

# The Solid State Bonding of Nickel to Alumina

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The paper describes the effect of sintering atmosphere (argon, hydrogen and vacuum), sintering temperatures (700 to 1300° C), sintering pressure ( $\frac{1}{2}$  to 6 tsi [7.7 to 92.4 MN. m<sup>-2</sup>]) and sintering time ( $\frac{1}{2}$  to 24 h) on the room temperature shear bond strength developed between nickel powder compacts and alumina single crystals: bond strengths of 3 to  $11 \times 10^3$  psi (20.7 to 75.9 MN. m<sup>-2</sup>) were developed and are satisfactory for composite strengthening. The spinel, NiAl<sub>2</sub>O<sub>4</sub>, was detected at the nickel/alumina interface. Heat treatment at 1100° C for 300 h resulted in gross chemical attack, but without degeneration of the bond strength. The variations in shear strength observed are discussed in terms of the nickel grain size and porosity and the differential thermal expansion of the two components.

## 1. Introduction

In the field of fibre-reinforced materials, it is important that a sufficiently high interfacial shear strength is developed between the fibre and the matrix to allow stress transfer from the fibre to the matrix to occur. Kelly and Davies [1] showed that for efficient use of the strength of fibres in a matrix, the interfacial shear strength, is related to the aspect ratio (length/diameter) and the strength of the fibre by the equation

$$\tau \geq \sigma_f \frac{d}{l}$$

where  $l$  and  $d$  are the length and diameter of the fibre and  $\sigma_f$  is the fibre breaking stress.

The bond developed between the fibre and the matrix may be either the result of a chemical reaction occurring at the fibre/matrix interface, or may be the result of a mechanical interaction arising due to differential thermal expansion effects, or combinations of these two effects. A further consideration are bonds of the Van der Waals type; however, surfaces need to be extremely clean for these effects to be prominent. In the preparation of practical fibre-reinforced materials such conditions are rarely met and Van der Waals type bonding is not considered, therefore, to be a dominating effect.

In the case of the strengthening of metals by very fine whiskers (1 to 10  $\mu\text{m}$  diameter) or fibres ( $\sim 25 \mu\text{m}$  diameter) gross chemical

reaction cannot be tolerated since the whisker (or fibre) strength would soon be impaired by small amounts of surface reaction. Sutton *et al* [2] and Ritter and Burton [3] have shown that chemical bonding between nickel and  $\alpha\text{-Al}_2\text{O}_3$  does cause gross deteriorations to the mechanical properties of the alumina at temperatures greater than the melting point of nickel. Sutton *et al* [2] however, also showed that providing the degree of chemical reaction at the interface is not greater than a critical amount, this reaction can be tolerated and is essential for the development of a good bond. A means of reducing the chemical reaction is to cause bonding at lower reaction temperatures.

Klomp [4] using nickel in the form of rolled foil 100  $\mu\text{m}$  in thickness and pressing at 1350° C with pressures of 0.225 to  $14 \times 10^3$  psi (1.5 to 98 MN. m<sup>-2</sup>) onto polycrystalline alumina, strengths in the range 7 to  $30 \times 10^3$  psi (49 to 210 MN. m<sup>-2</sup>) have been obtained.

Accordingly, a solid state bonding technique has been studied in this work to determine conditions of minimal attack at the nickel/alumina interface and at the same time develop bonds in accordance with the Kelly-Davies equation.

## 2. Experimental Techniques and Results

Specimens were prepared by a pressure bonding technique in which nickel powders were hot

pressed in contact with single crystal  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> discs\* with optically smooth surfaces (1  $\mu$ m finish) and with a common crystallographic orientation ((10 $\bar{1}$ 0) parallel to the polished surface of the disc). Electron diffraction studies on the polished surfaces of the crystals revealed the presence of a polycrystalline surface layer of alumina related to the abrasion marking direction and which could be removed by treatment at 1100° C for 2 h in vacuum. Prior to bonding all the alumina discs were treated in this manner.

### 2.1. Bonding of Nickel Powders

The nickel powder used in these experiments has been of three types:

- (a) Type A carbonyl nickel powder†
- (b) Type B carbonyl nickel powder†
- (c) 99.998% pure nickel powder‡

Type A and B powders differ in particle size, particle shape and in purity. The typical characteristics of the powders are shown in Table I. Other elements present Al, Si, Mg, Mn, B, Ca, Cu, Ag, Pb < 50 ppm/element.

TABLE I Characteristics of type A and B powders.

