

The wetting and bonding behaviour of some nickel alloy-alumina systems

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The effect of concentration on the wetting and bonding behaviour between nickel alloys and AL23 alumina or sapphire substrates has been investigated. The addition of 1 wt% chromium or 0.1 wt% yttrium produces a decrease in contact angles at 1570° C but not sufficient to cause wetting. Additions of up to 1 or 2 wt% chromium or 0.02 or 0.08 wt% yttrium improves the bonding between nickel and AL23 or sapphire respectively, but further additions cause a weakening. AL23 is less wetted but more strongly bonded than sapphire to the various alloys. The results are discussed in terms of possible correlations and their relevance to models of metal-ceramic interactions.

1. Introduction

This paper discusses the wetting and bonding behaviour of nickel-chromium and nickel-yttrium alloys with alumina and sapphire. The properties of such interfaces are of interest because of the role of metal-ceramic interactions in the development of alumina fibre-reinforced and dispersion-strengthened nickel alloy matrix materials for use in the aerospace and other high technology industries. Chromium and yttrium were chosen as the alloying elements to be used in this investigation because nickel-chromium alloys are the basis of most of the current range of nickel base super alloys and yttrium additions have markedly beneficial effects on the adhesion of alumina surface films formed, for example, on Fecralloy at high temperatures.

Several workers have investigated metal/alumina or metal/sapphire wetting and bonding behaviour and their conclusions are in broad agreement. Nickel does not wet alumina or sapphire at 1450 to 1600°C, contact angles in excess of 100° having been measured during studies conducted in vacuum or oxygen-free environments (e.g. [1-5]). However, wetting may be induced by alloying the metal with certain oxide-forming elements. McDonald and Eberhart [6] developed a model based on these observations in which the thermodynamic work of adhesion of the interface, which is a

function of wettability, was related to the oxide forming tendency of the added metal. Alloying with reactive metals also affects the (room temperature) strengths of solidified metal-alumina interfaces. In general it is observed that increasing the concentration of the reactive element at first strengthens, but ultimately weakens, the interfaces [7-9]. In earlier work one of the present authors found that maximum bond strengths of a number of alumina/nickel alloy interfaces were related to the reactivity of the alloying element and that the concentration at which the best bonding was achieved was similar to that at which the element most markedly affected wetting behaviour [9]. Thus there is some evidence to suggest that the McDonald and Eberhart model may also be relevant to bonding behaviour.

The objective of the work described in this paper is to extend the range of available information so that the emerging models of oxide-metal interaction processes can be tested more thoroughly. Data have been presented previously for the nickel-chromium/polycrystalline alumina system [1-9], and this paper presents similar information for the nickel-chromium/sapphire and nickel-yttrium/polycrystalline alumina or sapphire systems.

2. Materials and methods

The alumina used in this work was in the form of 20 mm diameter discs of AL23, which is silica-free and 99.5% pure, obtained from Degussa, Frankfurt/Main. The sapphire discs were smaller, with diameters of 10 mm, and were obtained from English Electric Ltd, Stafford. Nickel and chromium of spectroscopic purity and 99.8% pure yttrium were employed.

The sessile drop technique was used to evaluate wetting behaviour, to derive liquid surface energies and to produce samples for bond strength studies. In this technique, a small liquid drop rests on a horizontal substrate surface and the wetting behaviour is measured by direct observation of the contact angle subtended at the drop periphery by the liquid surface and the solid-liquid interface. Refined measurements of the drop profile enable liquid surface energy values to be derived. The room temperature strength of the interface created by the technique can be measured using the Sutton "push-off" test.

The vacuum furnace used to conduct the sessile drop experiments and the various manipulative techniques employed have been described previously in some detail [10-12]. Briefly, a ceramic disc was placed on a horizontal platform in the furnace chamber and the metal sample positioned on the ceramic so that it could be viewed, illuminated and photographed through diametrically opposed observation ports. The metal samples were in the form of small hollow nickel cylinders holding various amounts of chromium or yttrium which alloyed with the nickel when the sample melted. After loading, the furnace chamber was evacuated to a pressure of 1×10^{-5} mm of mercury and power supplied to the heating element to degas the sample by slowly raising the temperature to 1250 to 1300°C for 30 min. The temperature was then raised to 1570°C for 15 min, which previous work indicated to be sufficiently long for complete alloying and interfacial equilibrium to be achieved [13].

