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The Strength of Metal/Alumina Interfaces

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The room-temperature strengths of interfaces formed by melting aluminium, cobalt, gold, iron, nickel, palladium, silver, and uranium in contact with alumina have been measured. Correlations were sought between the strengths and the physical properties of the systems. Metals which formed void-free interfaces and were not subject to martensitic transformations bonded well to alumina. Metals subject to martensitic transformations (cobalt and uranium) were virtually non-adherent at room temperature.

1. Introduction

The strength of metal/ceramic interfaces is becoming an important material property as engineering requirements become more stringent and attempts are made to synthesise metal/ceramic combinations that will possess all the material properties required for some particular advanced technology project. Examples of such attempts are provided by the current work in many laboratories on the development of fibre composites.

Interest in fibre composites has been confined mainly to their mechanical properties, and particular attention has been paid to means of utilising very strong fibrous materials such as alumina whiskers. It can be demonstrated that the (length/diameter) rates of the fibres should be greater than the (fibre tensile strength/fibre-matrix interfacial shear strength) ratio if optimum utilisation of the fibre strength is to be obtained. Thus, if the fibres are strong, the fibre-matrix interface must also be strong if geometrical limitations on the fibre shape are not to be severe.

Ceramics such as alumina are not readily wetted by liquid metals, and it is frequently assumed that non-wetted interfaces (contact angle > 90°) will be weak. Many reports have appeared presenting the results of programmes employing techniques such as ceramic surface metallising and liquid metal alloying with reactive metals which were undertaken in an effort to improve the wetting and bonding behaviour of particular systems. However, it has not been established that non-wetting interfaces are necessarily weak, and there is in fact some evidence to the contrary. In a previous investigation [1] data were obtained for three metal/alumina systems (spectroscopically pure copper and nickel and high conductivity copper bonded to AL23 grade alumina) which had contact angles in excess of 90° and yet possessed good interfacial strengths.

The objective of the present programme was to examine the correlation between the wetting and the bonding behaviour of non-wetting metal/alumina systems. Accordingly, the contact angles and interfacial strengths of six more systems were determined and used in conjunction with the data already available.

2. Experimental Techniques

The metals employed in the programme were all spectroscopically pure and obtained from Johnson Matthey Ltd, Hatton Garden, London. The ceramic was in the form of Degussit AL23 alumina plaques, with a purity of more than 99.5% and free from siliceous binding agents, obtained from Degussa, Frankfurt/Main, West Germany.

The experimental specimens were produced by melting small cylinders, with diameters and heights of approximately 0.3 and 0.5 cm, on the alumina plaques in a vacuum-furnace. The metal cylinders were ultrasonically cleaned in methyl alcohol for 5 min, and dried with a hot air blast before insertion into the vacuum chamber. The vacuum at the specimen preparation temperature was always better than 3×10^{-5} torr and the specimens were degassed by holding at 200 to 300° C below the metal melting point for 30 min after the initial pump-down. Various superheat temperatures and times were employed with each system to produce sessile drops with differing contact angles. The furnace power was then switched off and the specimens removed from the furnace after they had cooled to room temperature.

The dimensions of the solidified drops were measured with a Baker travelling microscope, and their "contact angles" were derived from the dimensions by assuming the drop surfaces to be spherical. In some instances, the "contact angles" were measured directly but no significant difference was found between these values and those derived from the drop dimensions. Furthermore, there was little difference, less than 3°, between the "contact angles" of the solidified drops and the true contact angles measured at the preparation temperatures. The "contact angles", therefore, were used as a measure of wetting behaviour and measurements of the contact angles at the preparation temperatures were not made as a routine matter.

Interfacial strengths were assessed by placing the specimens in a shearing jig attached to a Hounsfield Tensometer and measuring the load needed to push the drop off the plaque. If the samples parted at the metal-ceramic interface, the bond strength was calculated simply by dividing the failure load by the interfacial area. The criterion of interfacial failure was that the metal fracture surface should appear to be free from adherent alumina to the unaided eye.

Seventy of the samples produced failed at their interfaces, and therefore, yielded valid bond strengths which could be compared with their wetting behaviour. Fifty-five differing preparation routes were used in the production of these samples. The full details of the routes have been given elsewhere [2], and table I gives an idea of their diversity.

3. Experimental Results

The experimental measurements of the interfacial strengths were such that the metals could be classified into three groups: (i) aluminium, gold, iron and silver, (ii) cobalt and uranium, and (iii) palladium. For clarity and conciseness the results obtained for each group will be presented in sequence.

