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The Solid State Bonding of Nickel, Chromium and Nichrome Sheets to α-Al_2O_3

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This paper describes experiments to measure the interfacial shear strengths of bonds formed between nickel, chromium and nichrome sheets hot pressed on to α-Al_2O_3 single crystal plaques. Nickel developed bonds of $\sim 8 \times 10^3$ psi (56 MN. m^{-2}) in shear when pressing was carried out under non-reducing conditions at 1100° C, 1 tsi (15 MN. m^{-2}) for 2 h: in the case of chromium, the effect of pressing temperature (1000 to 1300° C) pressing pressure ($\frac{1}{2}$ to 3 tsi [7.7 to 45 MN. m^{-2}]) and pressing time ($\frac{1}{2}$ to 7 h) on the bond was investigated. Nickel-chrome alloys produced from alternate nickel and chromium strips showed bond strengths up to 20×10^3 psi (140 MN. m^{-2}) whilst commercial nickel-chrome (containing a silicon impurity) was not as effective in bonding to alumina. In material prepared from alternate strips of nickel and chromium, the degree of alloy homogenisation was investigated using microprobe analysis and suggestions made as to the mechanism of the interfacial reactions with alumina.

1. Introduction

Alloys of nickel and chromium of all the metals offer the highest inherent resistance to oxidation at elevated temperature. A prerequisite of the use of such materials as matrices in high temperature composites is to investigate the extent of bonding with suitable refractory reinforcements. Such a study is reported in this paper, which in particular describes experiments designed to measure the bond strength developed between diffusion couples of nickel, chromium and nichrome in contact with alumina crystals. These experiments were designed to simulate the chemical stability conditions at the metal-alumina interface in composites prepared from these constituents and involving alumina as a reinforcing fibre. The couples were bonded using a hot pressing technique, since most dispersion hardened products are manufactured via a powder metallurgy route and a possible method of producing fibre reinforced composites is by hot pressing bundles of metallised whiskers.

2. Experimental Procedure

2.1. Preparation of Nickel, Chromium and Nichrome Sheet

2.1.1. Nickel Sheet

Nickel sheet was prepared in thicknesses of 0.025 to 0.254 mm by the thermal decomposition of nickel carbonyl ($Ni(CO)_4$) onto glass microscope slides. The deposited nickel could be stripped from the glass slide by filing away the excess of nickel which had grown around the edges of the slide allowing the nickel coating to roll away from the glass substrate.

2.1.2. Chromium Sheet

Chromium sheet in the form of discs has been directly produced electrolytically using a sulphuric-chromic acid electrolyte (chromic acid: sulphuric acid:citric acid in the ratio 100:1:1). The cathode of the cell was comprised of a copper sheet with its surface masked by a perspex sheet with the exception of holes 1.27 cm diameter. The cell produced several discs of chromium 0.0189 to 0.0508 mm thick during each run. This cell was developed to produce chromium discs directly in view of the very brittle nature of the electrodeposited film and the difficulty experienced in cutting the discs from deposited sheets. The chromium discs were stripped from the copper cathode by chemical solution of the copper using nitric acid.

2.1.3. Nickel-Chrome Sheet

This sheet was prepared by pressing together

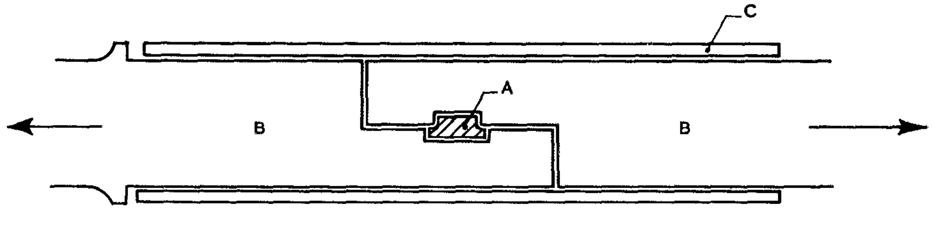

Figure 1 Schematic diagram of the shear testing device.

alternate layers of nickel and chromium sheet (manufactured as described in sections 2.1.1 and 2.1.2) at 1300° C for 2 h in vacuum when complete homogenisation of the alloy occurred (see section 3.3.2). Appropriate quantities of nickel and chromium sheets were used to prepare an 80:20 Ni:Cr composition. A further source of Ni/Cr alloy sheet was from British Driver Harris. This material contained 1.25% Si, 0.35% Fe, 0.03% Mn, and 0.04% C as impurities.