Contact angle and surface energy data were derived from photographs of the molten drops taken using a Nikon F 35 mm camera. The contact angles were measured quite simply using the rotating screen attachment of a Nikon CT6 projector and surface energy values were calculated from drop profile dimensions using the Bashforth and Adams method and tables [14]. Interface tensile strength values were calculated from the results of

Sutton push-off tests using the stress model developed to take account of sample shape variations caused by different degrees of wetting [12].

3. Experimental results

3.1. Nickel-chromium alloys

The contact angles between sapphire and nickel alloys containing up to 10 wt% chromium are presented in Fig. 1 and compared with data previously obtained for AL23 alumina [9]. The contact angles assumed on sapphire were unaffected or very slightly increased by alloying with up to 1 wt% chromium but a small decrease occurred with further additions. The behaviour found for AL23 substrates was similar but more marked, the low chromium alloys assuming larger contact angles and the decrease associated with additions of more

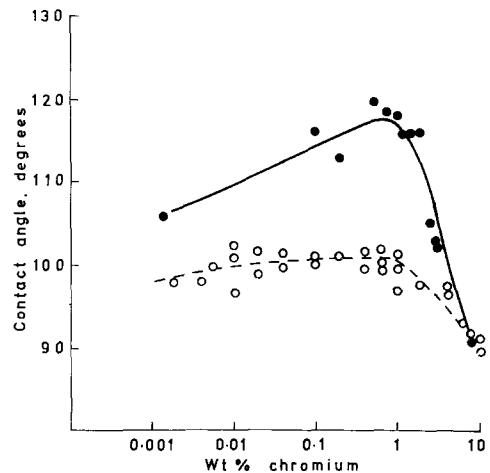


Figure 1 The effect of chromium on the wetting of AL23 (●) or sapphire (○) by nickel.

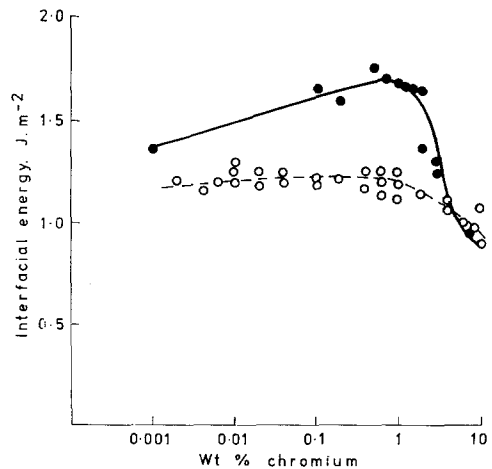


Figure 2 The effect of chromium on the interfacial energy between nickel and AL23 (●) or sapphire (○).

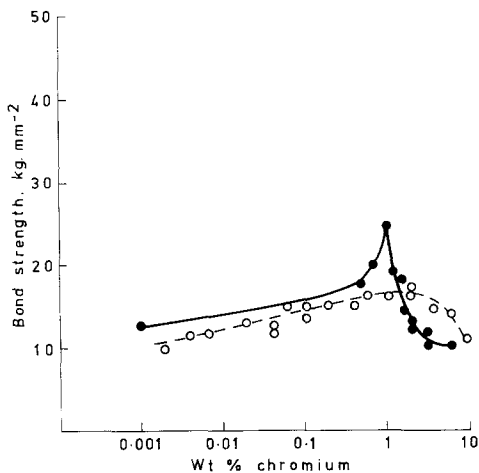


Figure 3 The effect of chromium on the bonding between nickel and AL23 (●) or sapphire (○).

than 1 wt% chromium being correspondingly greater. Published values for the surface energy of Al_2O_3 [15] and liquid nickel–chromium alloys [16] were used to calculate interfacial energies shown in Fig. 2 by substitution in the Young–Dupre equation. The variation in these energies with the chromium contents of the alloys closely resembles that observed previously for contact angle values.