The common characteristic of aluminium, gold, iron and silver is that they all consistently formed strong interfaces with the alumina plaques. The actual values of the bond strengths measured were markedly dependent on the "contact angles" of the individual samples as shown in fig. 1. This marked dependence at contact angles in excess of 105 to 110° was expected on the basis of a stress analysis of the push-off strength test published previously [1]. This analysis showed that the interfaces will fail in tension if the "contact angle" is greater than about 105 to 110° and that the bond strength, B, is related to the "contact angle", θ, by the expression,

$$B = 0.25U \cot(\theta - 90) \qquad (1)$$

where U is the tensile strength of the interface. At "contact angles" lower than about 105 to 110°, the bond strength will equal S, the shear strength of the interface, and be independent of the size of the angle. The experimental results are in qualitative agreement with the predictions of this stress analysis. The agreement was tested quantitatively by selecting U values which could be substituted into equation 1 to give a reasonable fit to the actual experimental bond strength values. The full lines drawn through the experimental data in fig. 1 were derived in this manner

TABLE I Summary of preparation routes.

Metal	Range of preparation		Preparation route producing the	
	Temperatures (°C)	Times (min)	maximum contact angle	minimum contact angle
Ag	980-1070	15-25	980° C, 15 min	1070° C, 15 min
Al	670-1018	5-15	670° C, 15 min	1018° C, 5 min
Au	1090-1416	1-15	1090° C, 1 min	1416° C, 15 min
Co	1513-1624	15	1513° C, 15 min	1624° C, 15 min
Fe	1550-1624	1-25	1550° C, 1 min	1624° C, 15 min
Pd	1580-1621	5-25	1603° C, 5 min	1617° C, 13 min
U	1200-1600	5-15	1200° C, 5 min	1600° C, 15 min

using the U values presented in table II. (Previously published U values for spectroscopically pure copper and nickel, and high conductivity copper bonded to AL 23 alumina, are included in the table to extend the range of metals for which comparisons and data analyses will be presented later.)

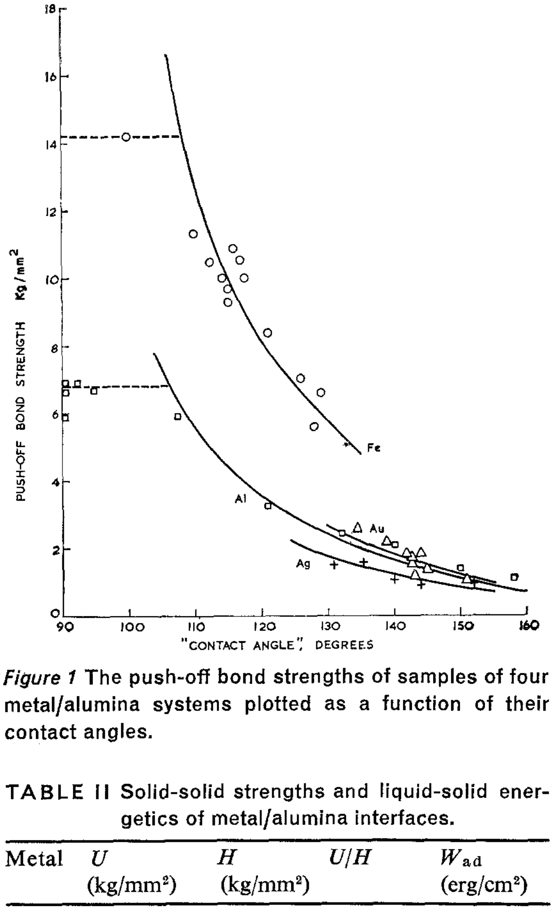

Figure 1 The push-off bond strengths of samples of four metal/alumina systems plotted as a function of their contact angles.

TABLE II Solid-solid strengths and liquid-solid energetics of metal/alumina interfaces.

Metal	U (kg/mm^2)	H (kg/mm^2)	U/H	W_{ad} (erg/cm^2)
U	0	203	0	429
Co	0→5.40	141	0→0.038	619
Pd	0→9.05	52.2	0→0.174	477
Ag	5.80	34.5	0.168	100
Cu	7.40	58.1	0.127	166
H.C.Cu	8.70	60.3	0.144	475
Au	8.80	32.4	0.272	114
Al	9.15	19.5	0.470	63
Ni	11.85	95.1	0.124	962
Fe	19.15	84.3	0.227	603

Although iron/alumina interfaces have a U value more than three times larger than that for silver/alumina interfaces, iron is far stronger than silver, and therefore the greater strength of the iron/alumina interfaces does not necessarily reflect a greater interfacial perfection. Two approaches were made in attempts to rank metals in the order of the efficiency with which they formed interfaces: (i) the metal fracture surfaces were examined for evidence of deformation and (ii) the Vickers diamond hardnesses, H, of the metal drops were measured and the U/H ratio used as an indication of relative interfacial strength. The aluminium fracture surface shown in fig. 2 is so heavily deformed that it suggests that failure occurred within the metal rather than at the interface, but the fracture surfaces of the other samples were not heavily deformed and had structures reminiscent of the alumina plaques. The U/H ratios listed in table II also show aluminium to differ from the other metals, having a ratio of nearly twice that of any of the other metals.

