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Wetting of Aluminium Oxide by Molten Aluminium and Other Metals

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The sessile drop technique has been used to measure the contact angle of molten aluminium, aluminium-nickel and aluminium-copper alloys, copper and gold, with sapphire, ruby and recrystallised alumina. Measurements were made *in vacuo,* and as a function of time and temperature over the range 800 to 1500° C. Cinematography and time-lapse photography were used. At temperatures below 950° C, sessile drops of aluminium reached equilibrium only after a period of time which increased with decrease in temperature and could be in excess of one hour. A rapid increase in contact area occurred around 900° C. Above 1150° C drops of aluminium and of the aluminium alloys were observed to spread and contract repeatedly. Contractions were observed with both polycrystalline and single-crystal alumina, although they were much more pronounced with the latter, and were associated with the formation of a series of reaction rings on the plaque. Ruby and sapphire behaved similarly. The shape of the rings depended on the crystallographic orientation of the plaque: the reaction profile tended to terminate in certain low index directions. Neither contractions nor reaction was observed with copper or gold. The observations are discussed in terms of the combined effects of evaporation, chemical reactivity and interfacial tensions in the system.

1. Introduction

The factors that affect the wetting of solids by liquid metals are of interest from the point of view of preparing metal/ceramic fibre and metal/ceramic powder composite materials. This is particularly so if the composites are prepared by liquid infiltration. The same factors are also important in the production of vacuum-tight joints between metal and ceramic components. An established method for studying these factors is to investigate the behaviour of a sessile drop of molten metal on a substrate of the relevant metal oxide under different physical conditions.

The behaviour of molten aluminium on aluminium oxide has been studied by several previous authors [1-3]. Livey and Murray [1], while studying a variety of oxides and carbides, found that molten aluminium did wet polycrystalline alumina at a temperature of 1255° C. Carnahan, Johnson and Li [2] studied the wetting of single-crystal and polycrystalline alumina by molten aluminium at temperatures near 1200° C. They found a significant difference in spreading behaviour on the two substrates: in the case of aluminium on recrystallised Al_2O_3, the contact angle attained a steady value, whereas on sapphire the drop was observed to spread and contract repeatedly. Wolf, Levitt and Brown [3] studied the wetting of aluminium on sapphire (α-alumina) over a temperature range 700 to 1150° C. Above about 925° C these authors found that the sapphire was partially dissolved by the aluminium and even below this temperature they found some evidence of attack.

The object of the present work was to study in more detail the wetting and spreading of a molten drop of aluminium on aluminium oxide over the temperature range 850 to 1500° C. A particular study has been made of the spreading and contracting behaviour at temperatures above 1150° C. Cinematography was used to record the rapid changes in profile that frequently occurred. Both polycrystalline (recrystallised) and single-crystal (sapphire and ruby) alumina have been studied: the latter with respect to the effect of crystallographic orientation. Molten drops of pure aluminium were used in most of the experiments, although some work was done with Al/Ni and Al/Cu alloys, and with copper and gold.

2. Experimental Apparatus

The experimental work was started using a fairly simple, bell-jar type of vacuum furnace whilst a more sophisticated, horizontal tube apparatus was being designed and constructed. In both pieces of equipment the specimen was heated in a vacuum or inert atmosphere inside a cylindrical susceptor of refractory metal coupled to a 40 kW 450 kcycle/sec rf generator. The wall thickness of the susceptors was appreciably greater than the skin depth at this frequency so that the specimen was heated by radiation alone.

The first apparatus was similar to that used by Morel [4]. It consisted of a water-cooled stainless steel bell-jar fitted with two diametrically opposite viewing ports to permit simultaneous visual observation and photography of the sessile drop. The rf heating current entered through a further inlet port. The chamber was evacuated by oil diffusion pump with a liquid nitrogen trap backed by a rotary pump. A vacuum of better than 10^{-5} torr was readily attained before heating was started: subsequently the degree of vacuum depended on the vapour pressure of the specimen. The sample rested on a flat alumina table placed so that it lay along the axis of the two viewing ports. The cylindrical susceptor and a concentric rf coil straddled the table to form the complete furnace unit. Temperatures were measured with a Pt/13% Rh/Pt thermocouple placed as close as possible to the sample and were controlled to within ±2° C. The specimen table was levelled using screw jacks fitted to the base of the frame of the apparatus so that the whole apparatus could be tilted.

The second apparatus was similar to that of Sutton [5] and consisted essentially of a horizontal, water-cooled, fused-silica tube vacuum furnace closed at each end by stainless steel caps containing glass viewing windows. The pump unit for this apparatus was similar to that used for the earlier equipment except that the rotary pump was isolated to avoid the transmission of vibration.

Specimens were placed on an alumina plate supported in the centre of the susceptor tube located concentrically inside the silica tube. Refractory metal radiation shields were placed around and at both ends of the susceptor. The susceptor was coupled to a rf coil wound round the outside of the furnace tube. Deposits due to evaporation from the specimen were contained within a smaller region than in the first apparatus and the walls being of silica rather than of steel were much easier to clean.

In the second apparatus the specimen could be levelled much more accurately. The furnace tube could be rotated about its axis and tilted along its length by means of fine adjusting screws. A small pendulum arm suspended at one end of the susceptor tube facilitated levelling in the vertical plane.

3. Experimental Procedure

The aluminium, aluminium-copper, aluminium-nickel, copper and gold used for the metal drops were analysed spectrographically in this laboratory and the impurities detected are listed in table I.

