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Contact angle measurements of E-glass with platinum group metals

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The measurement of the contact angles of E-glass sessile drops has been used to assess the wetting characteristics of platinum, iridium, palladium, rhodium and alloys of these materials. At each temperature studied platinum was wet more than palladium and iridium and markedly more than rhodium. The wetting behaviour has been associated with the stability of the metal oxide and a model has been proposed to explain qualitatively the relative degrees of wetting. The movement of molten glass drops situated at the junction between dissimilar metals is consistent with the proposed model.

1. Introduction

The way in which the platinum group metals are wetted by glass is an important factor in industrial processes, such as the continuous fiberizing of glass through platinum alloy bushings. Studies of wetting can assist in the development of alloys for these processes. To assess the wetting behaviour sessile drop experiments have been used to determine the contact angle between E-glass and certain platinum group metals and their alloys. The movement of glass drops in contact with sharp and graded junctions of dissimilar metals has also been observed.

This investigation, in which the initial glass composition is constant and the metal substrate is systematically varied, forms a part of a study of the glass-metal interface and the results help to establish the role of the metal in glass-metal interactions.

2. Experimental method

The experimental method was essentially that described in previous publications [1, 2] and involved observing and measuring E-glass sessile beads on metal substrates. E-glass is a commercial borosilicate glass, used in the production of continuous glass fibre and its contact behaviour with platinum alloys is, therefore, important in industrial processes.

Glass beads were prepared by spheroidizing chips of E-glass on a graphite block at 1573 K; the beads had a nominal diameter of 2 mm.

Substrates of commercially pure platinum, rhodium, palladium, iridium and their alloys were supplied by Engelhard Industries Limited in the form of 2 cm × 2 cm × 1 mm sheet. Bimetallic substrates were fabricated from 0.5 mm sheet in the following ways:

(a) electron beam welding of pure platinum to pure rhodium;

(b) argon arc welding of pure platinum to platinum–20% rhodium;

(c) argon arc welding of pure platinum to platinum–25% rhodium;

(d) argon arc welding of platinum–20% rhodium to platinum–25% rhodium.

All the substrates were prepared by standard metallographic grinding, polishing and degreasing techniques. Electron probe microanalysis was used to determine the composition profile of the bimetallic samples (Fig. 1).

Sessile drop experiments were performed in air at 1283, 1378, 1418 and 1453 K on the single-metal substrates and on the bimetallic junctions at 1378 K. The procedure involved heating the substrate to temperature and soaking for 15 min before the glass bead was introduced. The beads were then observed and photographed in profile until "equilibrium" conditions were achieved. Contact angles were subsequently determined from the photographs and a typical