The second group of metals, cobalt and uranium, were virtually non-adherent. Thirteen cobalt samples were produced with "contact angles" ranging from 131 to 115° but only three were adherent and even these had the relatively low U values of 1.85, 2.15, and 5.40 kg/mm^2. Six uranium samples were produced with "contact angles" ranging from 132 to 72°, but none were adherent. Although greatly different in interfacial strength characteristics, the cobalt and uranium fracture surfaces resembled those of the adherent metals. The topography resembled that of the surface of an alumina plaque, and there was no indication that voids had been present at the metal/alumina interface. The low interfacial strengths of the cobalt/ and uranium/alumina samples were not unexpected because the metals undergo a martensitic transformation on cooling [3]. If these transformations caused the non-adherence, the drops should have been adherent at an elevated temperature and should have become non-adherent only when cooled to some particular temperature. This possibility was examined in a series of experiments in which an invertible specimen platform was placed inside the vacuum-furnace. This platform could be rotated through 180° from time to time as the specimen was cooled, thus subjecting it to a tensile stress of about 5×10^{-5} kg/mm^2 (drop weight divided by interfacial area). Seven experiments were performed with cobalt-alumina samples cooled at a rate of 5 to 10° C/min; one sample was still adherent at room temperature and the others became non-adherent at 210, 150, 135, 130, 125, and 120 °C.

