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Observation of contact phenomena in glass/metal systems

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Microscopic observation of the wetting of glass sessile drops on platinum has revealed the presence of glassy droplets in the vicinity of the wetting edge. A study of the droplets has clarified the deposition process and the influence of the platinum grain structure on their nucleation and growth, and has allowed comment to be made on the mode of grain-boundary movement during grain growth.

1. Introduction

During the microscopic observation of alkali-silicate glass sessile drops on platinum substrates at high temperature, the formation of glassy droplets was noted, on the metal substrate, ahead of the advancing edge of the glass bead [1]. It was suggested that the formation of these droplets was by way of a vapour transport mechanism and that this played a part in the wetting process.

The present investigation was undertaken to establish the mode of droplet formation and its relationship to the structure of the platinum substrate, by microscopic monitoring of the phenomenon. It was hoped that this would contribute to a better understanding of the glass/metal wetting process at a microscopic level.

2. Experimental method

Glass beads of nominal composition 70 mol% SiO_2, 30 mol% Na_2O were prepared by spheroidizing chips of the glass on graphite at 1200°C; the beads had a nominal diameter of 2 mm. The beads were placed on platinum at 1100°C, the platinum having previously been prepared by standard metallographic grinding, polishing and degreasing techniques. Glass-on-platinum samples were removed periodically from the furnace, rapidly air quenched and metallographically examined to monitor the formation of the small glassy droplets which in earlier experiments had been observed to form on the substrate outside the periphery of the glass bead (Fig. 1).

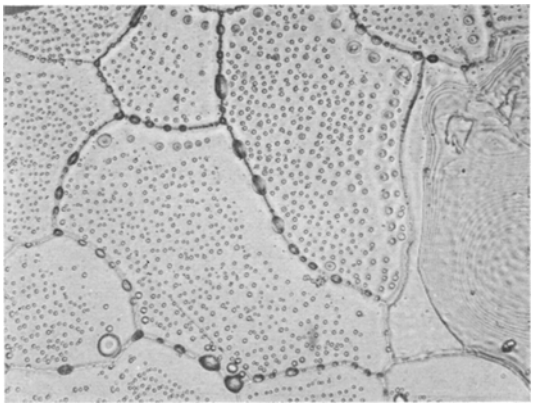

Figure 1 Droplet array outside the periphery of the glass bead after 21 h at 1120°C. × 550

Further specimens were observed continuously in a "Vacutherm"* hot-stage attachment to a metallurgical microscope during the wetting and droplet formation processes. The experiments were performed in nitrogen and also under nitrogen at reduced pressure with a small, continuous flow of nitrogen over the surface of the specimen.

3. Results and discussion

It was established that the droplet array formed in a very short time. Samples withdrawn from the furnace, within 1 min of the glass bead reaching the test temperature, showed arrays of droplets with diameters between 0.5 and 2.5 μm, over the whole substrate surface area (nominally 1 cm^2).

*Trade name of Reichert Co Ltd.

The rapidity of the droplet formation process strongly suggested that movement of the glass constituents took place by a vapour-transport mechanism.

At the test temperature the platinum grain boundaries became clearly visible after about 5 min due to thermal etching. The droplets showed a marked preference to deposit at grain boundaries and at residual scratches on the substrate.

Continuous microscopic observation of the droplet arrays at temperature showed that following the rapid deposition of droplets, further formation virtually ceased; further droplets being created only rarely. Evaporation of small droplets and the growth of larger droplets was observed to proceed at a slow rate. However, rapid droplet formation occurred whenever a platinum grain boundary moved to a new site, droplets being deposited almost immediately along the new grain boundary while the droplets at the location of the old grain boundary evaporated slowly over long periods of time. Thus, during an experimental run the platinum grain boundaries could be seen to change their position, the old and new sites being recorded by the lines of glassy droplets (Fig. 2).

The behaviour of the droplets suggested that the grain-boundary migration occurred in a series of discrete jumps [2]; a grain boundary disappearing and almost simultaneously reappearing at a new site between 5 and 50 μm away (Fig. 2). A new grain boundary was a favourable site for nucleation of droplets and its position was indicated by the immediate deposition of droplets before thermal etching of the boundary occurred.

The droplets situated along the old position of the grain boundary remained for a long time suggesting that evaporation took place only slowly from the region of the thermally etched "ghost" boundary; no new droplets were, however, observed to nucleate at these sites. Any misorientation across the old grain boundary which resulted in a residual sub-boundary dislocation array, would presumably present a more favourable site for droplets than the etched "ghost" grooves where perfect matching had occurred, but less favourable than a new grain boundary. Variations in the stability of residual droplets on "ghost" boundaries were observed.

