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The Adhesion of Metal/Alumina Interfaces

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Cylinders of copper and nickel have been melted under various conditions to form sessile drops on alumina plaques. The resultant metal/ceramic adhesion at room temperature has been measured using the commonly adopted test in which the drops are pushed off the ceramic plaques. The stress system involved in the test has been analysed and it has been shown that the standard interpretation of the test, as a measure of interfacial shear strength, is not valid; the revised interpretation makes it a measure of adhesion in tension. Results for the Cu/Al_2O_3 and Ni/Al_2O_3 systems show that non-wetted interfaces can be strong and have strengths that are independent of contact-angle changes caused by wetting-temperature variations.

1. Introduction

The current interest in the potential of alumina whiskers for fibre reinforcement has resulted in several investigations of the adhesion of metal/alumina interfaces. A simple and favoured technique used to assess interfacial strength has been to push off a solidified sessile drop of the metal from an alumina plaque [1-3] and to calculate an apparent shear strength from the load and the interfacial area. By measuring the contact angle of the drop at the wetting temperature, one sample yields information on both the wetting and bonding behaviour under the particular experimental conditions employed.

On the basis of these "shear" test results, a marked correlation appears to exist between the wetting and bonding behaviour. However, reservations have been expressed about the quantitative meaningfulness of the strength values – Sutton [1], for example, labelling them "apparent" shear strengths – in view of the complex geometry of the push-off test. These reservations were felt in this laboratory also, when the test was used with copper/alumina and nickel/alumina samples. In an attempt to clarify the situation, a calculation has been made of the variation in the apparent shear strength due to geometric changes in the test as the contact angle is altered. These calculations indicate that, for the majority of the observations, the failure criterion is actually a tensile one and that the variation with contact angle of the apparent shear strengths can be satisfactorily related to a unique tensile strength of the interface.

2. Experimental Techniques

The sessile-drop experiments were performed in a vacuum resistance furnace that has been described previously [4]. The vacua employed were always better than 3×10^{-5} mm of mercury, and the wetting temperatures were controlled to within $\pm 5°$ C. The contact angles were measured with a goniometer by viewing the levelled specimens at temperature through a horizontal observation port. The accuracy of the measurement was estimated to be $\pm 2°$.

The metals used were Johnson Matthey* spectroscopically pure copper and nickel, and a commercial high-conductivity copper, BSS 1433. The metal specimens were cylinders weighing 0.200 g with heights of approximately 1.5 diameters. The alumina was in the form of Degussit† AL23 discs. This material was chosen because of its purity, >99.5%, and availability. (As will be shown later, the precise grade of alumina may have only a minor influence on interfacial strength, the data obtained in this study being in good agreement with those of Sutton [1], who used single-crystal sapphire discs.) The specimens were ultrasonically cleaned in methyl alcohol for 5 min and dried in a hot air blast before insertion in the furnace. After

*Johnson Matthey Ltd, Hatton Garden, London

†Degussa, Frankfurt/Main

the furnace was pumped down, the specimens were degassed by holding at 1000° C for 30 min prior to being heated to the wetting temperature.

The apparent shear strengths of the interfaces at room temperature were obtained from measurements of the interfacial area, and of the load, applied parallel to the interface, required to push the solidified drop off the plaque; an attachment to a Hounsfield tensometer, similar to that described by Sutton [1], was used for the test. All the values to be quoted are for true interfacial failures (i.e. the type 1 fracture of reference 1).

3. Experimental Results and Discussion

The experimentally measured contact angles and push-off bond strengths for the three metal/alumina systems employed are summarised in table I.

It will be noted that the time at temperature was not kept constant for all the tests. This was because a correlation between the bond strength and the contact angle was being sought, and the contact angle of a sessile drop can often be decreased by holding at temperature. Thus the contact angles of specimens 601, 668, 840, 718, 674, and 672 are anomalously low because of the unusually long times for which they were held at temperature.

The experimental results demonstrate a clear correlation between the contact-angle data and the push-off bond-strength values, as shown in fig. 1; variations in the experimental conditions leading to a lower contact angle almost invariably resulted in a higher push-off bond

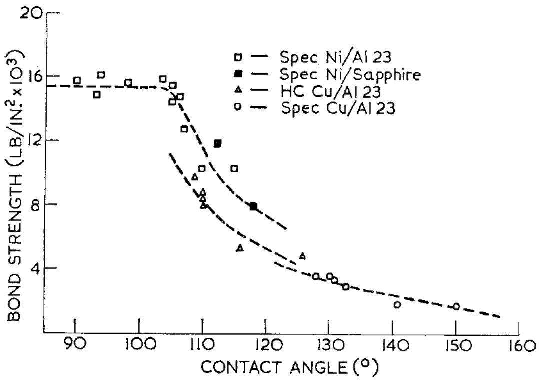

Figure 1 Correlation between the wetting and bonding behaviour of three metal/alumina systems (1 lb/in.^{2} = 7×10^{-2} kg/cm^2).