Powder characteristics	Grade A	Grade B
<i>Impurities</i>		
Carbon	500 to 1000 ppm	1000 to 2000 ppm
Oxygen	1000 ppm	1000 to 2000 ppm
Sulphur	< 10 ppm	< 10 ppm
Iron	< 100 ppm	< 200 ppm
Nickel	Balance	Balance
<i>Particle size</i>	4 to 7 $\mu$ m	3 $\mu$ m
<i>Particle shape</i>	Granular rather than spherical	Chainlike structures

The high purity powder (99.998%) had the analysis shown in table II and a particle size of < 300 mesh. This material was air elutriated to produce a fraction of reduced particle size ( $\sim$  10  $\mu$ m) for the experiments.

TABLE II Analysis of high purity powder.

Impurity	- 300 Mesh powder	Elutriated Fraction
Carbon	0.07%	95 ppm
Silicon	3 ppm	10 to 50 ppm
Iron	3 ppm	< 10 ppm
Magnesium	2 ppm	None detected
Silver	2 ppm	< 10 to 50 ppm
Calcium	< 1 ppm	None detected
Copper	< 1 ppm	10 ppm

\*Prepared by Salford Electrical Industries Ltd.

†International Nickel Ltd.

‡Halewood Chemicals Ltd.

Bond production was carried out in a machinable alumina lined, graphite hot pressing die in which a  $\frac{3}{8}$  in. diameter powder plug was pressed onto the central region of a  $\frac{1}{2}$  in. diameter alumina single crystal disc at temperatures in the range 700 to 1300° C, pressures of 0.5 to 10 ton f/in.<sup>2</sup> (7.7 to 154 MN. m<sup>-2</sup>) for pressing times up to 24 h (fig. 1). Provision was also made in the apparatus to allow various sintering atmospheres to be introduced. The cooling rate for the bonded specimens was constant at  $\sim$  100° C/h. The bond developed between the nickel and the alumina was tested in shear at 20° C.

The effect of the following variables on the interfacial shear strength were studied:

- (i) sintering atmosphere
- (ii) sintering temperature
- (iii) sintering pressure
- (iv) sintering time.

The resulting observations collected from tests on 250 bonds are summarised in figs. 2 to 4 and table III.

TABLE III Interfacial bond strength as a function of pressing atmosphere.

Atmosphere	Bond lbf. in. <sup>-2</sup>	Strength (MN. m <sup>-2</sup> )
Argon	4460	(30.7)
Argon - Hydrogen (200 mm Hg)	6650	(45.8)
Vacuum (10 <sup>-4</sup> torr)	8000	(55.2)

In the case of the investigation of bonding as a function of atmosphere (table III) the pressing conditions were constant throughout the experiments namely 1100° C, 2 tonf. in.<sup>-2</sup> [30.8 MN. m<sup>-2</sup>] for 2 h. The results referred to in table III were measured on Type A nickel powder and it was concluded that bonding under vacuum conditions afforded the optimum interfacial shear strengths and the further studies (figs. 2 to 4) were conducted solely under this condition. Bonding did not occur with type B powder or with the 99.998% high purity powder under these conditions and the further studies (figs. 2 to 4) were carried out with type A powder. Generally, the bonding was satisfactory (8 to 10  $\times$  10<sup>3</sup> lbf. in.<sup>-2</sup> [55 to 69 MN. m<sup>-2</sup>]) but certain features are worth comment.

(a) With increasing pressing temperature, a

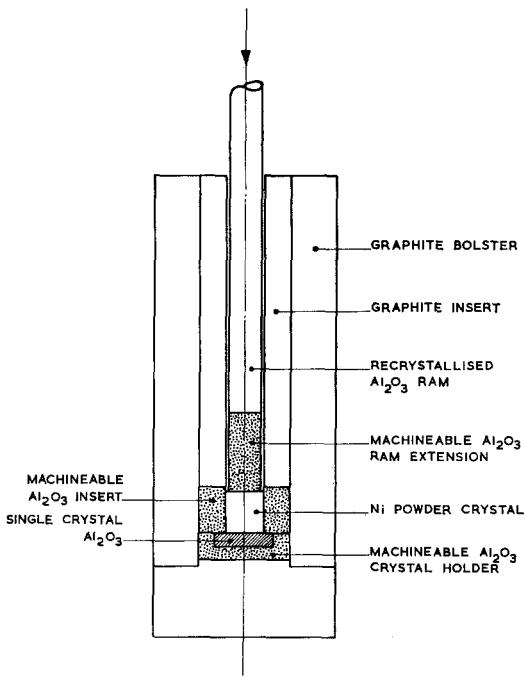


Figure 1 Hot pressing die arrangement.

maximum occurs in the bond strength at  $1000^{\circ}\text{C}$  and this corresponds to an almost complete densification of the nickel plug.