2.2. Preparation of Bonding Couples

The metallic sheets prepared as described in section 2.1 have been bonded between two α-Al_2O_3 single crystal discs* of diameter 12.70, 9.525 mm under pressures between limits of $\frac{1}{2}$ and 3 tsi at temperatures between the limits of 900 and 1300° C under reduced pressure (1 to 10 μm Hg vacuum). Various combinations of the elemental discs have been used together to give the overall Ni—20Cr composition during the bonding operation. The systems that have been studied fall into the following categories:

(1) Al_2O_3—Ni—Al_2O_3
(2) Al_2O_3—Cr—Al_2O_3
(3) Al_2O_3—Ni—Cr—Ni—Al_2O_3
(4) Al_2O_3—Cr—Ni—Cr—Al_2O_3
(5) Al_2O_3—Ni/Cr alloy—Al_2O_3

The difference between categories (3) and (4) is the element in contact with the Al_2O_3 disc (i.e. Ni or Cr), although the overall composition of the layers as a whole was Ni—20Cr in both cases.

Shear testing was carried out in the device illustrated schematically in fig. 1 at room temperature.

3. Results

During the course of experimentation the relevance of several parameters with respect to the interfacial bond strength (temperature, pressure, the metal adjacent to the Al_2O_3 plaques, time, furnace atmosphere) were studied. The distribution of nickel and chromium in the couples prepared from elemental strips was studied, using the electron microanalyser, with respect to the time and temperature of bond preparation. A target figure of 2.5 × 10^3 psi (17.5 MN. m^{-2}) for interfacial bond strength on the basis of the Kelly-Davies equation [1] is proposed.

3.1. Ni-Al_2O_3 Bonding Couples

Bonds between carbonyl nickel and alumina were prepared from 0.050 mm thick nickel films, packed together to give an overall thickness of 0.203 mm and pressed between alumina single crystals. Bonding was carried out in three types of pressing die: (1) all graphite, (2) graphite with alumina inserts and (3) stellite with alumina inserts. These die materials were assumed to promote varying degrees of reducing atmosphere. (CO) in the region adjacent to the bond, (1) being most reducing and (3) being a neutral atmosphere. The effect of the die material was assessed on bonds formed at 1100° C under 1 tsi for 2 h, table I.

TABLE I Effect of die material on bond formation between nickel and alumina

Die material	Range of bond strength (psi)	Average bond strength (psi)
Graphite	0 to 2453 (5 specimens)	709
Graphite-alumina inserts	0 to 6546 (15 specimens)	1324
Stellite-alumina inserts	4090 to 8454 (5 specimens)	7109

Klomp [2] pressing nickel foil onto polycrystalline alumina at 1350° C showed bond strengths in excess of these values [7 to 30 × 10^3 psi (49 to 210 MN. m^{-2})]. This difference may

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*The α-Al_2O_3 single crystals were supplied by Salford Electrical Industries Ltd.

stem from the use of higher bonding temperatures and the polycrystalline nature of the sintered alumina allowing possible mechanical keying at the grain boundaries. Further the purity of the alumina can have a marked effect on bonding and the sintered alumina contained ~ 2000 ppm unspecified impurity (cf 100 ppm impurities in the single crystals).

Previous work [3] has shown that the bond formation between nickel powder compacts and alumina, arises from the interaction between nickel oxide and alumina to form the spinel, $NiAl_2O_4$. It is suggested that if the reducing potential of the bonding environment is lowered then more nickel oxide is available for the spinel reaction and results in the formation of stronger bonds.

3.2. Cr—Al_2O_3 Bonding Couples

Bonds have been produced between alumina and electrolytically deposited chromium as described in sections 2.1.1 and 2.2. In this case, bonding is best carried out under a vacuum of 10 μm; bonds produced in a vacuum of < 1 μm had very low bond strengths. Under a vacuum of ~ 10 μm, sufficient oxygen is present to produce controlled amounts of chromia and cause enhanced bonding due to its solid solubility in alumina. The results are summarised in figs. 2 to 4 in which the bond strength is measured as a function of pressing temperature (1000 to 1300° C), pressing pressure ($\frac{1}{2}$ to 3 tsi) (7.7 to 45 MN. m^{-2}) and pressing time ($\frac{1}{2}$ to 7 h). Generally, the bonding was satisfactory at 1100° C (~ 10 × 10^3 psi) (~ 70 MN. m^{-2}) from the fibre reinforcement aspect, see section 3, although there is a sudden loss of strength at pressures greater than 2 tsi (30 MN. m^{-2}). Increasing pressing, temperature, or pressing time does not lead to large bond strength improvements.