Flame-fusion grown single-crystal sapphire (undoped α-alumina) and ruby (chromium-doped α-alumina) were used for most of the substrates. These plaques were supplied in a cut and polished condition from Agate Products*. A few ruby crystals were used that had been grown, by the fluxed-melt process [6], and polished in this laboratory. The results of the analysis of these substrate materials are also given in table I. The orientation of the single-crystal plaques was determined by Laue X-ray back reflection, or by the use of crossed Nicols, and is included in table II. The polycrystalline alumina used was Degussit AL23 discs cut and polished in this laboratory; X-ray examination indicated random orientation of the grains.

The alumina plaques were cleaned in AR acetone for 15 min, to remove any surface film, and then dried. The cylindrical pieces of aluminium, generally weighing 0.2 g, were etched for 15 min in 10% NaOH solution, thoroughly washed in deionised water, rinsed in acetone, and dried. After the furnace was evacuated the specimens were degassed by heating at a temperature of 500° C for 15 min

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TABLE I Spectrographic analysis of materials (ppm by weight).

	Cr	Fe	Pb	Mg	Si	Mn	Cu	Ni	Ag	B	Ca	Na	Zn
Aluminium	—	15	—	30	10	—	1	—	<10	—	<10	<10	—
Aluminium/Copper	—	20	—	30	40	—	*x*	<10	—	—	—	—	—
Aluminium/Nickel	—	20	—	30	10	—	20	*y*	—	—	—	—	—
Copper	—	<5	<5	—	—	—		1	10	—	—	—	<10
Gold	—	—	—	—	2-20	—	2-20	—	—	—	—	—	—
Sapphire (S)	<5	<10	<5	<0.1	0.1	<1	<0.5	—	—	<2	< 1	—	—
Ruby (R(0.05))	500	<15	<5	<0.1	<0.1	<1	<0.1	—	—	<3	< 1	—	—
Ruby (R(0.16))	1600	15	<5	0.3	<0.1	<1	<0.1	—	—	<2	< 1	—	—
Ruby (RF)	300	15	600	0.1	0.4	—	0.1	—	—	<2	—	—	—
Degussit AL23 (P)	10	150	<5	250	3.0	2	<0.1	5	—	<3	< 1	1200*	—

No other impurity elements were detected. By chemical analysis, $x = 25.6$ wt %, $y = 19.8$ wt %.
*By chemical analysis.

before increasing to the working temperature.

In the early experiments single-shot 35 mm photography was used. Later the profile of the drop was photographed on 16 mm film using either a cine camera or a time lapse camera.

Contact angles were generally measured directly from a projected image of the film. Estimating the position of the tangent to the liquid curve at the point of contact introduced an error of $\pm 2°$ for the same observer or $\pm 5°$ from one observer to another. A more precise method proved to be to measure the diameter and height of the projected image of the drop and to calculate the contact angle θ from the well-known formula for a spherical cap: this procedure reduced the above errors by a factor of two. The volume and free (liquid-vapour) surface area of the drop were calculated in a similar manner. These calculations assume that the flattening of the drop due to gravity is negligible, which assumption is reasonable for the small, low-density metal drops studied and was checked by measuring several samples: in each instance the drop profile was circular within the limits of experimental error.

In general, the shape of a sessile drop results from a balance between surface tension which tends to make the drop spherical, and gravity which tends to flatten it. Consequently it is possible in principle to determine the surface tension of the liquid from the shape of the drop. Such determinations could not be made from the present observations due to the negligible effect of gravity previously mentioned.

4. Results

Preliminary experiments, carried out with the bell-jar apparatus, showed that when a drop of aluminium was heated on a sapphire plaque and at a constant temperature below about 950° C, the contact angle decreased with time and did not reach a constant value for a considerable time. For example, at 950° C a constant contact angle was first reached after 15 min; at 850° C the angle was still changing after 50 min.

A series of experiments conducted at temperatures between 950 and 1150° C showed that the final steady value of the contact angle decreased with temperature as shown in fig. 1. (Also shown for comparison are the results of Wolf, Levitt, and Brown [3] for commercially pure aluminium on sapphire.) On the basis of the criterion $\theta = 90°$, wetting occurred above about 1050° C.

In these experiments a series of samples was heated to different temperatures, allowed to reach equilibrium and then cooled. The bases of the frozen sessile drops were photographed through the bottom of the plaques and the areas of contact determined. The contact area showed no marked change until about 950° C at which point there was a rapid increase of about $2\frac{1}{2}$ times.

At temperatures above 1150° C, a new phenomenon appeared: the drop extended so as to increase the solid-liquid interfacial area with the liquid-vapour surface area remaining constant (see below); this extension was followed by a sudden contraction, and the process was repeated continuously. This phenomenon was investigated in some detail with a variety of specimens. In most experiments, photographs of the drop profile were taken at intervals of 2 sec, but a few films were shot at 8 frames per sec. The latter showed that the actual contraction was complete in less than 1/8 sec. Fig. 2 shows a series of adjacent frames taken at intervals of 2 sec and including a contraction: a marked change in shape of the drop profile is seen