(b) With increasing pressing pressure (at  $1100^{\circ}\text{C}$ ) there is a sudden loss of bond strength at pressures  $> 5 \text{ tonf. in.}^{-2}$  [ $> 77 \text{ MN. m}^{-2}$ ].

(c) With increasing pressing time (at  $1100$ ,  $1200$  and  $1300^{\circ}\text{C}$ ) the bond strength curves pass through a number of maxima and minima.

## 2.2. The Zone of Interaction between Nickel and Alumina

### 2.2.1. Electron Microscopic Examination of the Interface

An extensive study of the interfacial region between the nickel and alumina and of the surface of the sapphire plaques using the electron microscope revealed

(a) that the surface of the discs had been lightly etched compared with the as-received discs fig. 5 and

(b) the reaction zone at the interface is  $1.0$  to  $1.5 \mu\text{m}$  in thickness.

### 2.2.2. Microanalysis

An analysis of the aluminium concentration in the nickel at various depths underneath the interfacial zone has been carried out. At the

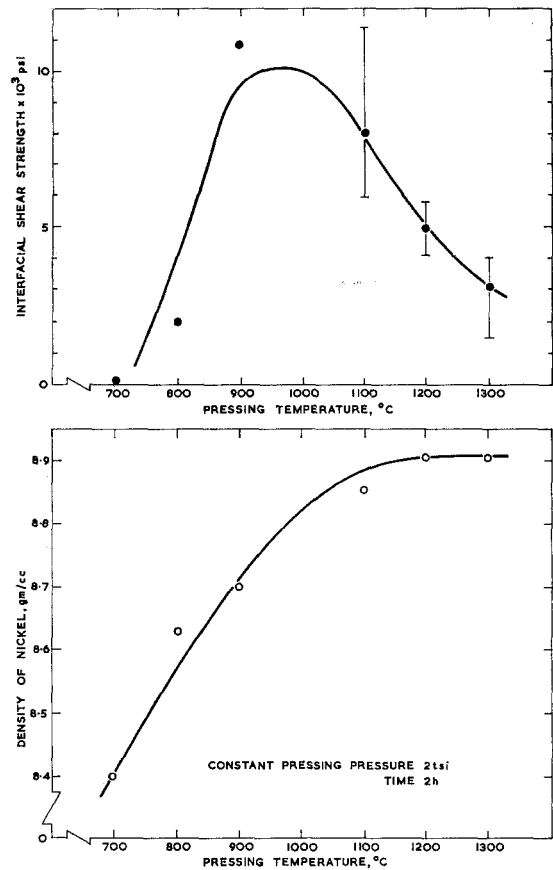


Figure 2 Shear strength of the nickel/alumina interface and the density of the nickel plug as a function of pressing temperature.

interface itself, a concentration gradient of aluminium occurs varying from  $0.8\%$  at the edge of the bond where a three phase region exists (nickel and alumina in contact with some third gaseous phase, probably oxygen or carbon monoxide) to  $0.1\%$  in the centre of the bond (two phase region). A similar concentration gradient exists at a depth of  $10 \mu\text{m}$  from the interface varying from  $0.1\%$  at the edge of the bond to non-detectable amounts at  $200$  to  $250 \mu\text{m}$  towards the centre of the bond.

A similar investigation has been carried out on the fractured surfaces of a sheared bond. Intense regions of attack occurred on both halves of the bond; in the case of the nickel half these regions were found to contain alumina, oxygen and trace amounts of silicon and in the case of the alumina half were found to contain nickel associated with trace amounts of silicon. It is probable that the silicon (found as discrete particles on as-received