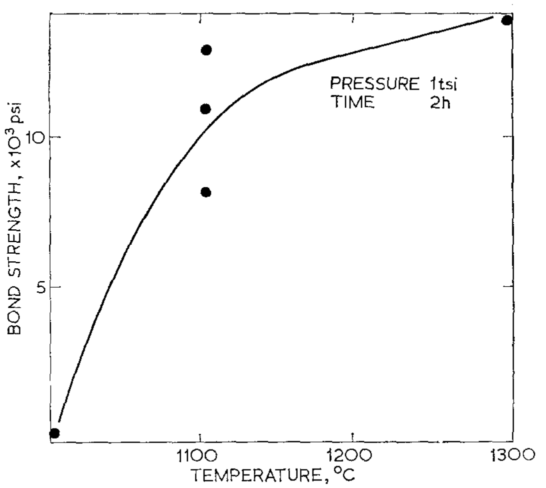

Figure 2 The effect of bonding temperature on the interfacial shear strength between chromium and alumina.

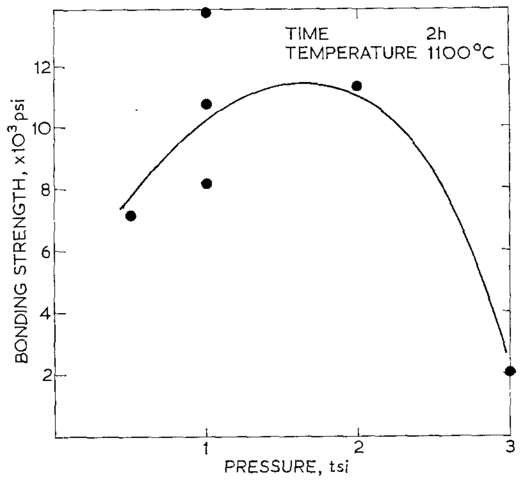

Figure 3 The effect of bonding pressure on the interfacial shear strength between chromium and alumina.

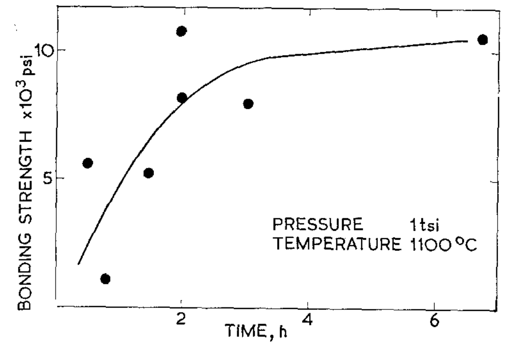

Figure 4 The effect of bonding time on the interfacial shear strength between chromium and alumina.

3.3. Nickel/Chromium—Al_2O_3 Bonding Couples

3.3.1. Bonding

The bonding of nickel-chromium alloy (80 - 20 composition) was carried out in three ways. The first two ways involved the pressing of alternate layers of nickel and chromium sheets between alumina single crystals and differed only in the element placed next to the alumina crystals. It was hoped that during the hot pressing to produce a bond, a homogeneous nickel-chromium alloy would also be produced. This type of approach was designed to simulate the production of nickel-chromium alloy-alumina whisker composites prepared by hot pressing whiskers, sequentially plated with layers of nickel and chromium. The third method involved pressing nickel-chromium alloy sheet (80 – 20) between alumina crystals; the sheets being prepared commercially (ex-British Driver Harris) or by pre-pressing and homogenising layers of nickel and chromium.

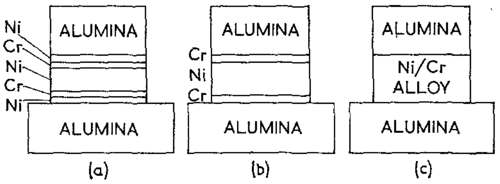

Figure 5 The distribution of nickel, chromium and nichrome sheets between alumina plaques for the bonding of nichrome to alumina.