TABLE I Summary of experimental contact-angle and bond-strength results.

Specimen no.	System	Wetting temperature (° C)	Time at temperature (min)	Contact angle (°)	Bond strength (lb/in.^{2})*
561	Spec Cu/AL23	1120	15	150	1600
602	,,	1170	15	141	1830
563	,,	1210	10	133	2800
567	,,	1260	15	131	3050
564	,,	1480	10	130	3450
601	,,	1255	30	128	3380
663	HC Cu/AL23	1120	5	126	4850
662	,,	1240	5	116	5300
664	,,	1465	5	110	7900
669	,,	1376	5	110	8250
668	,,	1150	15	110	8800
666	,,	1390	5	109	9800
761	Spec Ni/AL23	1455	3	115	10 250
658	,,	1460	3	110	10 200
660	,,	1470	5	107	12 600
684	,,	1505	10	106.5	14 600
653	,,	1540	20	105	14 300
846	,,	1585	5	105	15 400
681	,,	1610	10	104	15 900
840	,,	1330	35	98	15 700
718	,,	1513	135	94	16 050
674	,,	1610	35	93	14 900
672	,,	1485	185	90	15 900

*1 lb/in.^{2} = 7×10^{-2} kg/cm^2

strength. The two results derived from Sutton's [1] work included in the figure are for nickel of the same purity as that employed in the present work and obtained from the same source.

In an attempt to interpret these data, the forces and bending moments acting on the interface during the strength testing were analysed. For this purpose, four explicit assumptions were made.

(*a*) The drop surface was spherical.

(*b*) The ultimate tensile strength, U, of the interface was uniform over the entire contact area.

(*c*) The interface was planar and remained so during the test.

(*d*) The interface was only elastically strained prior to fracture.

The analysis, which is presented in detail in the Appendix, predicted that the interfaces of drops with contact angle θ greater than 107° would fail in tension rather than shear if the shear strength S of the interface is $0.8U$, and that the contact angle at which transition from tensile to shear failure occurs will be less than 107° if the shear strength is greater than $0.8U$.

The predicted relationship between

$$\frac{\text{Push-off bond strength}}{\text{True tensile bond strength } (U)}$$

and the drop contact angle is shown in fig. 2.

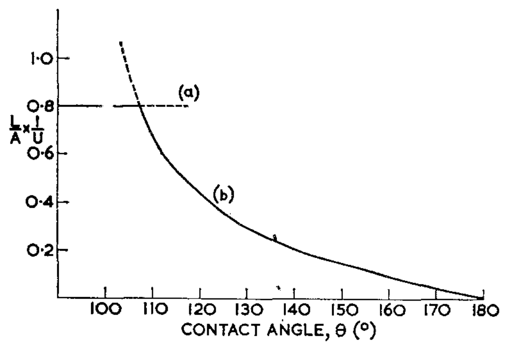

Figure 2 The calculated variation of push-off bond strength with U, the interfacial ultimate tensile strength, and the contact angle: (a) $S = 0.8U$, shear failure; (b) $L/A = [U\tan(\theta - 90)]/4$, tensile failure ($L$, load; A, area).

Examination of the data presented in table I in terms of this analysis showed that the observed variation of bond strength with contact angle was of the same general shape as that predicted. The strength data for spectroscopically pure nickel plotted against the contact angle display a "knee" at a value of 105°. (It was not found to be practical to produce specimens of the other systems with contact angles below that at which a tensile/shear failure transition is expected.) Quantitatively, the observed variation of bond strength with contact angle could be accounted for by a single U value for each of the three systems; that is, it is not necessary to assume that the interfacial tensile strength is a function of the contact angle. The U values that best describe the observed bond-strength variations are 10 800 lb/in.^{2} (1 lb/in.^{2} = 7×10^{-2} kg/cm^2) for spectroscopically pure copper, 12 300 lb/in.^{2} for high-conductivity copper, and 17 000 lb/in.^{2} for spectroscopically pure nickel. The dashed lines drawn in fig. 1 were calculated from the predicted relationship using these values. For comparison, annealed copper and nickel have ultimate tensile strengths ~30 000 and 45 000 lb/in.^{2} respectively [5].