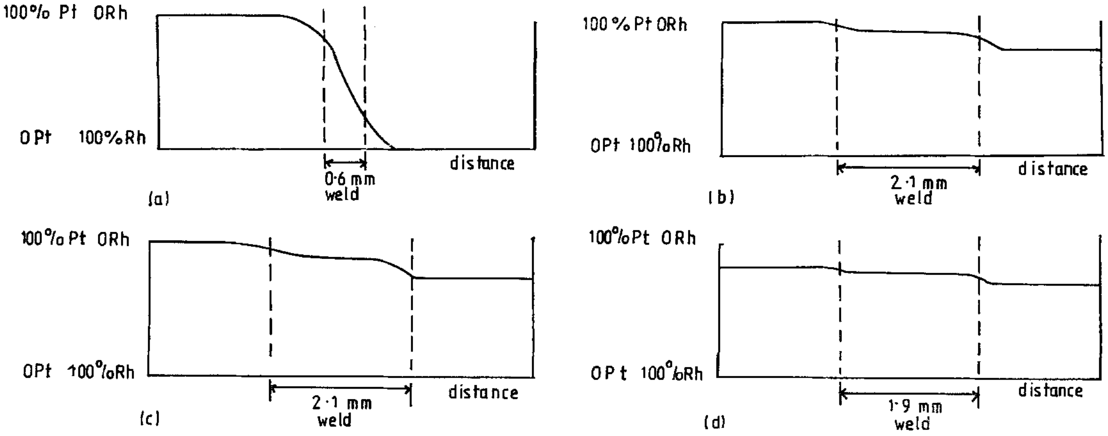

Figure 1 Composition profiles of bimetallic samples. (a) Pure platinum electron beam welded to pure rhodium. (b) Pure platinum argon arc welded to Pt–20% Rh. (c) Pure platinum argon arc welded to Pt–25% Rh. (d) Pt–20% Rh argon arc welded to Pt–25% Rh.

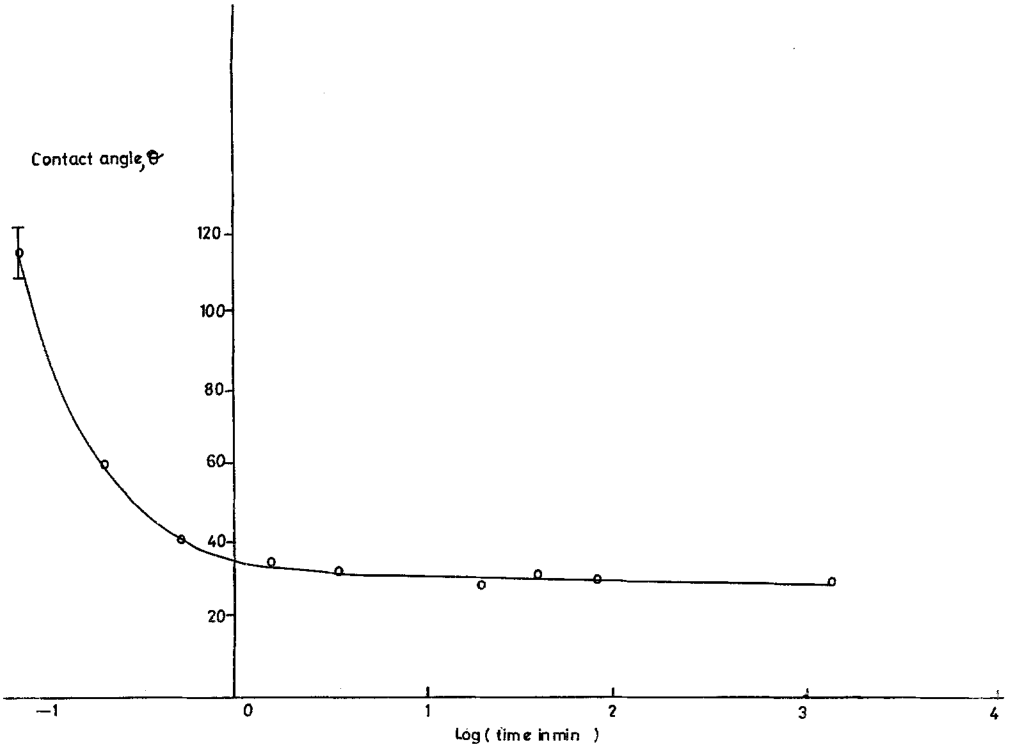

Figure 2 Typical curve showing variation of contact angle with time; E-glass of platinum at 1378 K.

curve showing the variation of contact angle with time is shown in Fig. 2.

The beads were placed on the bimetallic substrates with particular care to straddle the junction or weld zone. These beads were observed and photographed in a direction normal to the substrate with a weld zone visible as a reference line. The sequence of photographs shown in Fig. 3, recording the migration of the glass bead, was taken using an intercepted quench technique. This procedure was adopted to achieve good resolution for these photographs.

The beads and substrates were examined metallographically after cooling to room temperature.