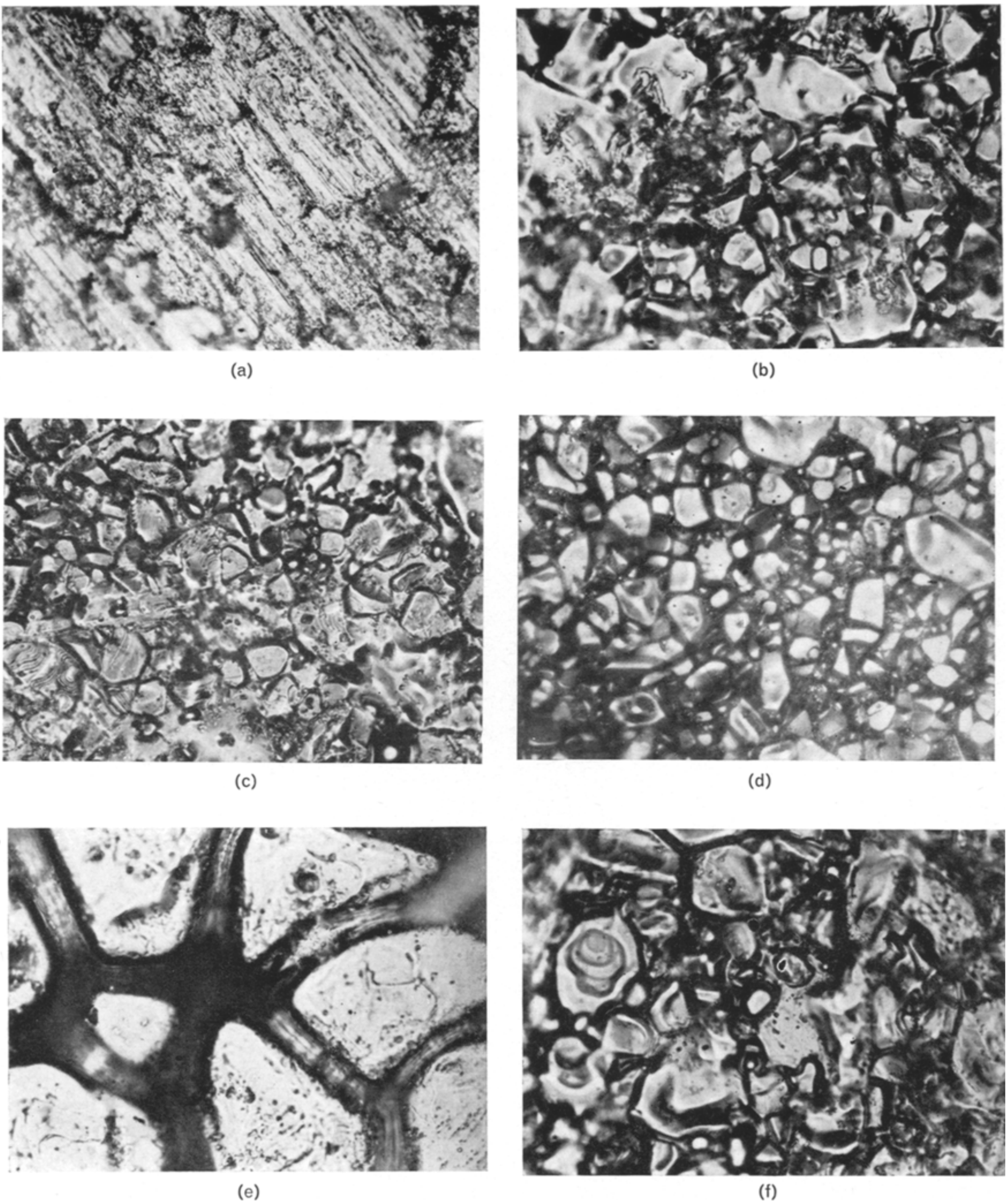

Figure 2 Fracture surface structures of several metal/alumina systems (× 632). (a) Aluminium; (b) iron; (c) silver; (d) alumina; (e) palladium, $U = 0$ kg/mm^2; (f) palladium, $U = 9.05$ kg/mm^2.

The behaviour of the palladium/alumina samples was unique. Thirteen samples were produced with "contact angles" ranging from 133 to 104°. Seven samples were non-adherent, and the other six had bond strengths which yielded values for U of 0.76 to 9.05 kg/mm^2. The average value of U was 5.45 kg/mm^2. A correlation was found between the strengths of the individual samples and the appearance of their metal fracture surfaces. The seven non-adherent samples had many large voids at the metal-alumina interfaces, but the palladium fracture surfaces of the six strong samples were nearly void-free and resembled the topography of the alumina plaque surfaces, fig. 2. The reason for the lack of contact of the non-adherent samples is not known but the void shapes suggest gas evolution. A similar effect was noted with palladium-sapphire samples.

4. Discussion

The objective of this study was to examine the possibility of a correlation between the wetting and bonding behaviour of metal/alumina systems. The basis of this correlation is the assumption that the work needed to separate an interface is equal to W_{ad}, the work of adhesion on the interface. W_{ad} is defined by the equation

$$W_{\mathrm{ad}} = \sigma_{\mathrm{A}} + \sigma_{\mathrm{B}} - \sigma_{\mathrm{AB}} \qquad (2)$$

where σ_{A} and σ_{B} refer to the surface energy of components A and B and σ_{AB} to the energy of their interface. The assumption, therefore, implies that no work is consumed in the deformation of the components during the separation, a condition which is unlikely to be satisfied in practice. Values for σ_{AB} are known for very few solid-solid interfaces, and, therefore, it has been argued that W_{ad} values for temperatures just above the metal melting point can be used as an approximation. If component A is liquid, equation 2 can be rewritten as

$$W_{\mathrm{ad}} = \sigma_{\mathrm{A}} (1 + \cos \theta) \qquad (3)$$

Equation 3 has been taken as implying that non-wetting systems, for which $\cos \theta$ is negative, will have weak interfaces.

The data presented in table II in fact show that non-wetting systems can form strong interfaces, and therefore, that this simplified approach is invalid. This lack of correlation is emphasised by comparing the U and liquid-solid W_{ad} values presented in the table. There is, at best, only a general trend discernible. The W_{ad} values were calculated using literature values for σ_{A} [4, 5] and the highest values of the "contact angles" mentioned in the text or plotted in fig. 1.

While a correlation between wetting and bonding seems lacking there does appear to be a qualitative correlation between the bonding behaviour of the various systems and the structural stability of the appropriate metals. Cobalt and uranium are polymorphic and subject to martensitic transformations. It is likely that the shear associated with the transformations will stress the interfaces severely, and this could account for their weakness and even non-adherence. The invertible platform experiments showed that cobalt/alumina samples were adherent at high temperatures and that the temperature at which non-adherence occurred was low and fairly reproducible. This behaviour is consistent with the hypothesis that a martensitic transformation was responsible for the non-adherence even though it is not proof.