Because of the possibility that the agreement between the measured bond strengths and those predicted on the basis of unique U values was merely fortuitous, an investigation was made of the variation of apparent shear strength with contact angle for a model system in which U did not vary. The model chosen consisted of steel ball bearings upon which variously sized flats had been ground, bonded to brass plates by a thin layer of Araldite. Two batches of specimens were prepared, but the Araldite strength was assumed to be constant since the same proportions of adhesive and hardener were used and the curing conditions were identical. The push-off strengths of these model samples are plotted against their "contact" angles in fig. 3. It can be seen that there is no appreciable difference between the data obtained with the two batches. A "knee" occurs in the observed bond-strength variation at a "contact angle" of about 108° and there is good agreement with the predicted variation, shown by the dashed line, calculated by equating U to 7000 lb/in^2.

The good agreement between prediction and practice for both the metal/alumina and the model systems gives rise to a reasonable degree of confidence in the validity of the analysis and the conclusions that can be derived from it. The analysis enables sets of push-off bond-strength data to be compared even if the contact-angle values do not overlap, and permits the interpretation of the experimental strength data to yield meaningful U values.

The experimental data obtained demonstrate

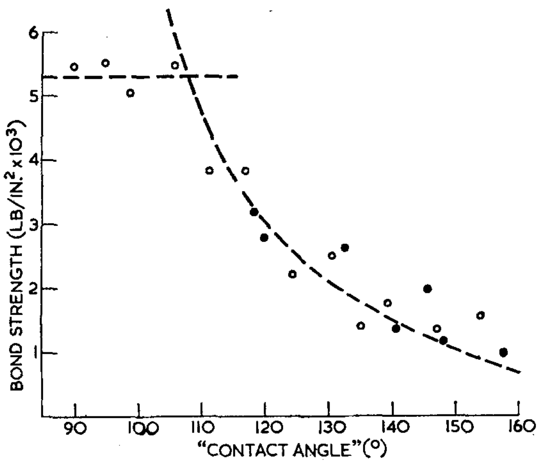

Figure 3 The variation of bond strength with "contact angle" for steel ball bearings bonded to brass plates with Araldite: ● – batch A; ○ – batch B.

that U is independent of the sessile-drop contact angles and wetting temperature but is dependent upon the purity of the metal employed, AL 23/high-conductivity copper interfaces being 14% stronger than AL 23/spectroscopically pure copper interfaces. An impurity effect can be demonstrated also for nickel bonded to sapphire by calculating U values from the bond-strength data of Sutton [1] and Ritter and Burton [3]. These values, summarised in table II, show that the effect is complex. Thus an increase in nickel impurity level from <15 ppm to 31 ppm increased by 41% the interfacial strength of Sutton's samples, while Ritter and Burton's samples decreased in strength by 22% when the metal impurity level was raised from 10 ppm to 91 ppm. It should be noted that these strength changes are quantitatively different from the bond-strength changes; Sutton's bond strengths increased by about 130% and Ritter and Burton's decreased by only 7%.

If Sutton's two results and Ritter and Burton's single result for high-purity nickel are assumed to be representative, two other comparisons can be made using the data presented in table II. First, Ritter and Burton obtained a lower interfacial strength than did Sutton, even though nickel of comparable purity was employed. This difference suggests that the identity as well as the amount of impurity can influence interfacial strength. Second, the present results obtained with polycrystalline AL 23 are in good agreement with those Sutton obtained with single-crystal sapphire specimens. This agreement may be merely chance, but it could also be interpreted as indicating that a U value is a material parameter, independent of structure. Clearly, much more work is needed before this possibility can be assessed properly.

4. Conclusions

(*a*) The variation of push-off bond strength with sessile-drop contact angle can be analysed to yield a meaningful interfacial tensile strength value; shear strengths are not generally measured by this test.

(*b*) The experimental results obtained can be described in terms of a unique interfacial tensile strength for each system; that is, it is not necessary to postulate a variation in interfacial strength with contact angle.

(*c*) The tensile strengths of alumina interfaces with spectroscopically pure nickel and copper, and with high-conductivity copper are 17 000, 10 800, and 12 300 lb/in.², respectively.

(*d*) Sutton's data for Johnson Matthey nickel

TABLE II Summary of push-off bond-strength data for nickel/sapphire interfaces formed in a vacuum at 1500°C.

Reference	Metal purity (ppm)	Source	Contact angle (°)	Push-off bond strength (lb/in.²)*	U (lb/in.²)*
Sutton	<15	Johnson Matthey	118	7860	16 700
,,	,,	,,	112	11 900	19 200
Ritter and Burton	10	?	111.3	8700	13 500
Sutton	<31	MRC†	101	22 200	24 700‡
,,	,,	,,	,,	23 700	26 300‡
Ritter and Burton	91	?	108.1	8100	10 500

*1 lb/in.² = 7×10^{-2} kg/cm²
†Materials Research Corp, Yonkers, NY, USA
‡assuming $S = 0.9U$

and Ritter and Burton's data for nickel of a similar purity bonded to sapphire single crystals can be analysed to yield interfacial tensile strengths of 18 000 ± 1200 and 13 500 lb/in.[2] respectively.

