Interfacial Effects Between Molten Aluminium and Sapphire

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The sessile-drop technique has been used to examine the interfacial effects that occur between molten aluminium and single-crystal α-Al_2O_3 when heated *in vacuo*. In the region of 1300°C the growth of crystallites, probably of α-Al_2O_3, at the liquid-solid and liquid-vapour interfaces has been observed, together with the formation of etch pits on the sapphire plaque as the result of vapour attack. These effects are described and discussed.

1. Introduction

Brennan and Pask [1] have reported work on the wetting of sapphire (single crystal α-Al_2O_3) by molten aluminium under vacuum. Using the sessile-drop technique they have found evidence for the formation of complex surfaces on the sapphire at temperatures above about 900 to 1000° C.

In a previous paper [2] we noted a rapid increase with temperature in the contact area of a sessile drop on sapphire at about 950° C. Reference to fig. 1 of this earlier paper also shows a change in slope at about 950 to 1000° C for the variation of contact angle with temperature. These results thus lend support to the views of Brennan and Pask. Differences in points of detail between the two sets of results may well be due to the differences in cleaning procedures.

Brennan and Pask reported the formation of small angular needle-like crystals at the aluminium-sapphire interface in some of their experiments, but did not comment on their form or on the fact that the crystals appear to be aligned in their published photomicrograph. We have also observed crystallisation at the aluminium-sapphire interface but in more than one form and, in addition, at the aluminium-vapour interface.

2. Crystal Growth at Interfaces

Our experiments were carried out as described previously [2]. Crystal growth was observed to occur at the aluminium-sapphire interface only with specimens that had been heated to temper-

atures above about 1270° C. Examples of the various forms of crystallisation are shown in fig. 1.

The fine network structure shown in fig. 1a persists as a background to the larger crystallites shown in figs. 1b and c, although it is not so readily discernible in the photomicrographs. There is also a suggestion of a similar sort of fine structure in fig. 6 of Brennan and Pask [1]. The identity of the network has not been established but it may be Al_2O_3, possibly formed during the cooling down of the specimen when an oxide species previously dissolved in the aluminium is precipitated.

The acicular crystals shown in fig. 1b appear somewhat similar to those of Brennan and Pask. They appear to be aligned and to have nucleated near their mid-points, each crystal growing out in two branches at a small angle to one another; one branch is approximately parallel to the trace of an *a*-direction and the other to the trace of the *c*-direction. The two branches are rather similar to the well-known A- and C-type forms of sapphire whiskers [3]. (The slight departure from parallelism between the crystallites is reminiscent of a somewhat similar phenomenon which can occur with the epitaxial deposition of a thin film of material by evaporation on to a crystalline substrate [4].) Some of the crystals extend beyond the final boundary of the aluminium, which has been reduced due to evaporation.

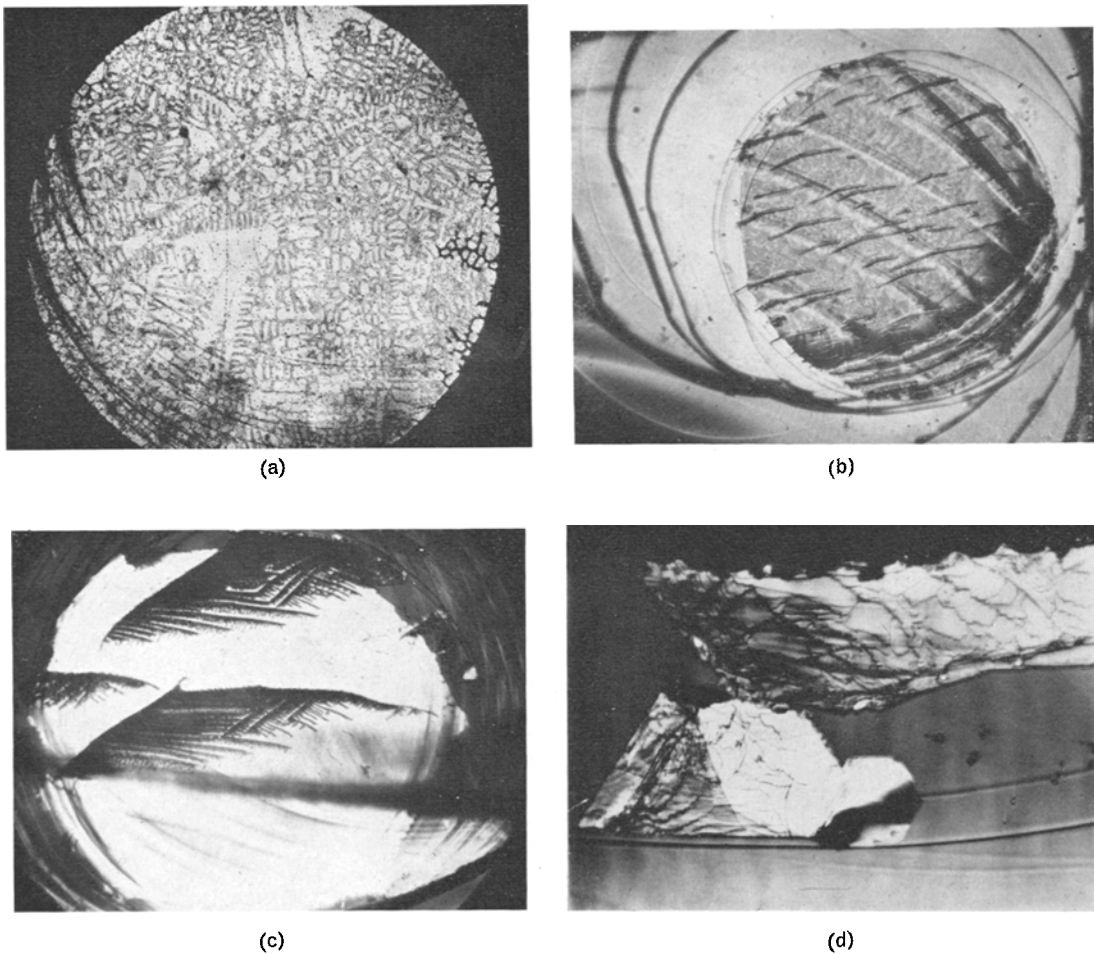Fig. 1c shows the further development in a

