solid interface. The measurements were all made by viewing the liquid drop through a telescope while it remained in the furnace.

Effects of Atmospheric Conditions

The contact angle of sodium disilicate glass on gold at a temperature of 1000°C was found to be virtually unaffected by atmosphere. In vacuum, or in atmospheres of oxygen, carbon dioxide, water vapour, hydrogen, argon, helium or nitrogen from 10^{-3} mm to 1 mm of mercury, the contact angle remained substantially the same, about 60°. Platinum, however, was found to be very sensitive to the atmospheric conditions; in vacuum at 1000°C the contact angle was 60°, in helium it was also 60°, but in hydrogen it was only 43°, indicating a lesser degree of wetting, while in air or oxygen complete wetting was observed. Palladium, because of its affinity for hydrogen, behaved somewhat differently and was more strongly wetted in hydrogen than was platinum. In atmospheres containing oxygen at very low pressures, the degree of wetting was diminished by increasing the oxygen concentration up to a pressure of 10^{-3} mm of mercury; above this pressure the degree of wetting became continually greater.

The initial decrease is due to the adsorption of oxygen on the platinum surface lowering the surface tension; the increase at higher pressure can be shown to be due to absorption of oxygen into the bulk metal. The absorbed gas migrates to the glass-metal interface and causes the decrease in interfacial energy. The behaviour of platinum in other atmospheres can be explained on an analogous basis.

Electrochemical Properties

The phenomena of wetting have also been studied by Dr Coenen of the Max Planck Institute, Würzburg, and the results of his work were incorporated in a paper given to the German Society of Glass Technology at a meeting in Freudenstadt in May 1958 (4). This author considers that the relationship between the wettability of rhodium-platinum, gold-platinum and beryllium-platinum alloys by molten soda-lime glass is related to the reversibility of the electrochemical properties of these alloys. He considers that the cause of this relationship is the diffusion of oxygen atoms, which are essential links in the glass network and are capable of diffusing in the noble metal alloys.

Glass Fibre Bushings

Two Russian workers, M. G. Cherniak and G. G. Naidus (5) were concerned with the behaviour of the alloys used in bushings for glass fibre manufacture, and they sought to collect quantitative data on the behaviour of different materials in contact with molten glass in order to improve the efficiency of furnaces for fibre manufacture. A suitable material must have adequate mechanical strength at 1180°–1200°C and must resist the action of molten glass. Tests were made on samples of the following metals and refractories:

(1) Unalloyed platinum; (2) 7 per cent rhodium-platinum; (3) 1 per cent chromium-platinum; (4) 25 per cent palladium-platinum; (5) 25 per cent platinum-palladium; (6) 5 per cent nickel-platinum; (7) Unalloyed palladium; (8) Fused silica; (9) Alumina.

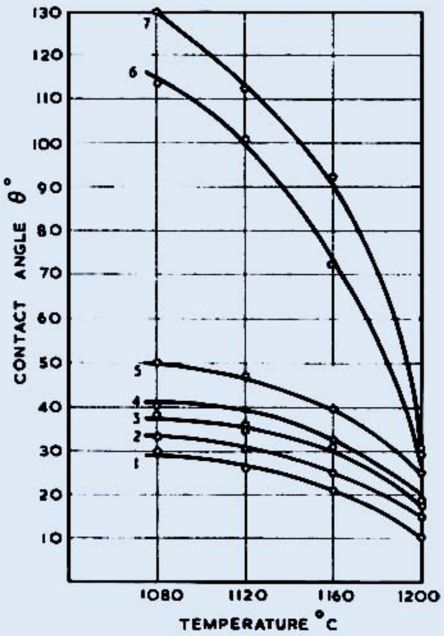

Fig. 1 The wetting of solid surfaces by Glass I (Cherniak and Naidus)

1 *Palladium*
2 *25 per cent Pt-Pd*
3 *25 per cent Pd-Pt*
4 *Platinum*
5 *7 per cent Rh-Pt*
6 *Fused quartz*
7 *Special ceramic*

Two glasses were used, one containing principally 55 per cent SiO_2, 17 per cent CaO, 11 per cent B_2O_3 and 11 per cent Al_2O_3; the other 74 per cent SiO_2, 15 per cent Na_2O and 7 per cent CaO.

The experimental technique differed from that of the American workers, in that the specimens were examined by the "frozen drop" method, as plates on which a 0.1 g glass specimen was mounted. Each sample was

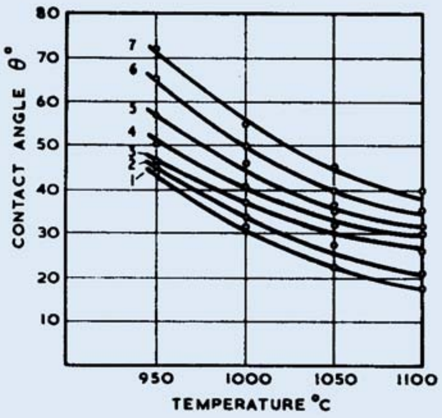

Fig. 2 The wetting of solid surfaces by Glass II (Cherniak and Naidus)

1 *Fused quartz*
2 *Palladium*
3 *25 per cent Pt-Pd*
4 *25 per cent Pd-Pt*
5 *Platinum*
6 *7 per cent Rh-Pt*
7 *Special ceramic*

placed for 30 minutes in an electric furnace at a chosen temperature, in the range 1080 to 1200°C for glass I, and 850 to 1100°C for glass II, then removed and rapidly cooled to fix the shape of the drop. The profile of the fixed drop was optically projected and the contour was traced. Although the profile was not exactly the same as at the temperature of experiment, the variation in contact angle was found to be only 1.5 to 2° of angle.

The results obtained by these investigators are shown in Figs. 1 and 2. No values are shown for 1 per cent chromium-platinum, which had the same wettability as unalloyed platinum, or for 5 per cent nickel-platinum which was easily oxidised at the temperatures of experiment. The resistance to wetting increased in the following order:

(1) Unalloyed palladium
(2) 25 per cent platinum-palladium
(3) 25 per cent palladium-platinum
(4) Unalloyed platinum
(5) 7 per cent rhodium-platinum

Available data on the ease of oxidation of the metals was correlated with the experimental results and a direct correspondence was found between the resistance to wetting and the resistance to oxidation, which was in the same sequential order: more easily oxidised metals or alloys are more easily wetted.

Although the results of these various workers are not directly comparable, they all indicate the great importance of the nature of the atmosphere surrounding the glass metals system, and the probability that the phenomena of wetting are related to the reactivity of the metals and alloys towards the gases in the atmosphere, and that wettability is controlled by changes in the surface energies at the respective interfaces.

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