The effects of alloying on the room temperature strength of sapphire–solidified metal interfaces are shown in Fig. 3. The bond strength values increased from 10 kg mm^{-2} for pure nickel to 17.5 kg mm^{-2} for a nickel–2wt% chromium alloy and then decreased to 11 kg mm^{-2} for a nickel–10wt% chromium alloy. These changes are similar to those observed for alloys in contact with AL23 [9], although the maximum bond strength attained is lower and the optimum chromium content is somewhat higher. The change from strengthening to weakening with increasing chromium concentration was accompanied by a greater tendency for the samples to fracture within the sapphire, although all the values plotted in Fig. 3 relate to true interfacial failures. As the concentration of chromium increased, so did the plastic deformation of the metal prior to interface separation and the erosion of the sapphire.

3.2. Nickel–yttrium alloys

The experimental observations made with these alloys were qualitatively similar to those reported for the nickel–chromium alloys. The contact angles assumed by molten drops on both substrates increased with very small additions of yttrium but

noticeably decreased when concentration exceeded 0.08 wt%. The angles were larger for sessile drops on AL23 than on sapphire substrates, and the angular decrease at 0.08 wt% yttrium was also larger as shown by Fig. 4. Careful measurements of the sessile drop profiles revealed that additions of more than 0.01 wt% yttrium reduced the liquid drop surface energy values by about a third to approximately 1 J m^{-2} as shown in Fig. 5. These data were then used with the angular values referred to previously to calculate the interfacial energies of the various samples. Fig. 6 shows that the variation of this energy with yttrium concentration differed for the two substrates. The values for interfaces formed with sapphire substrates decreased very slowly as the yttrium concentration was increased to 0.08 wt%, but a further increase

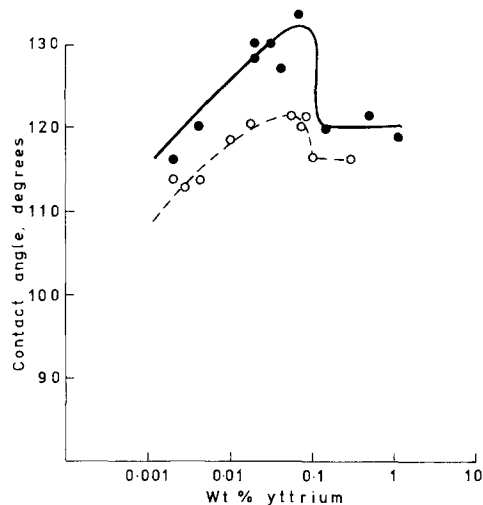


Figure 4 The effect of yttrium on the wetting of AL23 (●) or sapphire (○) by nickel.

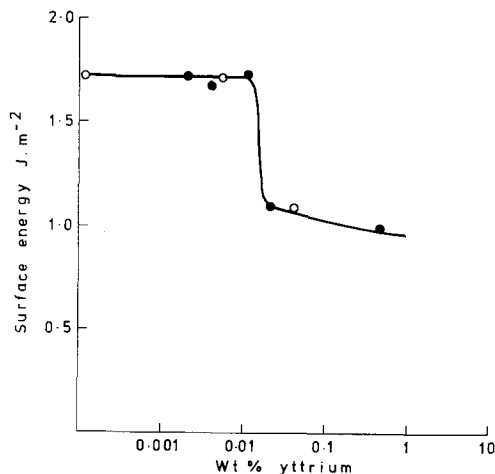


Figure 5 The effect of yttrium on the surface energy of nickel when in contact with AL23 (●) or sapphire (○).