Appendix

The stresses involved in the push-off test were analysed using a model, shown in fig. 4, consisting of a metal drop having a spherical surface and a planar interfacial zone of contact with a ceramic plaque. The interface was assumed to remain planar during the test and to be elastically strained only until failure started at F, the point on the periphery of the contact area at which the zy plane, in which the external load L is applied, intersects the xy plane. The ultimate tensile strength and the ultimate shear strength of the interfacial zone were assumed to have unvarying values U and S throughout the zone. In calculating the stresses on point F, it was assumed that the sums of the forces acting in the x, y, and z directions were zero and that the sums of the moments about any axis in the system were zero also.

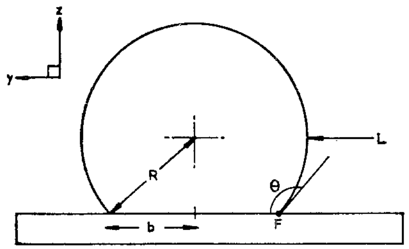

Figure 4 Elevation in *yz* plane through centre of drop/plaque contact area. Load *L* in plane of paper and *x* direction normal to paper.

The shear stress acting in the xy plane at F, τ_{xy}, was calculated by summing the forces in the y direction.

$$(\pi\,[R\cos(\theta-90)]^2)\tau_{xy} - L = 0 \quad (1)$$

$$\tau_{xy} = \frac{L}{\pi[R\cos(\theta-90)]^2} \quad (2)$$

The tensile stress acting in the z direction at F, σ_z, can be calculated by summing moments about MM′, the x direction axis through the centre of the drop/plaque contact area. The moment of the external load is $-LR\sin(\theta-90)$ and, if that of the tensile stresses acting on the entire contact area is M_T,

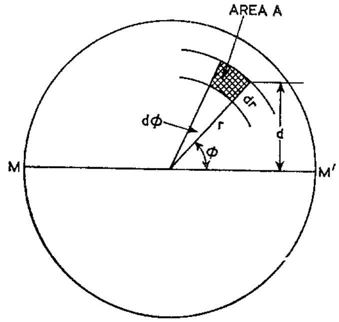

Figure 5 Symbols used in calculating M_T.

$$M_T - LR\sin(\theta-90) = 0 \quad (3)$$

The tensile stress $\sigma_z{}^A$ acting on the small element A shown in fig. 5 will be proportional to the element's distance from MM′, d, since the deformation is elastic, thus

$$\sigma_z{}^A = C_1\,E\,d = C_2\,d \quad (4)$$

where C_1 and C_2 are constants and E is Young's modulus of the interface. The moment of $\sigma_z{}^A$ about MM′ is $(r\mathrm{d}\phi\mathrm{d}r\ C_2 r\sin\phi)\ r\sin\phi$. Hence

$$M_T = \int_{r=0}^{r=b}\int_{\phi=0}^{\phi=2\pi} r\mathrm{d}r\mathrm{d}\phi\,(C_2 r\sin\phi\ r\sin\phi) = \frac{\pi C_2 b^4}{4} \quad (5)$$

From equation 4, σ_z at F is equal to $C_2 b$, and, substituting this into equations 3 and 5, we get

$$\sigma_z = \frac{4L\tan(\theta-90)}{\pi b^2}$$

The failure criterion for the model is that the load L is such that σ_z is equal to U, or τ_{xy} to S. Stresses larger than σ_z and τ_{xy} act on planes lying in the alumina and inclined to xy, but it was assumed that these stresses do not result in failure because of the very high tensile and shear strengths of the alumina in comparison with U and S.

In order to predict the value of the contact angle at which the change from tensile to shear failure occurs, it is necessary to define S as a function of U. Such a definition can be made for homogeneous systems that fail in a ductile or brittle manner, but the present system is inhomogeneous and no theoretical treatment is available which defines S as a function of U. Nevertheless, S is probably less than U*, and, for the purpose of illustrating the conclusions which can be drawn from the analysis, S will be taken arbitrarily to be $0.8U$. As fig. 2 illustrates, the analysis predicts that there will be a marked and rapid increase in the failure load and bond strength (failure load/contact area) as the drop contact angle decreases from 180 to 107°. Over this range of contact angles, the interfaces fail in tension, but drops with contact angles of less than 107° fail in shear at bond strengths that are independent of the contact angle. The contact angle at which the transition from tensile to shear failure occurs is not very dependent upon the S/U ratio of the interface, the appropriate angles for S/U ratios of 1.0 and 0.6 being 104 and 112° respectively.

*The experimental data for the nickel/alumina and ball-bearing/Araldite/brass-plate systems suggest S values of 0.90 U and 0.75 U respectively.

Acknowledgements

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