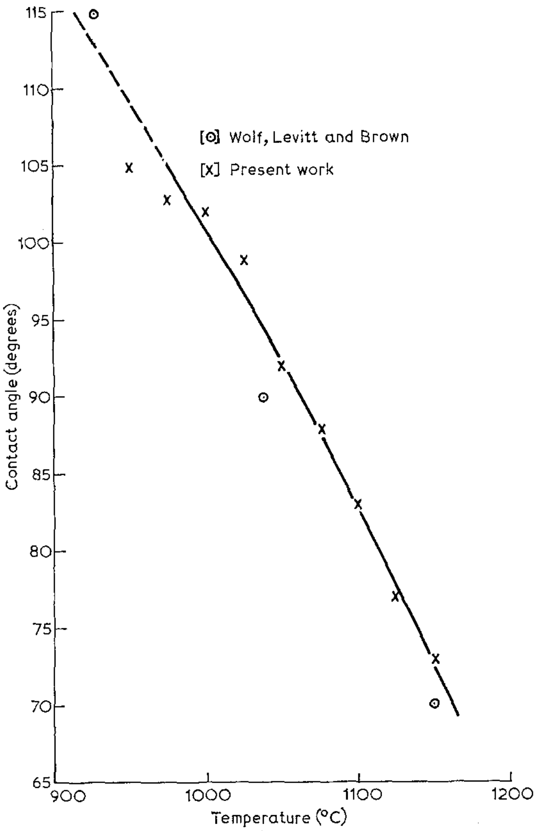


Figure 1 Variation of contact angle with temperature up to 1150° C. Aluminium on single-crystal sapphire.

between the second and third frames. (The pendulum arm used in levelling is visible in these photographs.)

Most of these experiments were performed in the horizontal tube apparatus with pure aluminium on sapphire or ruby, but the effect of aluminium on recrystallised alumina, and of other metals and alloys on single-crystal alumina, was also investigated.

The variation of contact angle with time from measurements on films is shown for a typical specimen of aluminium on sapphire in fig. 3a. A corresponding plot of free (liquid-vapour) surface area and volume of the same drop is shown in fig. 3b. The points on the graphs result from measurements made on every 30th frame (i.e. at time intervals of 1 min) and in addition just before and just after each contraction. It may be noticed that the free surface area shows a sudden decrease at each contraction but remains sensibly constant in between,

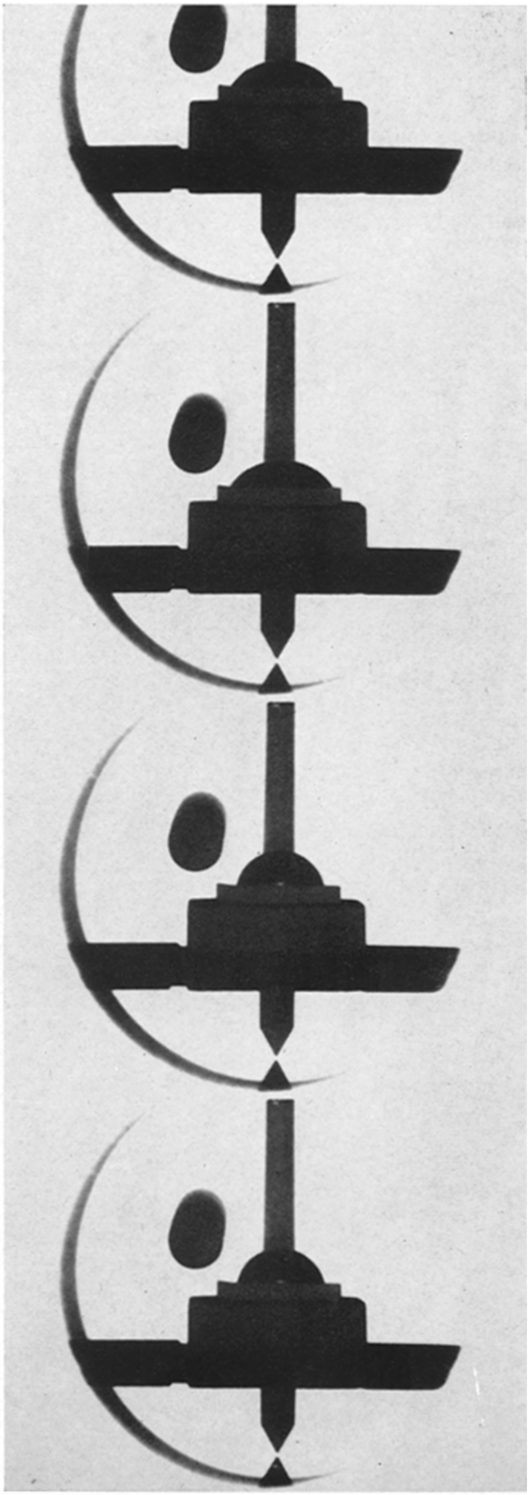
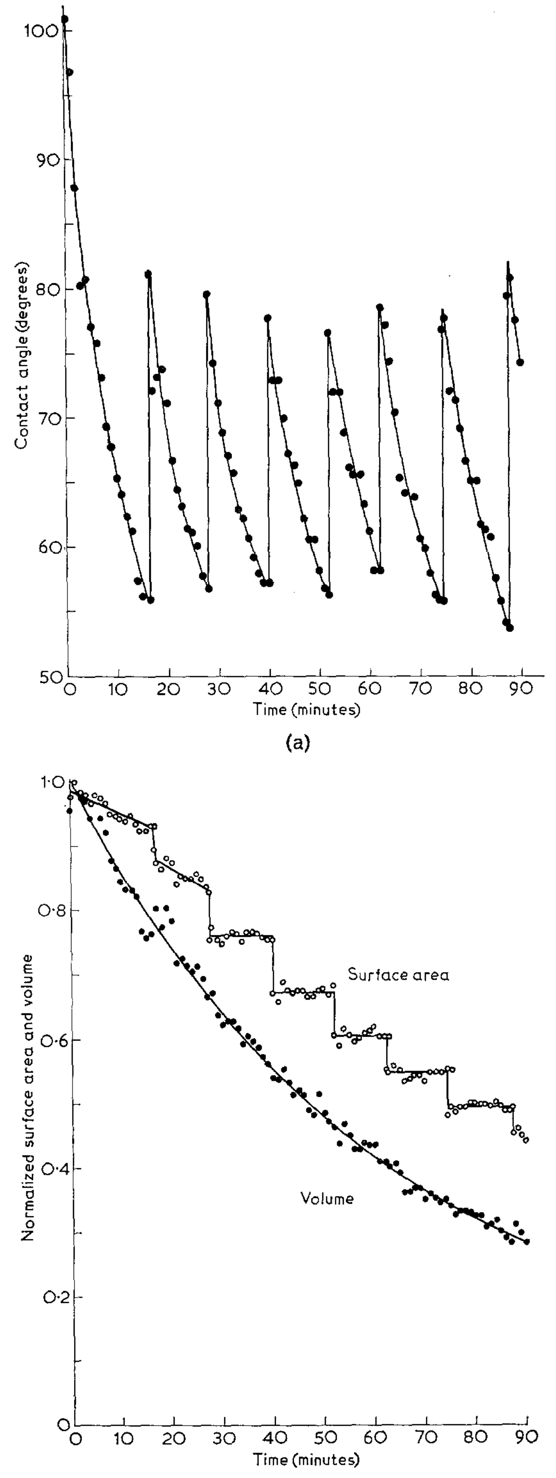