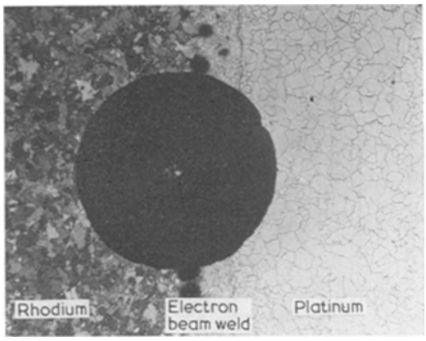

Figure 3 E-glass drop on the welded junction between pure rhodium and pure platinum after 40 sec at 1373 K (× 22).

3. Results

3.1. E-glass on the pure metal substrates

The equilibrium contact angles for E-glass drops on the pure metal substrates at the four test temperatures are listed in Table I.

TABLE I Equilibrium contact angles (in degrees) for E-glass on noble metal substrates at 1283, 1378, 1418 and 1453 K

	Temperature (K)				
	1283	1378	1418	1453	Average angle (degrees)
Platinum	25	18	23	20	22
Palladium	40	31	33	34	35
Iridium	33	34	—	37	35
Rhodium	60	51	50	50	52

At each temperature platinum was wet the most by E-glass, rhodium the least. Palladium and iridium behaved in a similar manner with wetting characteristics between platinum and rhodium. Increasing the temperature had the effect of decreasing the contact angle (increasing the wetting) and of increasing the rate of approach to the equilibrium situation.

The relative degrees of wetting were maintained when the metals were alloyed. Table II shows the equilibrium contact angles, at the same temperatures, for binary and ternary alloys of platinum, palladium and rhodium.

Small additions of rhodium to platinum produced a marked increase in contact angle; additions of palladium to platinum significantly increased the contact angle.

TABLE II Equilibrium contact angles (degrees) for E-glass on alloys of platinum, palladium and rhodium at (a) 1283, (b) 1378, (c) 1418 and (d) 1453 K

Alloy			Contact Angle (degrees)			
Pt	Pd	Rh	(a)	(b)	(c)	(d)
90	—	10	38	34	39	33
80	—	20	45	44	44	41
75	—	25	45	43	45	41
60	—	40	49	48	46	48
80	20	—	35	38	22	37
60	40	—	27	31	—	26
—	80	20	54	52	56	51
80	10	10	44	38	41	36
70	20	10	44	40	42	38
50	30	20	51	40	46	45
50	40	10	48	45	46	48

3.2. E-glass on the junction between dissimilar metals

In these experiments the glass bead was placed on the bimetallic substrate, at 1378 K, so that parts of the bead were in contact with both metals in the cases where the welded junction was very narrow, or on the concentration gradient between the metals where the junction was wide. In each case as wetting proceeded the glass bead migrated to the high platinum side of the junction, leaving the other side of the couple unwetted.

The rate of movement apparently depended upon the difference in platinum concentration on either side of the junction. The rate was greatest on the platinum-rhodium couple when the bead moved about 1.5 mm in 2 h. In each case the shape of the bead changed during the migration process. Initially the bead had a circular outline; within a few minutes it became elliptical with a major axis at 90° to the direction of the weld. Subsequently, the drop spread on the platinum or platinum-rich side of the junction and developed an elliptical shape with the major axis now parallel to the weld and the trailing edge of the bead aligned along the weld line. Eventually the bead resumed a circular outline but now situated on the platinum side of the junction (Figs. 3 to 7). The region near the drop shown in Fig. 7, has a higher reflectivity than the unwetted surface due to the removal by

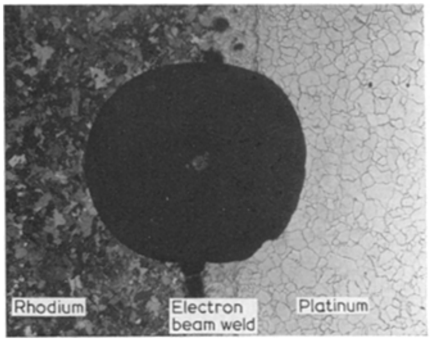

Figure 4 Drop shape and position after 1½ min (× 22).