Clearly the droplets in the grain-boundary grooves would present a smaller surface area to the atmosphere, for a given volume of glass, than those on a flat surface; they would thus evaporate at a slower rate.

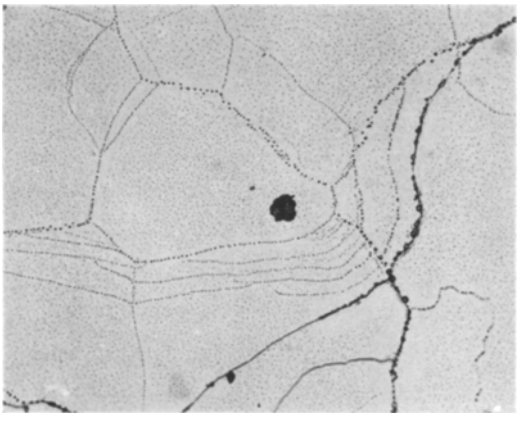

Figure 2 Droplet array after 22 h at 1100°C showing a relatively stable grain-boundary configuration and successive sites of the platinum grain boundaries. × 200.

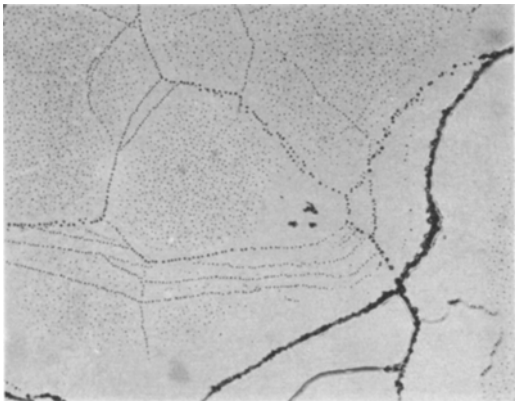

Figure 3 Same field as Fig. 2 after 87 h at 1100°C showing the aggregation of droplets at deeply etched grain boundaries and denuded zones near the grain boundaries. × 200.

The migration of the grain boundaries had no apparent effect on the position of the existing droplets; in no case did we observe any tendency for the droplets to be dragged along by the movement of the boundary. This behaviour is not consistent with the observations of Ashby and Centamore [3] on the dragging of small (0.4 μm), included oxide particles by internal grain boundaries, but it is not possible to directly compare surface and internal behaviour. Clearly factors such as the forces experienced by surface and internal particles, the diffusion paths

available and the influence of the free surface are quite different in the two cases.

After a considerable length of time, relatively steady state conditions were realized and there was little further grain-boundary movement (Fig. 2). On holding the specimen at temperature for considerably longer times, deep thermal etching of the final grain-boundary configuration occurred and the droplets in these grooves joined together often producing almost continuous lines of glass. The droplets on either side of the grain boundary apparently acted as sources of glass for those in the grain boundary with the creation of zones denuded of droplets along the sides of the grain boundaries. This denudation occurred, but to a lesser extent near the "ghost" thermal grooves. This is shown in Fig. 3.

Observation of the main bead, at temperature, in the "Vacutherm" unit showed that the glass/metal/atmosphere triple junction was in a state of flux; rapid wetting and de-wetting of grains being evident even as "steady-state" conditions were being approached. The experimental conditions did not however allow any correlation of the observations of overall wetting and de-wetting and droplet formation and evaporation.

Under conditions of reduced pressure and with a stream of nitrogen directed on to the specimen surface, droplets that were initially present evaporated and eventually disappeared, the vapour of the glass constituents being extracted with the carrier gas. Subsequent examination of these specimens revealed no droplets. This again is strong evidence that droplet formation is due to vapour-phase transport.

4. Conclusions

1. The formation of glassy droplets on the metal substrate during sessile drop wetting experiments occurs by vapour transport of the glass constituents.
2. Grain boundaries, surface scratches and possibly other crystal defects act as favourable nucleation and growth sites for the glass droplets.
3. Nucleation occurs rapidly once the test temperature is attained but then becomes a rare occurrence until new nucleation sites are created by, for example, grain growth in the substrate. Old grain boundary sites remain as "ghost" thermal grooves and retain their glassy droplets, while new grain boundaries are rapidly decorated with droplets.
4. Droplets sited at a grain boundary were not dragged to the new position when the boundary moved.
5. Droplet formation presents a convenient method of decorating and studying surface grain structure. Thus examination of the droplets identifies the changes which take place in the surface grain-boundary configuration. These observations suggest that the platinum surface grain boundaries move in discrete jumps of 5 to 50 μm during grain growth at 1100°C.

References

1. G. J. COPLEY, A. D. RIVERS, and R. SMITH, *Glass Technol.* **13** (1972) 50.
2. J. NUTTING and S. R. ROUZE, Fifth International Congress for Electron Microscopy (Academic Press, London, 1962).
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