Fig. 5 shows schematically the configuration of the constituents pre-hot pressing of the three methods referred to above, and fig. 6 summarises the effect of the pressing temperature on the bond strength generated between the alloy and the alumina crystals for these methods.

3.3.2. Studies on Alloy Homogenisation

Bonds of nickel-chrome alloy with alumina prepared by route 1 (section 3.3.1) with the nickel layer adjacent to the alumina crystal have been prepared at 1100, 1200, and 1300° C for pressing times varying from ¼ to 5 h. The specimens have been sectioned normal to the bond and the chromium content monitored across the bonded region using microprobe analysis. Fig. 7 shows the results of this investigation. After 2 h pressing at these three temperatures only the bond region of the specimen manufactured at 1300° C showed any semblance towards alloy homogeneity. After 5 h holding at temperature at 1200° C alloy homogenisation results, whereas lowering the time to ¼ h at 1300° C does not allow sufficient time for homogenisation to occur.

An interesting feature of these curves (fig. 7) is the very high chromium concentrations occurring at the alumina/matrix interface after 2 h at 1200° C. This concentration effect seemingly defies the laws of diffusion since the concentration of chromium at the interface (originally zero) is much higher than at the original position of the chromium layer. This "uphill" diffusion effect can only have arisen by the chromium at the interface having some chemical affinity for the alumina, which maintains the high interfacial chromium concentration, whilst over the rest of the alloy the chromium content evens out to a much lower level. After 5 h at 1200° C and at 1300° C the concentrations at the interface no longer exist; these have probably disappeared

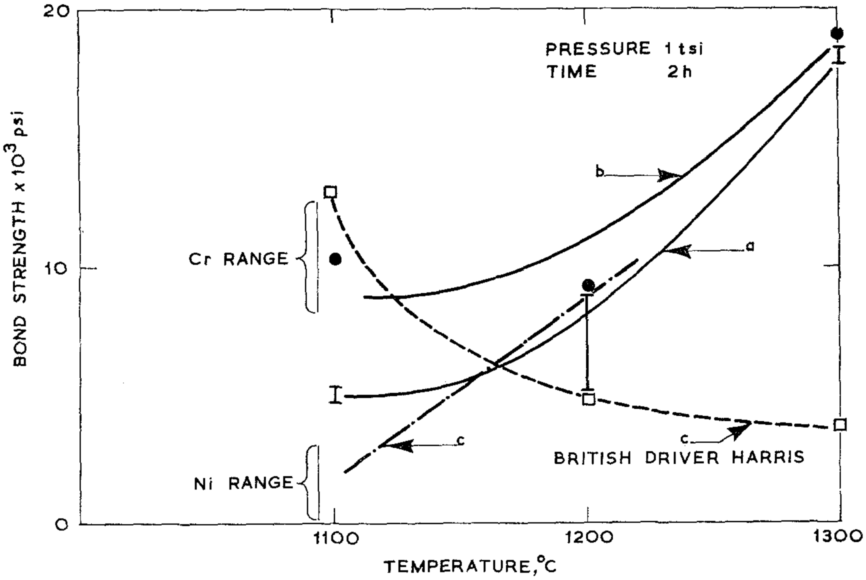

Figure 6 The effect of bonding temperature on the interfacial shear strength developed between nichrome and alumina.

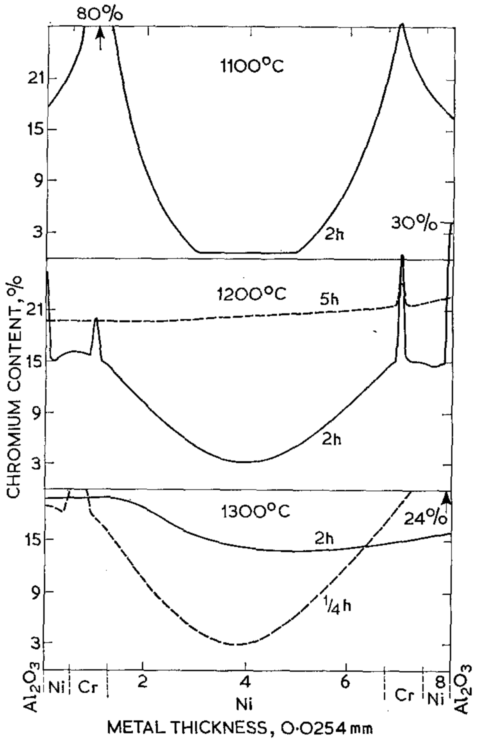

Figure 7 The chromium distribution in nichrome bonded to alumina.

either into the alumina itself to form alumina-chromia solid solution or back into the nickel-chromium solid solution.