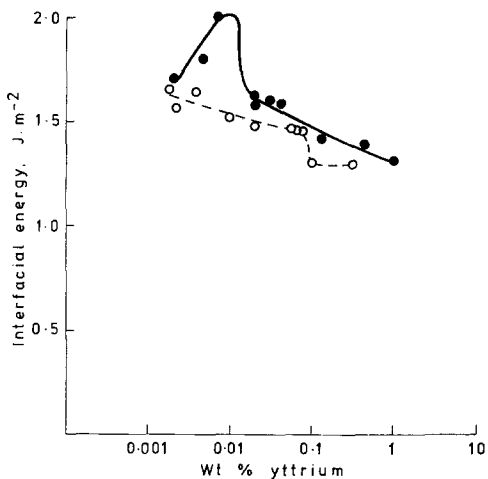


Figure 6 The effect of yttrium on the interfacial energy between nickel and AL23 (●) or sapphire (○).

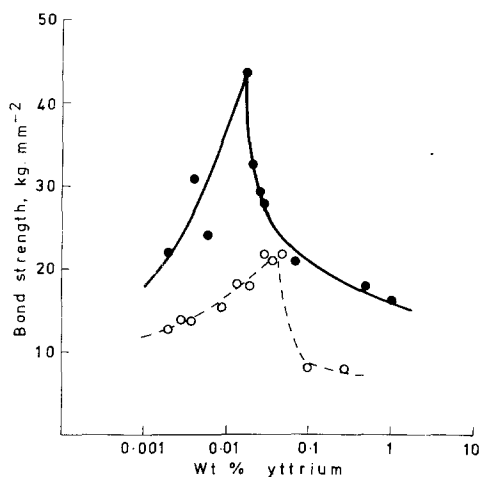


Figure 7 The effect of yttrium on the bonding between nickel and AL23 (●) or sapphire (○).

to 0.10 wt%, reduced the value by a small but detectable amount. In contrast, the energies of interfaces formed with AL23 substrates became larger as the yttrium concentration was increased to 0.007 wt%, but a further increase to 0.02 wt% markedly reduced the energy value.

The room temperature strengths of interfaces formed with sapphire increased from 12.5 to 22 kg mm⁻² as the yttrium content of the nickel was increased from 0.002 to 0.06 wt%, and thereafter decreased. As shown in Fig. 7 this effect of yttrium concentration occurred in a more marked form with samples produced using AL23 substrates the strength values peaking at 44 kg mm⁻² when a nickel-0.018 wt% yttrium alloy was used.

4. Discussion

The results obtained for the four material combinations compared in this programme are reasonably self-consistent and in broad agreement with the data reported or conclusions drawn previously. Thus the addition of the reactive alloying elements chromium or yttrium brought about steplike improvements in the wetting behaviour at well defined compositions. The improvement in the case of the chromium alloys occurred at concentrations of 1–2 wt% which is comparable to the 1–8 wt% found by other workers using vacuum or inert atmospheres [8, 16, 17]. Yttrium is far more oxygen active than chromium and produced improvements when present in far lower concentrations, only 0.08–0.10 wt%. No directly comparable literature data for yttrium additions are known, but it may be relevant that titanium, which is also more oxygen active than chromium, produces improvements in wetting when present at concentrations of less than 1 wt% [8, 16, 17].

Limited comparisons can be made also for the interfacial strength data. Thus the chromium concentrations producing the strongest bonding, approximately 1 wt% with AL23 substrates [9] and 2 wt% with sapphire substrates, which are similar to previously reported values of 1–5.3 wt% for sapphire substrates [7, 8, 17] although the strength levels differ. No direct comparison is possible for nickel–yttrium alloys, but the production of very strong bonds obtained with the optimum alloying addition is consistent with the high oxygen affinity