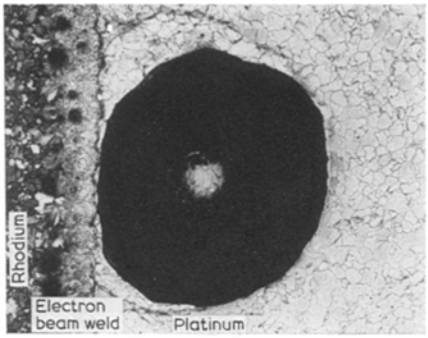

Figure 7 Drop shape and position after 2 h 20 min (× 22).

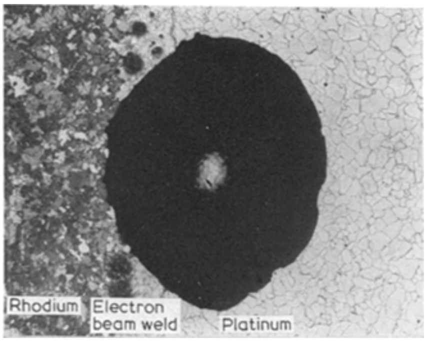

Figure 5 Drop shape and position after 13½ min (× 22).

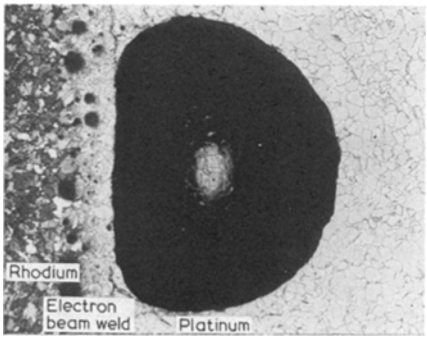

Figure 6 Drop shape and position after 34 min (× 22).

the drop of the glassy droplets formed on the platinum during wetting [2].

4. Discussion

The degree of wetting of E-glass on platinum, palladium, iridium, rhodium and their alloys appears to be related to the stability of the oxides of the pure metals. Platinum oxide decomposes at normal pressure at a temperature less than 773 K; palladium oxide at about 1173 K while rhodium oxide is stable up to 1673 K. Thus at the temperatures used in these experiments there will be no bulk oxide on the platinum surface but there will be oxide on the rhodium surface [3]. Palladium and iridium will occupy an intermediate position, the oxide probably just being unstable. The presence of glass may increase the temperature at which a bulk oxide can exist beneath the glass drop by changing the surface energy and increasing the pressure at the glass-metal interface.

The wetting behaviour may be related to the demand for oxygen by the metal surface. The force which causes the glass to spread is regarded as originating in the requirement for the metal atoms in the substrate surface to form bonds with oxygen. In the case of platinum this demand cannot be met by atmospheric oxygen since the bulk oxide is unstable. The platinum atoms can, however, partly satisfy their requirements by sharing the non-bridging oxygen ions in the molten glass. The degree of wetting will then be governed by the competition between the substrate metal ions and the cations present in the glass for non-bridging oxygen ions (Fig. 8). (This view will be expanded with further experimental evidence in a subsequent paper [7].)