4. Discussion

4.1. Bond Strength

The strength of bonds developed between nickel-chromium alloy and alumina crystals, where the nickel-chromium is generated during pressing from alternate nickel and chromium layers, increases with increasing pressing temperature. At 1100° C, there is a marked difference between the alloys, depending on which element (nickel or chromium) is in contact with the alumina crystal. Bonds prepared with chromium in contact with alumina are stronger (10×10^3 psi) (70 MN. m^{-2}) than those with nickel adjacent to the crystal (5×10^3 psi) (35 MN. m^{-2}). This difference is due to the bonding ability of nickel or chromium separately with the alumina, since chromium bonds with strengths varying between 8 to 13×10^3 psi (56 to 90 MN. m^{-2}) and nickel (in graphite dies) bonds with strengths varying between 0 to 3×10^3 psi (0 to 21 MN. m^{-2}). As the identity of the interface changes from nickel or chromium to a nickel-chromium (80 - 20) alloy, with increasing temperature, so the bond strengths of the two configurations increase and run together, with the result that after a 1300° C pressing, the two bond strengths are in the range 19 to 20×10^3 psi (133–130 MN. m^{-2}). For commercial nichrome strip (ex-British Driver Harris) the bond strength decreases rapidly with increasing bonding temperature. Such a decrease is probably a result of the 1.25 % silicon content, in this particular commercial product and results in gross attack on the alumina, weakening the alumina and thus causing a weak bond zone.

4.2. Interfacial Reactions

Using the microanalyser, large concentrations of chromium at the alumina/matrix interface have been noted. These concentrations disappear after further annealing, although ingress of chromium into the alumina crystal has not been detected by the microanalysis technique. Due to the finite width of the microanalyser beam ($\sim$ 5 μm), the chromium cannot have penetrated the alumina to a greater depth, otherwise a positive identification would have been possible. It is therefore suggested that the high chromium concentration diffuses back into the nickel-chromium alloy to produce a homogeneous nickel - 20 % chromium material and that diffusion into the alumina does not penetrate to a greater depth than 5 μm.

It has been noted, in the course of this work that bonding both chromium and nickel-chromium alloy occurs to a greater degree when pressing is carried out under a positive oxygen potential. The mechanism of bonding is thought to be due to solid solution of chromium (as chromia) into the alumina.

5. Conclusions

(1) Nickel and chromium sheet will each form adequate bonds with alumina single crystals providing the surrounding atmosphere is neutral in the case of nickel, and is oxidising in the case of chromium.

(2) The bond with chromium increases with increasing pressing temperature and time, the rate of increase falling rapidly when a bond strength of 10 to 12×10^3 psi (70 to 84 MN. m^{-2}) has been generated. Increasing pressing pressure $>$ 2 tsi ($>$ 30 MN. m^{-2}) causes a sudden loss in bond strength.

(3) Adequate bonds have been produced between nickel-chrome alloy and alumina. In the case of pure material prepared from alternate

nickel and chromium strips, the bond strength increases with pressing temperature up to 20 × 10^3 psi (140 MN. m^{-2}) after pressing at 1300° C. Commercial material containing silicon bonds decreasingly well with alumina with increasing pressing temperature.

(4) Full alloy homogenisation in material prepared from alternate strips of nickel and chromium occurs only after prolonged annealing at 1200° C. (5 h) and after 2 h at 1300° C. High chromium concentrations occur at the alumina/matrix interface contrary to the laws of diffusion. These concentrations indicate chemical affinity between alumina and the chromium species.

(5) Microprobe analysis does not show chromium diffusion into the alumina crystal. However, due to the finite size of the micro-analyser beam (5 μm) penetration of this order would not be picked up by this technique and it is possible, therefore, that chromium does penetrate the alumina to this extent.

(6) It is suggested that bonding between chromium and alumina and also between nickel-chromium alloy and alumina is due to the solid solution of chromia.

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