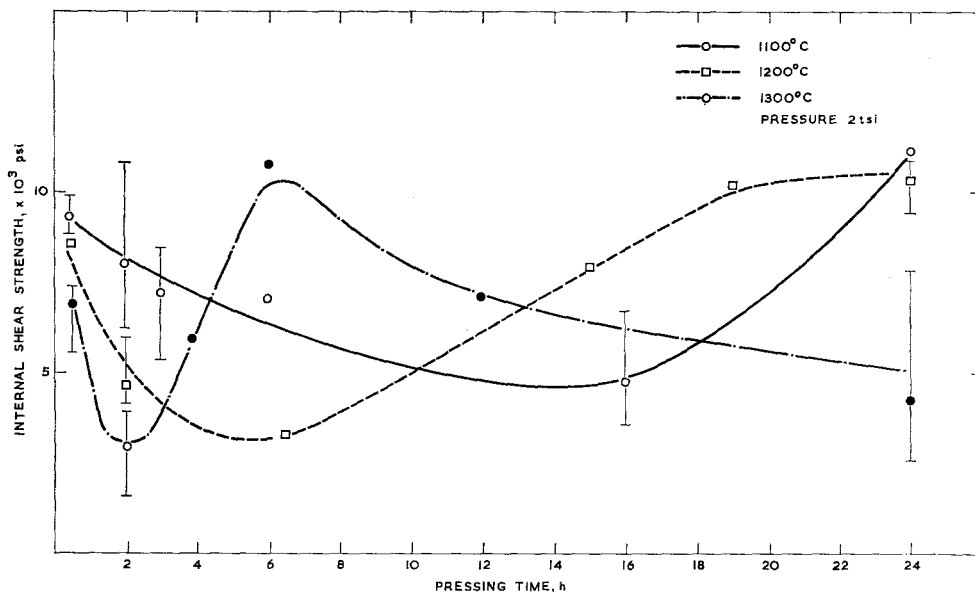


Figure 3 Shear strength of the nickel/alumina interface as a function of pressing time.

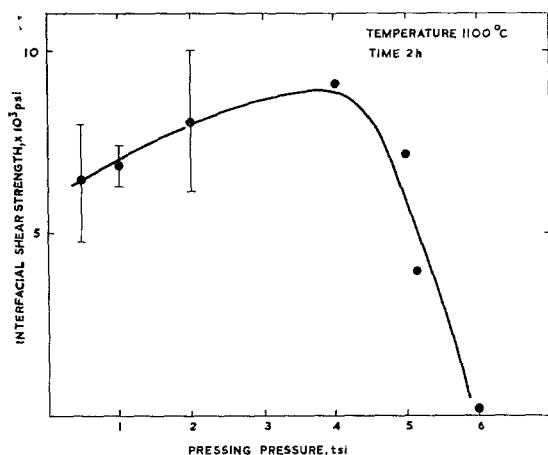


Figure 4 Shear strength of the nickel/alumina interface as a function of pressing pressure.

discs and resulting from the use of silicon bearing lubricant used in polishing the discs) enhances the interaction between nickel and alumina.

### 2.2.3. Electron Diffraction

Reflection electron diffraction studies have been carried out on the surfaces of bonded specimens after shearing and also on specimens in which a "no-bonding" condition prevailed and on which shearing of the interface was unnecessary. Three types of specimen were generated showing:

(i) diffraction rings corresponding to the spinel,

nickel aluminate,  $\text{NiAl}_2\text{O}_4$ . These were generally associated with the no-bonding conditions in which no shearing of the interface was necessary. (ii) diffraction rings corresponding to nickel and alumina on both halves of the nickel-alumina bond. These were particularly associated with bonded specimens in which shearing was necessary to separate the two halves.

(iii) diffraction rings which could not be identified with nickel,  $\alpha$ -alumina, nickel aluminate, nickel oxide,  $\text{AlNi}$ ,  $\text{Al}_3\text{Ni}_2$ ,  $\text{AlO}_4\text{C}$  or  $(\text{Al}_3\text{Ni}_2)\text{SH}$ . There are, however, certain resemblances to the  $d$  spacing spectra of  $\text{NiAl}_2\text{O}_4$  and it is suggested that these may be associated with the dissolution of  $\alpha$ -alumina into the aluminate. This type of pattern was associated with the interface that could be examined without shearing (i.e. no-bond condition and thin nickel films on alumina). A series of these " $d$ " spacings are shown in the appendix as examples of the three types referred to above.