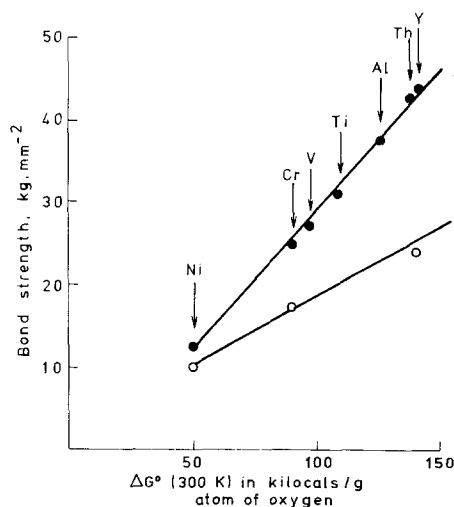


Figure 8 Correlation between the chemical reactivity of alloying additions and the maximum strengths of bonds formed by nickel-base alloys with AL23 (●) or sapphire (○).

of yttrium as shown by Fig. 8 which also includes data from [9].

The results obtained in this programme have shown that the contact angles assumed by the non-wetting drops were larger and the bonds formed were stronger with AL23 than with sapphire substrates. These differences could be due to the effects of small unidentified, compositional variations but another possible explanation is that they are reflections of the differing roughnesses of the two substrates. Comparison of the wetting and bonding data suggest that the roughness (actual surface area/nominal surface area) of the AL23 alumina samples could be 20 to 90% greater than that of the sapphire samples. This estimate received some support from the results of Talystep I direct contact stylus measurements that showed AL23 alumina samples to have a linear roughness 30 to 40% greater than that of sapphire samples.

In previous work with AL23 substrates, an empirical correlation was observed between the alloying concentrations needed to produce maximum bonding and improvements in wetting behaviour. This same correlation seems valid for the new data obtained for sapphire/nickel–chromium samples, but the data for nickel–yttrium alloy bonding presented in Figs. 4, 6 and 7 suggest that a better and more meaningful correlation can be obtained with the concentrations causing a change in interfacial energies. The establishment of such a correlation would strengthen the emerging pattern that relates that effect of alloying additions to changes in the wetting and bonding behaviour of metal/ceramic systems and lends support to the suggestion that the McDonald and Eberhart model [2] is relevant to both the thermodynamic work of adhesion and the practical adhesive strength.

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References

1. B. E. ALLEN and W. D. KINGERY, *Trans. Met. Soc. AIME* **215** (1959) 30.
2. W. H. ARMSTRONG, A. C. D. CHAKLADER and J. F. CLARKE, *J. Amer. Ceram. Soc.* **45** (1962) 115.
3. V. N. EREMENKO, V. I. NIZHENKO and N. I. SKLYARENKO, *Sov. Powder Met. Ceram.* **5** (1965) 372.
4. M. HUMENIK and W. D. KINGERY, *J. Amer. Ceram. Soc.* **37** (1954) 18.
5. V. I. TUMANOV, V. F. FUNKE and L. I. BELENKAYA, *Zh. Fiz. Khim.* **36** (1962) 1574.
6. J. E. McDONALD and J. G. EBERHART, *Trans. Met. Soc. AIME* **233** (1965) 512.
7. W. H. SUTTON, Report R-64 SD44, G. E. Space Sciences Lab., U.S.A. (1964).
8. J. E. TITTER and M. S. BURTON, *Trans. Met. Soc. AIME* **239** (1967) 21.
9. M. NICHOLAS, *Sci. Ceramics* **5** (1969).
10. M. NICHOLAS and D. M. POOLE, AERE-R4843 (1965).
11. E. N. HODKIN, D. A. MORTIMER, M. NICHOLAS and D. M. POOLE, *J. Nuclear Mat.* **39** (1971) 59.
12. M. NICHOLAS, R. FORGAN and D. M. POOLE, *J. Mater. Sci.* **3** (1968) 9.
13. M. NICHOLAS, AERE-R5961 (1968).
14. F. BASHFORTH and I. C. ADAMS, "An attempt to test theories of capillary action" (University Press, Cambridge, 1883).
15. W. D. KINGERY, *J. Amer. Ceram. Soc.* **37** (1954) 42.
16. C. R. KURKJIAN and W. D. KINGERY, *J. Phys. Chem.* **60** (1956) 961.
17. P. GRENIER and M. MARCHAL, *Rev. de Met.* **65** (1968) 345.

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