Figure 2 Successive photographs, taken at intervals of 2 sec, of a sessile drop of aluminium on single-crystal ruby at 1350° C showing a contraction (specimen 66).

whereas the volume shows a steady decrease. Ruby gave similar results to sapphire, but the contractions with the polycrystalline material, although clearly discernible visually, were much smaller, more frequent and more irregular, and were only observed on polished material. The results for the whole series of experiments are summarised in table II. It may be seen from this table that the magnitude of the contractions was often quite large, exceeding 40° on occasions. The mean value of the contact angle shows little variation, however. The interval between contractions was often rather irregular but tended to decrease at higher temperatures.

In fig. 4 the variation with time of the diameter of the liquid-solid interface is plotted for aluminium on single-crystal ruby and on polycrystalline alumina. With the ruby the contractions are very pronounced and the spreading of the drop between contractions is very evident. The effect



(a)

(b)

Figure 3 Aluminium on single-crystal sapphire: specimen 51, 1350° C; (a) variation of contact angle with time, (b) variation with time of free surface area and volume of drop, normalised to time $t = 0$.

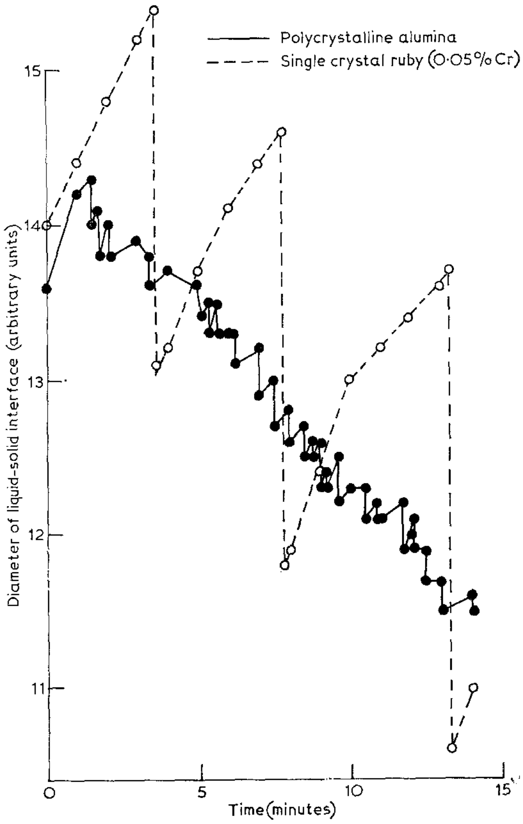


Figure 4 Variation with time in diameter of liquid-solid interface at 1350° C for (i) aluminium on single-crystal ruby: specimen 66 (broken line); (ii) aluminium on polycrystalline alumina: specimen 58 (full line).

TABLE II Summary of sessile drop experiments at 1250 to 1500° C.

Specimen no.	Metal	Plaque		Temp. (° C)	Time (min)	Mean θ (deg)	Max. contraction (deg)	Mean contraction (deg)	Mean contraction interval (min)	Reaction rings	Interface
		Material	Orientation (deg)								
51	Al	S	90*	1350	90	69	36	30	11.8	RCF	A
69	Al	S	90	1350	90	67	24	9	1.7	RF60	A
70	Al	S	90 ± 3	1350	90	68	24	16	2.4	RF60	A
55	Al	S	0	1350	90				4.6	RF90	A
48A	Al	S	0	1350	90				4.0	RF90	A
71	Al	S	0	1250	90	55	26	22	20.0	RF90	A
50	Al	R(0.05)	90 ± 2	1350	90	60	44	36	15.0	RF60	A
52	Al	R(0.05)	90 ± 2	1350	90	68	38	17	4.7	RCF	A
53	Al	R(0.05)	90 ± 2	1400	90	70	18	12	4.2	RF60	A
66	Al	R(0.05)	0	1350	15	64	36	29	4.7	RF60	A
54	Al	R(0.16)	90	1400	90				1.1	RC	A
57	Al	R(0.16)	90	1250	94	66	17	9	8.4	RC	A
67	Al	RF	90 ± 1	1350	90	69	24	19	4.5	RF60†	A
68	Al	RF	90 ± 1	1350	90				1.5	RF60†	A
56	Al	PU	—	1350	90				—	N	A
58	Al	PP	—	1350	90	61	7	3	?	RW	A
59	Al/25% Cu	S	90	1350	15	67	24	17	5.5	RC	G
64	Al/25% Cu	S	90	1350	15	62	14	10	4.5	RC	SG
62	Al/25% Cu	S	90	1350	15				4.0	RC	SG
63	$CuAl_2$	S	90	1350	15				1.5	RC	X
73	Cu	S	90	1200	30					N	B
60	Cu	S	0	1400-1535	30					N	A
72	Cu	S	0	1500	30					N	C
47	Al/20% Ni	S	90	1350	15				—	N	DG
61	Al/20% Ni	S	90	1350	15				8.2	RW	G
65	Al/20% Ni	S	90	1350	15				5.0	RC	G
74	Au	S	90	1350	15					N	B
75	Au	S	90	1350	15					N	B
76	Au	R(0.05)	0	1450	180					N	A