In summary, two mechanisms will primarily control the degree of wetting. Firstly, the demand by the substrate metal to bond with non-bridging oxygen ions in the glass and secondly the demand from cations in the glass for non-bridging oxygen ions. If the former is greater then the total energy of the system will be

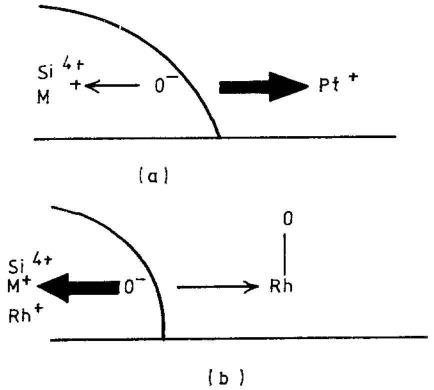

Figure 8 Schematic representation of the competition for non-bridging oxygen ions from cations in the glass and at the metal surface. (a) E-glass–platinum; (b) E-glass–rhodium.

lowered if the bead spreads. If the latter is the greater, spreading will be restricted.

According to this model the degree of wetting of E-glass on rhodium is small (high contact angle) because there is little demand from the substrate rhodium ions for non-bridging oxygen ions, since their bonding needs already are satisfied by a stable bulk oxide. Also, some rhodium oxide will be taken into solution in the glass and the rhodium ions thus dissolved will add their charge to the cations already in the glass, in competing for non-bridging oxygen ions; there will thus be less charge available from the less polarizable non-bridging oxygen ions for bonding with or screening rhodium atoms in the substrate.

In the case of platinum the bulk oxide is unstable and metal ions will compete strongly for the non-bridging oxygen ions in the glass and their bonding needs will be satisfied as the drop spreads. Further, because there is no bulk oxide, the tendency for platinum to dissolve in the glass will be low (compared with rhodium) and there will be less competition for non-bridging oxygens from the cations in the glass (again compared with rhodium). Both mechanisms contribute to a low contact angle. The two cases are summarized diagrammatically in Fig. 8.

The difference in the strength of interaction between the glass and platinum and glass and rhodium is reflected in the behaviour of the glass bead at the junction between the two metals. The strength of the interaction on the platinum side is sufficient to overcome the viscous and surface tension forces to attenuate the drop and eventually move it to the platinum side of the substrate.

The addition of small amounts of rhodium to platinum markedly reduce the contact angle of E-glass, probably reflecting a decrease in the requirement for oxygen bonding due to the presence of rhodium and rhodium oxide. The rate of movement of the glass bead is slower at a platinum/platinum–rhodium junction.

The observations described in these studies are consistent with those of Katzschmann [4] and Pask *et al.* [5] the latter workers associated the high contact angle of glass on rhodium with the formation of van der Waal's bonds between glass unsaturated with rhodium oxide and rhodium metal. The good wetting of platinum was interpreted by the same workers in terms of a chemisorbed oxygen or oxide layer, tightly bound to the platinum, which interpenetrates the glass lattice and helps to screen the cations at the glass surface.

If the propensity to wet is associated with chemical interaction in the formation of Pt–O^-–Si or Rh–O^-–Si bonds then according to Adamson and Ling [6] there can be no general thermodynamic relationship between the contact angle and the surface free energies (or between the interfacial surface tensions and the work of adhesion). The interpretation used in the present paper does, however, allow the prediction of a relationship between contact angle and the difference in bond strength between platinum and oxygen and between the cations in the glass and oxygen. This relationship describes the present results in a qualitative way and further work has allowed the relationship to be expanded in a more quantitative way [7].

5. Conclusions

(1) The degree of wetting of E-glass on certain platinum group metals has been associated with the stability of the bulk metal oxide at temperature; thus platinum is wet more than palladium and iridium and markedly more than rhodium.

(2) Alloying the metals changes their wetting characteristics between those of the components; thus the addition of rhodium or palladium or iridium to platinum reduces the degree of wetting by E-glass.

(3) The propensity to wet has been regarded as originating in the demand by the substrate metal atoms to form bonds with the non-bridging oxygen ions in the molten glass; the degree of wetting has been related qualitatively to the

competition for non-bridging oxygen ions between the substrate metal and the cations in the glass.

(4) The migration of glass drops at the junction between dissimilar metals is always in the direction of the most-wet metal or alloy and is consistent with the proposed model.

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