All the other metals were capable of forming strong interfaces with alumina. Before discussing the group as a whole, special comments need to be made about the palladium and iron data. Some palladium samples were non-adherent and contained many large voids at their interfaces. The strongest samples that had void-free interfaces, however, had strengths and U/H ratios that fell well within the range found for the other monomorphic metals. Like cobalt and uranium, iron is polymorphic and can undergo a martensitic $\gamma \rightarrow \alpha$ transformation. Bibby and Parr [6] found that a cooling rate of 35000° C/sec was needed to induce such a transformation in Johnson-Matthey spectroscopically pure iron. The cooling rate through 900° C was only about 1° C/sec in the present work, so the $\gamma \rightarrow \alpha$ transformation will have proceeded by a process of nucleation and diffusion-controlled growth, and the iron/alumina interfaces will not have been subjected to severe shearing stresses during cooling.

Eight of the ten systems evaluated in this and the previous study can form strong interfaces. Seven of these, the exception being aluminium, have U/H ratios lying between 0.124 and 0.272, with an average value of 0.177. Since the yield strength of a metal is approximately one-third of its Vickers hardness, the interfaces had, on average, a strength of half of the yield strength of the bulk metal.

The fact that interfacial failure occurred at stresses apparently too small to produce yielding within the metal is consistent with the metallographic appearance of the fracture surfaces. This similarity in the U/H ratios suggests that the various metal/alumina interfaces have a similar degree of perfection. By analogy, the grain-boundary/surface energy ratios of many face-centred cubic metals lie between 0.25 and 0.37 owing, it can be argued, to a similar extent of lattice disarrangement at the grain-boundaries.

The exception to this general pattern of behaviour, aluminium, has a U/H ratio of 0.470, indicating that U is approximately one-and-a-half times the metal yield strength. Even this high value is probably not a true reflection of the strength of aluminium/alumina interfaces because the fracture surfaces suggested that failure may have occurred within the metal rather than at the interface. The reason for this high U/H ratio, and, presumably, great interfacial perfection, is not known, but is consistent with the tenacity of naturally-formed oxide films on aluminium and the absence of interfacial separation in push-off strength tests performed by Wolf, Levitt, and Brown [7] on aluminium/sapphire samples.

While there does not appear to be a correlation between wetting and bonding behaviour for metal/alumina systems, there is some evidence of a correlation between the U values and W_{ad} values for solid-solid interfaces. Pilliar and Nutting [8], and Williams and Greenough [9] have reported W_{ad} values for a few solid-solid metal/alumina interfaces. These are listed in table III.

TABLE III The work of adhesion, W_{ad}, of solid-solid metal/alumina interfaces.

Metal	Environment	Temp (°C)	W_{ad} (erg/cm^2)	Ref.
Ag	H_2	700	435	8
Cu	H_2	850	475	8
Au	Air	1000	530	8
Ni	H_2	1000	645	8
	Ar	1400	518	9
Fe	H_2	1000	810	8

The difference in the W_{ad} value for nickel/alumina interfaces found by the two sets of workers is relatively small and probably due to the different experimental environments employed. Pilliar and Nutting's values rank the systems in the same order as the U values in table II, but this agreement must be viewed with considerable reserve because it is unlikely that surface and interfacial energy effects as such play a dominant role in room temperature fracture processes. Hull *et al* [10], for example, have shown that the work needed to fracture notched tungsten rods at room temperature is two to three orders of magnitude greater than the associated increase in surface and interfacial energy. Nonetheless, the apparent correlation is interesting and may be another indication that the various metal/alumina interfaces were of comparable perfection. Further comparisons should be made when additional data become available.

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References

1. M. NICHOLAS, R. FORGAN, and D. M. POOLE, *J. Materials Sci.* **3** (1968) 9.
2. M. NICHOLAS, AERE report R5681 (1968).
3. J. W. CHRISTIAN, "Phase Transformations" (Oxford University Press, Oxford, 1966).
4. O. FLINT, *J. Nucl. Matls.* **16** (1965) 233.
5. B. C. ALLEN, *Trans. Met. Soc. AIME* **227** (1963) 1180.
6. M. J. BIBBY and J. G. PARR, *J. Iron Steel Inst.* **202** (1964) 100.
7. S. M. WOLF, A. P. LEVITT, and J. BROWN, *Chem. Eng. Progr.* **62** (1966) 74.
8. R. M. PILLIAR and J. NUTTING, *Phil. Mag.* **16** (1967) 181.
9. D. I. T. WILLIAMS and A. P. GREENOUGH, *Powder Met.* **10** (1967) 318.
10. D. HULL, P. BEARDMORE, and A. P. VALENTINE, *Phil. Mag.* **12** (1965) 1021.