Alloying additions are in weight per cent. S, sapphire; R, ruby (% Cr in brackets); RF, ruby, flux grown, 0.03% Cr; PU, polycrystalline, unpolished alumina; PP, polycrystalline, polished alumina; orientation only nominal unless otherwise stated; *subsequently found to be 12° off; N, no reaction rings; RW, faint reaction rings; RC, reaction rings circular; RCF, reaction rings slightly flattened; RF60, reaction rings with flats at 60° to each other; RF90, reaction rings with flats approximately 90° to each other; A, good bond at interface; B, bubble at interface; C, plaque fractured; DG, deep cracks within plaque; G, cracks within plaque; SG, slight cracks within plaque; X, no bond; †see remarks in text.

of evaporation is shown by the overall decrease in diameter with time. With polycrystalline alumina, although the contractions are smaller, they are clearly shown by this mode of presentation, since the error in measurement of this single linear dimension is much less (about 0.7%) than in the determination of the contact angle. The effects of spreading and of evaporation are again evident.

As well as with aluminium, contractions were observed on single-crystal alumina plaques with aluminium-copper and aluminium-nickel alloys, but not with copper or gold. All the pure aluminium drops on solidification formed a good bond to the various substrates, but this was not generally so with the other metals and alloys (see table II).

Invariably, at the end of an experiment in which contractions had been observed, the plaque showed a series of reaction rings, an example of which is shown in fig. 5. In those experiments in which relatively few contractions had occurred at least, it was established that the number of contractions equalled the number of rings. The profile of the reaction rings was examined by interference microscope and with a talysurf. A typical talysurf record (for specimen 50) is shown in fig. 6.

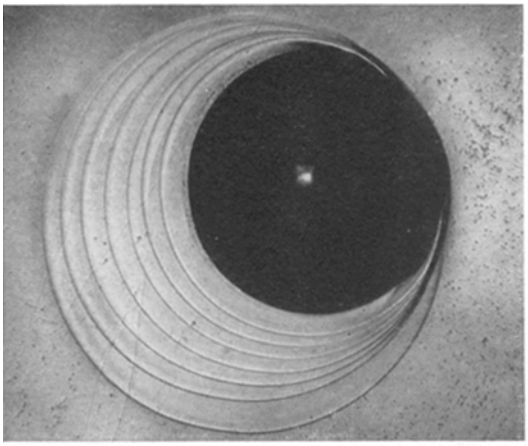


Figure 5 Specimen 51 at end of experiment showing solidified Al drop and reaction rings. The sapphire plaque is 20 mm square (×7).

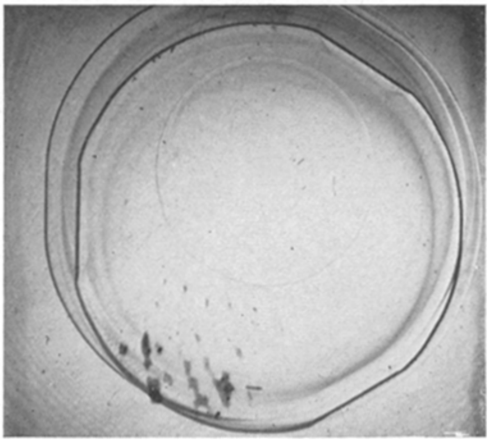


Figure 7 Surface of single-crystal ruby plaque, basal plane orientation, after reaction with aluminium at 1350° C (specimen 50) (× 7.5). The talysurf trace of fig. 6 was taken across the horizontal diameter of this specimen.

In general the reaction rings on polycrystalline and single-crystal alumina surfaces were circular as shown in fig. 5. If, however, the *c*-axis was accurately perpendicular to the surface, the rings showed straight portions at right angles to the three *a*-directions, (i.e. in the $\langle 10\bar{1}0 \rangle$ directions) as shown for specimen 50 in fig. 7. When the *c*-axis departed by only a few degrees from the perpendicular, then the rings had straight portions corresponding to the projection of the $\langle 10\bar{1}0 \rangle$ directions on the plane of the plaque. If the *c*-axis was inclined at more than about 10° to the perpendicular, then circular rings and no flat portions were obtained (cf the circular rings reported by Carnahan *et al* for 60° plaques). If the *c*-axis lay nearly in the plane of the plaque, rings with flats were again obtained, but this time the direction of the straight parts appeared to correspond to the projection on to the plane of the plaque of two of the $\langle 10\bar{1}0 \rangle$ directions and the *c*-direction, [0001] (see fig. 8). In some instances the periphery of the solidified drop clearly followed the outline of a reaction ring, including straight portions.