(a)

(b)

(c)

(d)

Figure 1 The interface between aluminium drops and sapphire plaques after heating to various temperatures. (a) After heating to 1300° C for 10 min, viewed through the plaque from the underside (specimen 30) ($\times$ 17). (b) After heating to 1350° C for 90 min viewed through the plaque from the underside (specimen 55: orientation of plaque near to $\{10\bar{1}0\}$; reverse view of specimen shown in fig. 2 of [2] where the reaction rings, seen prominently here, are discussed) ($\times$36). (c) After heating to about 1400° C for 10 min, viewed through the plaque from the underside (specimen 8) ($\times$ 19). (d) Part of specimen 8 (fig. 1c) viewed from the upper surface ($\times$ 146).

dendritic form. Part of the growth which extends beyond the outline of the solidified drop is shown viewed from the other (upper) side in fig. 1d. This photograph suggests that the growth has a layered-terrace structure, and this was more evident on examination of the same area in the scanning electron microscope. In other specimens, various degrees of crystal growth were seen, intermediate between those shown in figs. 1b and c.

Fig. 2a shows an example of the crystallites which grew at the aluminium-vapour interface. Some of the crystals appeared yellowish in colour when viewed optically, probably due to the presence of some impurity such as Mg. The

original Al contained 30 ppm of Mg [2] and this could become much more concentrated as the drop was reduced in volume by evaporation. The coloration would imply that growth occurred from the liquid rather than the vapour-phase.

Fig. 2b shows the regular hexagonal form of two crystallites which grew on the top surface of the aluminium drop in one particular instance.

The larger crystals, such as those shown in figs. 1b, c and d, and 2a and b, are almost certainly α-Al_2O_3, since their morphologies are very similar to corundum crystals (sapphire and ruby) grown by other techniques [5]. Additionally, all the crystallites examined in the scanning electron microscope appeared brighter than the
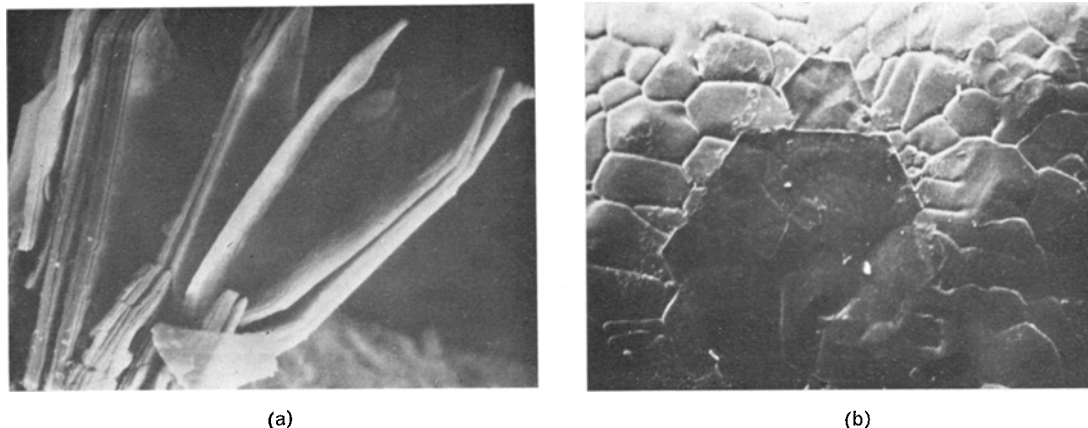
(a)   (b)

Figure 2 Scanning electron micrographs showing crystallites that had grown at the aluminium-vapour interface. (a) At the lower part of an aluminium drop (on sapphire) after heating to 1400° C for 1 min (specimen 152) (× 364). (b) On the top of an aluminium drop (on sapphire) after heating to 1400° C for 15 min (specimen 147) (× 40).

aluminium due to their higher emissivity: bulk alumina has a higher secondary emission coefficient than aluminium. It may also be noted that Yanagida and Kröger [6] have shown that Al and Al_2O_3 are the only solid phases that are stable in the Al–O system at normal temperatures and pressures.