Two experiments were performed with aluminium on flux-grown ruby crystals. With these plaques the *c*-axis was accurately perpendicular to the face, but the crystals were composed of a series of adjacent twins. At the end of the wetting experiments these plaques showed rings with straight portions mutually at 60° within a twin, but a rotation through 180° in these features from one twin to the next, see fig. 9 (cf the rotation of etch pits across a twin boundary noted in previous work [6]). The photographs of the rings, figs. 7 and 9, also show some interesting detail on the inner edge of some of the rings. This detail is reminiscent of a cellular or possibly dendritic type of interface observed under certain crystal growth

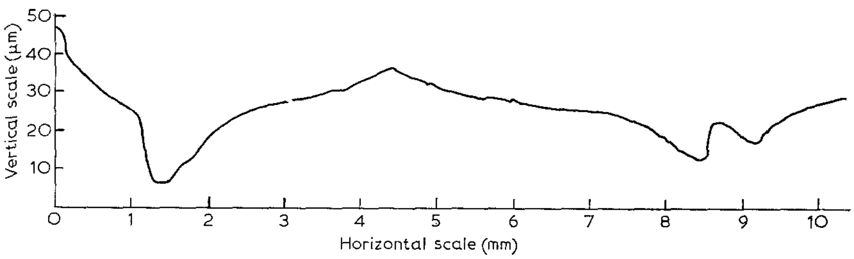


Figure 6 Talysurf record of the profile of reaction rings formed at 1350° C with Al on single-crystal ruby (specimen 50). The trace was made across two adjacent rings. On the left of the figure the rings overlap, on the right they are distinct (see also fig. 7).

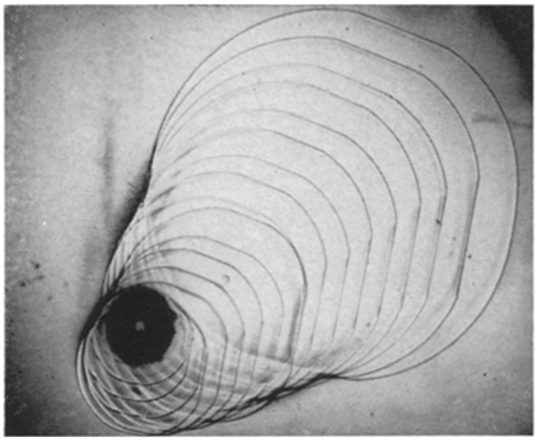


Figure 8 Surface of single-crystal sapphire plaque, near to $\{10\bar{1}0\}$ orientation, after reaction with molten aluminium at 1350° C (specimen 55) (× 14).

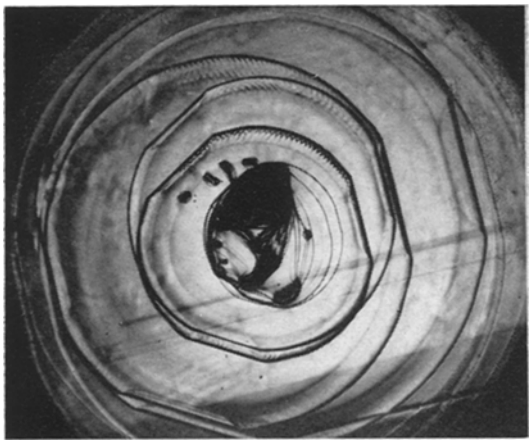
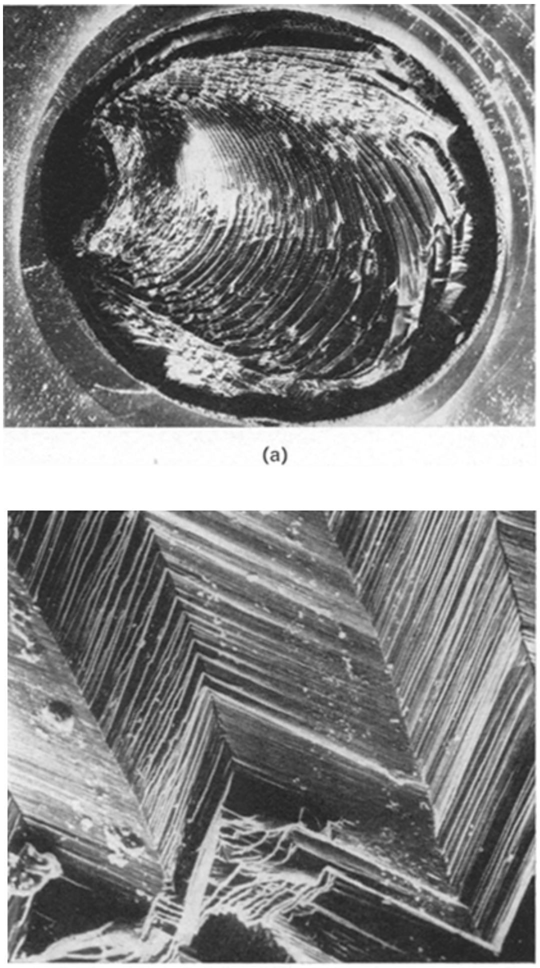


Figure 9 Surface of flux-grown ruby crystal, basal plane orientation, after reaction with molten aluminium at 1350° C (specimen 68). The asymmetry of the flats on the outer rings is caused by a twin boundary running across the crystal (× 14.5).

conditions, and is presumably associated with the reaction process, but does not seem to have been reported previously.

With Al, $CuAl_2$, Cu, and Au on single-crystal Al_2O_3, there was little attack of the central area of contact, although with copper and gold bubbles tended to form at the interface. With Al/25% Cu and Al/20% Ni, and to a lesser extent with Al/4% Cu alloys, it was observed that although the solidified drop adhered firmly to the sapphire immediately in contact with it, cracks appeared within the sapphire, ~1 mm below the metal-sapphire interface, in some cases causing the sapphire to fracture, leaving a lens-shaped piece of sapphire firmly adhering to the solidified metal. Fig. 10a shows one such fractured sapphire surface, and fig. 10b an enlarged view taken on a scanning electron microscope: this shows what seems to be shear lines. The effect appeared to be more intense if the metal had not been previously outgassed.



(a)

(b)

Figure 10 Fractured surface of single-crystal sapphire plaque, basal plane orientation, after reaction with Al/20% Ni at 1350° C (specimen 47); (a) optical photograph (× 5.5); (b) scanning electron micrograph (× 110).

Microscopic examination of the surface of the single-crystal α-alumina plaques at the end of an experiment also showed that, when aluminium or an aluminium alloy had been used, the area outside the outermost reaction ring had been etched. Often a large number of triangular etch pits were visible on basal plane surfaces. (The form of the pits resembled those produced on α-Al_2O_3 by chemical [6] or thermal [7] etching.) The area enclosed within the outer ring, all of which has at some time been covered by molten metal, had a chemically polished appearance. Neither thermal etching nor polishing occurred when a plaque was heated in the absence of the metal to the same temperature for the same time under the same vacuum conditions.

The results shown in table II were all obtained using the horizontal tube apparatus. When similar experiments were performed in the bell-jar type apparatus it was noticeable that evaporation of the metal occurred more rapidly and the contractions were more frequent and their frequency increased with temperature to a greater extent.

5. Discussion

The preliminary experiments carried out at temperatures below 950° C and mentioned at the beginning of section 4 show that the value of contact angles in the aluminium/α-alumina system must be treated cautiously, and accepted with due regard to the substantial time factor needed to reach equilibrium. The contact angle values obtained by Wolf, Levitt and Brown [3] for commercially pure aluminium on sapphire of similar, basal plane, orientation agree quite well with the present results obtained between 950 and 1150° C (see fig. 1). The rapid increase in area of contact that occurs between 900 and 1000° C indicates the onset of some form of interfacial action producing the transition from the non-wetted ($\theta > 90°$) to the wetted ($\theta < 90°$) state. This observation is in general agreement with the ideas of Wolf and co-workers.

The reported contractions and associated reaction observed at higher temperatures appear to be similar to the phenomenon reported by Carnahan, Johnson and Li [2] for aluminium on sapphire near 1200° C. The variation in contact angle with time shown in fig. 3a for single-crystal corundum is similar to that reported by Carnahan and co-workers, except that there is a definite tendency for the slope of the curves to decrease, rather than remain constant, between contractions. The fact that, after the first two contractions, the free surface area of the drop was essentially constant between contractions (fig. 3b) also agrees with Carnahan's results. Carnahan found a linear change in volume of the drop with time: fig. 3b of this paper shows that the volume decreased continuously, but at a decreasing rate. Probably this difference was only apparent due to the greater fraction of the drop evaporating in the present experiments.

Reaction rings were also reported by Wolf, Levitt and Brown [3] at 1150° C. From the work of Ritter and Burton [8] it seems that similar rings are formed with Ni/20% Cr on sapphire at 1500° C. Carnahan *et al* also examined polycrystalline alumina at ~1240° C and observed some very fine rings, but did not detect any contractions. In the present work both contractions and rings were observed at the higher temperature of 1350° C although the effect was much less marked than with single-crystal material; the contractions were only detectable with a fairly rapid rate of photography.

Carnahan, Johnson, and Li studied their rings on single-crystal sapphire by an optical interference technique and reported step heights of 3 to 4 μm and distances between adjacent rings of 150 to 200 μm. Their diagram of the cross-section through the sapphire plaque as revealed by the interference fringes is probably somewhat idealised in view of the rather asymmetric contours that were obtained using a talysurf in the present work. The talysurf record shown in fig. 6 is of a specimen (No. 50) that showed large contractions (see table II) and comparatively deep (10 to 20 μm) rings. The average step heights and distances between adjacent rings were similar to those of Carnahan *et al* mentioned above.

There appears to have been no previous mention in the literature of reaction rings of the type shown in figs. 7, 8 and 9 with straight portions in certain directions, although one photograph of Wolf *et al* [3] does indicate some departure from a circle. In the present work it seemed that the condition for obtaining flats at 60° to each other, as shown in figs. 7 and 9, was quite critical with respect to orientation. If the *c*-axis departed by more than about 10° from the normal to the surface, circular rings were obtained (Carnahan *et al* used plaques cut with the *c*-axis at 60° to their plane). The condition for straight portions to occur when the *c*-axis lay nearly in the plane of the plaques appeared to be similarly sensitive to orientation. The production of straight portions of the reaction rings may be related to the phenomenon observed by Pankove [9]. He was studying the alloying of indium to germanium and found that the shape of the alloy front was determined by surface tension forces and a tendency to terminate in (111) type plane. In the present work, straight portions in $\langle 10\bar{1}0\rangle$ directions indicated that the advance on a basal plane is slowest in the *a*-directions.

The present work seems in general to support the basic explanation for the formation of the reaction rings put forward by Carnahan *et al.* The rings quite definitely seem to be formed as the result of reaction between the molten aluminium (or aluminium alloy) and the plaque. (Neither contractions nor rings were observed with the non-reactive metals copper and gold.) The profile of the rings, as exemplified in fig. 6, shows that the reaction is more vigorous near the periphery of the drop. It was found that the rate of contractions increased with temperature and was dependent on environment: less reaction occurred if the specimen was heated in helium rather than in vacuum, or if the pumping rate in the vicinity of the specimen was reduced. These observations are consistent with a chemical reaction giving rise to a gaseous product.