It seems very unlikely that these larger crystals, especially those at the aluminium-vapour interface, would have grown in the very short cooling down period. More probably they grew at the working temperature when a much longer time was available and when the drop was being reduced in volume by evaporation. It is suggested that crystals may grow as a result of the Al_2O which is formed at the aluminium-sapphire interface [2, 7] combining with oxygen from the residual gas atmosphere at the appropriate interface.

Data for the diffusion coefficient of oxygen in aluminium do not appear to be available, but those which are available for other species in aluminium suggest that oxygen would diffuse through a thickness of aluminium corresponding to the size of the molten drop, in a matter of minutes at 1350° C. At temperatures below about 1270° C, where no crystal growth was observed, the diffusion process is possibly too slow to supply the oxygen; alternatively the reduced rate of reaction at these lower temperatures would result in insufficient Al_2O being available.

Fig. 3 shows an example of the cellular detail observed on the inner rings formed as a result of the reaction between aluminium and corundum [2]. The detail is reminiscent of the cellular inter-
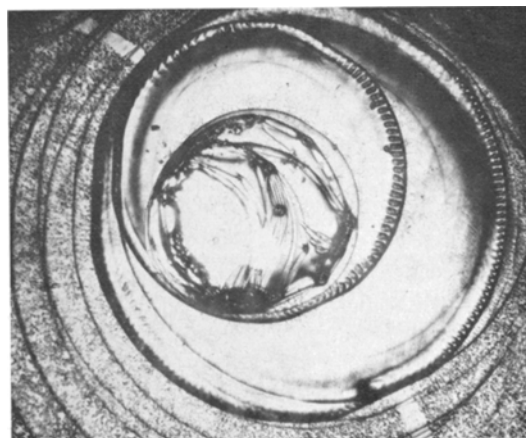

Figure 3 Top surface of sapphire plaque, basal plan orientation, after reaction with aluminium at 1350° C for 90 min (specimen 69) (× 16).

face that frequently occurs in growth from a melt containing some impurity [8] and may indicate some regrowth of α-Al_2O_3 under conditions of constitutional supercooling [9] with the rejection of the impurity at the cell boundaries. This detail was observed with corundum plaques in which the impurities (chiefly Cr and Pb) may vary between very wide limits (typical analyses given in [2]), so that the impurity rejected is more likely to have come from the aluminium. The highest metallic impurity in the Al is Mg at 30 ppm and it is just conceivable that this could be responsible, as concentration could occur as the drop evaporates. On the other hand the impurity could be Al_2O which would be virtually impossible to detect. Microprobe analysis of a plaque

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over the cellular region detected no impurity at the 0.1 % level.

3. Etching of Sapphire

In addition to the above crystallisation effects the etching of sapphire by Al vapour previously reported by Carnahan, Johnson and Li [7] has been further investigated. Many of the ruby and sapphire plaques used in experiments above 1200° C showed a mass of etch pits on their upper surface (see fig. 3). The intensity of the etching was much greater outside the region covered by the reaction rings, and often brought into prominence (at higher magnification) numerous polishing scratches. The area that had at one time been covered by molten aluminium had a more chemically polished appearance and far fewer etch pits. Outside the reaction rings the etching became less intense with distance from the aluminium and no attack was detected on the underside of the plaques. From examination of numerous sessile-drop specimens, and from subsidiary experiments designed specifically to test the hypothesis [10], it has been established that the attack is more severe on those plaques oriented with the c-axis at 90° to the surface than those oriented at 0°. On occasion plaques with the former orientation showed well-defined hexagonal etch pits. The above observations are in general accord with previous results on the action of other chemical polishes and etchants on corundum [11].

4. Summary

In summary it appears that a rather complex situation exists in the Al–Al$_2$O$_3$ system represented by a sessile drop resting on a plaque in a vacuum. Both attack of the Al$_2$O$_3$ by Al, in either the liquid or the vapour state, and regrowth of α–Al$_2$O$_3$ at the aluminium-sapphire and aluminium-vapour interfaces are possible, depending on time and temperature.

Acknowledgement

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Letters

Influence of Structure on the Conductivity of Thin Films of Bismuth

The conductivity of thermally grown films of bismuth show very erratic behaviour with thickness [1, 2] below 3 µm. Explanations of this effect have involved the orientation of the crystallites [3], scattering at grain boundaries [1] and a size effect [4] due to the long mean free path of electrons in bismuth. Neuman [1] tried to relate this unusual behaviour to the structure of the films, using electron microscopy; however, two-dimensional pictures do not reveal the peculiar growth of the films reported here.

We prepared several thin films of bismuth by thermal evaporation in a vacuum of 10^{-5} torr on glass substrates at 20° C and have varied the evaporation rates. The films were studied using scanning electron microscopy. Figs. 1 and 2 clearly show the unusual growth pattern of the