It is postulated that the volatile oxide of aluminium, Al_2O, is formed, according to the equation

$$4Al + Al_2O_3 = 3Al_2O$$

(A mass spectrographic analysis by Porter, Schissel and Inghram [10] of the vapour in thermodynamic equilibrium with Al/Al_2O_3 showed that the predominant species were Al and Al_2O, and gave thermodynamic properties for Al_2O in agreement with those obtained by Brewer and Searcy [11]. The latter authors showed that Al_2O gas is evolved when Al_2O_3 is heated with aluminium or another reducing metal.)

The rate at which this reaction proceeds would be governed by the rate at which the Al_2O is removed from the interference. Now Al_2O probably has a low solubility in the molten aluminium (Kubaschewski and Hopkins [12] give the solubility of oxygen in aluminium as 0.006 at. % at an unspecified temperature). Also, the pressure on the interface due to the weight of the aluminium is likely to exceed the vapour pressure of Al_2O, except near the periphery (Brewer and Searcy [11] give the vapour pressure of Al_2O over liquid Al and solid Al_2O_3 mixture at 1350° C as about 3×10^{-4} atm: this pressure will exist at a depth of about 1 mm of molten Al). Thus the reaction represented by the above equation will only tend to move towards the right hand side at the periphery of the drop and so a reaction ring will be formed. Brewer and Searcy [11] also give the vapour pressure of aluminium at 1350° C as about 1×10^{-4} atm, so that the observed decrease in the volume of the drop is likely to be due to the evaporation of both Al_2O and Al.

The ensuing discussion of the resolved forces acting at the periphery of the drop when reaction is taking place follows closely that of Carnahan *et al.*

Before appreciable reaction has taken place the interfacial tensions γ_{sv}, γ_{lv}, and γ_{ls}, and the "pseudo-equilibrium" contact angle* θ will be related by the Young equation (see fig. 11a)

$$\gamma_{sv} = \gamma_{lv} \cos \theta + \gamma_{ls}$$

After reaction has occurred γ_{ls} will no longer act horizontally, but will be deflected downwards at some angle α. So now (see fig. 11b)

$$\gamma_{sv} > \gamma_{lv} \cos \theta + \gamma_{ls} \cos \alpha$$

Thus the drop will tend to spread outward under the influence of γ_{sv} until a new equilibrium situation is reached given by (see fig. 11c)

$$\gamma_{sv} = \gamma_{lv} \cos \theta' + \gamma_{ls} \cos \alpha'$$

where θ' and α' are the limiting values of θ and α. Throughout this period, however, the drop will be losing mass by evaporation, so that θ will tend to decrease further to θ''. But then (see fig. 11d)

$$\gamma_{sv} < \gamma_{lv} \cos \theta'' + \gamma_{ls} \cos \alpha'$$

This effect will cause the drop to contract to a new pseudo-equilibrium position (fig. 11e), and so the process will be repeated. The above discussion assumes that γ_{lv} and γ_{ls} are unchanged as the aluminium absorbs any of the reaction product. Since, as mentioned above, the solubility of oxygen in aluminium is so minute, this assumption would seem to be justified.

The reason for the reaction profile tending to terminate in certain low-index directions remains somewhat open. It could either be due to the reaction proceeding more slowly in these directions, or to an asymmetry in the interfacial tensions. In summary, good wetting is possible

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*See, for example, Mykura [13].

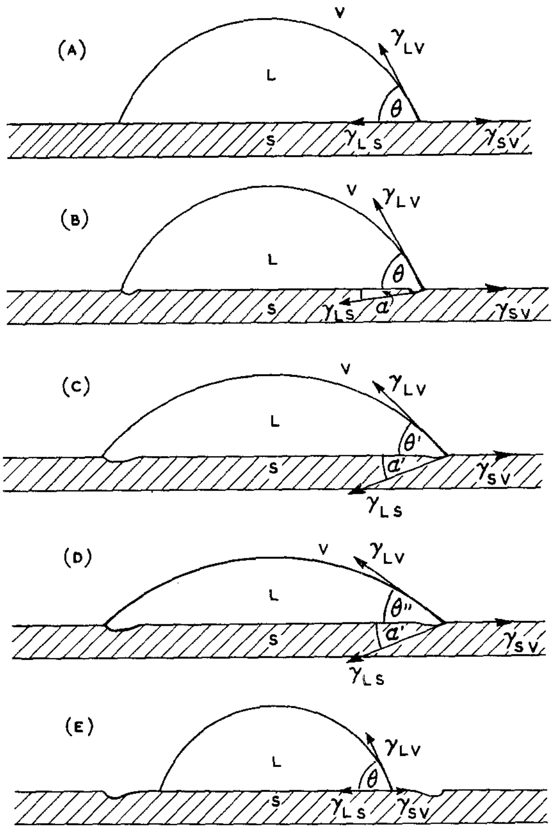

Figure 11 Diagram of resolved forces acting at the periphery of the drop when reaction takes place. (a) Initial situation $\gamma_{sv} = \gamma_{lv} \cos\theta + \gamma_{ls}$; (b) situation after reaction has started: $\gamma_{sv} > \gamma_{lv} \cos\theta + \gamma_{ls} \cos\alpha$; (c) situation after drop has spread: $\gamma_{sv} = \gamma_{lv} \cos\theta' + \gamma_{ls} \cos\alpha'$; (d) situation after drop has spread and there has been some evaporation, immediately prior to a contraction: $\gamma_{sv} < \gamma_{lv} \cos\theta'' + \gamma_{ls} \cos\alpha'$; (e) situation immediately after a contraction.

with aluminium on alumina at elevated temperatures but some chemical reaction then occurs. This implies that there may be an optimum temperature for the incorporation of corundum whiskers into an aluminium matrix by liquid infiltration if good wetting is to be obtained without excessive chemical attack.

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