## 3. Discussion of Results

### 3.1. The Effect of Matrix Properties on Bond Strength

The study of the nickel/alumina system has revealed the disturbing interaction between these two materials to produce  $\text{NiAl}_2\text{O}_4$  under the conditions proposed for the manufacture of alumina whisker reinforced nickel composites. This interaction is essential for the development

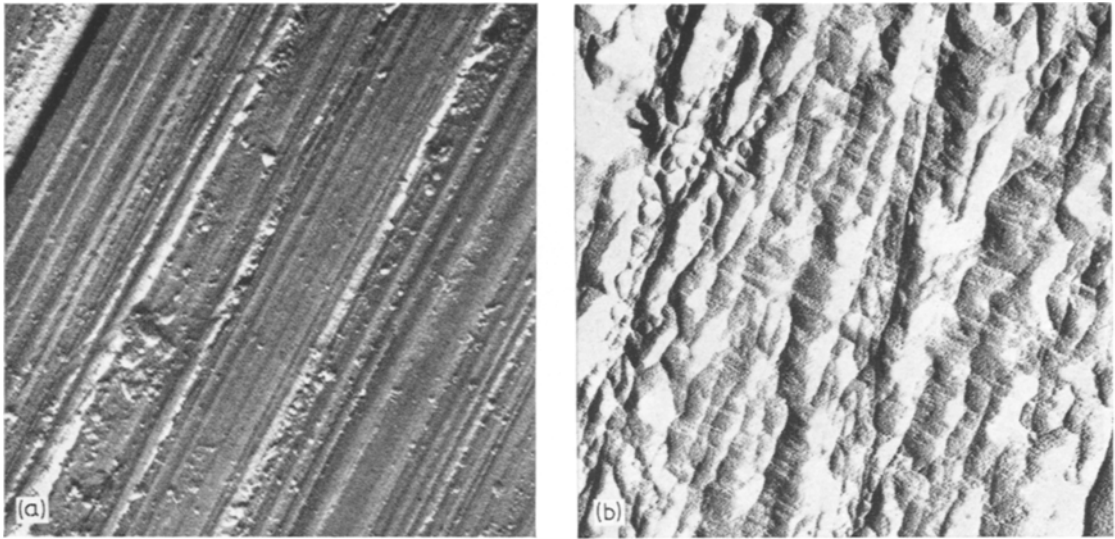


Figure 5 Degradation of sapphire surface after bonding with nickel (a) As-received, (b) After bonding. ( $\times 20$  K).

of a chemical bond at the interface between the metal and ceramic, but nevertheless is of sufficient extent (§ 2.2.1) to cause severe degradation in whisker properties where whiskers have diameters 1 to 5  $\mu\text{m}$ . Further, there are other significant factors which affect matrix/whisker bond strength even if the reactivity aspect was overcome. These factors are due to the metallurgical condition of the matrix material.

The thermal coefficients of expansion at 100 and 1000° C for nickel and alumina are compared in table IV.

TABLE IV Comparison of coefficients of thermal expansion in nickel and alumina.

Material	Coefficient of expansion in./in. °C $\times 10^{-6}$	
	100° C	1000° C
Ni	13.25	16.50
Al <sub>2</sub> O <sub>3</sub>	6.00	8.20

On cooling from the bond manufacturing temperature (1100° C), stresses are set up at the nickel alumina interface which act to disrupt the bond. Such a cooling cycle would leave the  $\alpha$ -alumina surface in compression and the adjacent nickel surface in tension. The apparent interfacial shear strength of this interface is a measure, then, of the true bond strength less any residual disrupting stresses formed as a result of the expansion differential. Interfacial stress relief is possible during cooling by plastic flow in the

matrix and, it can be argued, that this occurs more easily when

(a) the nickel is porous at the interface, and  
(b) the grain size of the nickel is large (Petch relationship).

Further, the more stress relief that occurs by plastic flow during cooling, the greater is the apparent measured interfacial shear strength at room temperature.

Fig. 6 shows all the factors affecting the apparent measured interfacial shear strength:

Curve (1). This represents the formation of the bond between nickel and alumina by a chemical reaction which slows down with reaction time.

Curve (2). As reaction between nickel and alumina progresses, the alumina surface becomes roughened and its strength deteriorates because of its notch sensitivity.

Curve (3). In the early stages of sintering the nickel plug is porous at the interface and the pores are removed with respect to time in a logarithmic manner [5]. Curve (3) represents the removal of stress at the interface by the porosity with time.

Curve (4). This is a schematic representation of the decrease of yield strength with increasing grain size and hence the ease of stress relief with increasing grain size. In practice, yield strength varies from 5 to  $2.5 \times 10^8$  lbf. in<sup>-2</sup> [34 to 17.2 MN. m<sup>-2</sup>] (at 700° C) in nickel as the grain size varies from 100 to 400  $\mu\text{m}$  diameter. Grain sizes at the interface in actual bonding specimens vary between 50 and 2000  $\mu\text{m}$  depending on manufacturing variables and hence the stress relieving

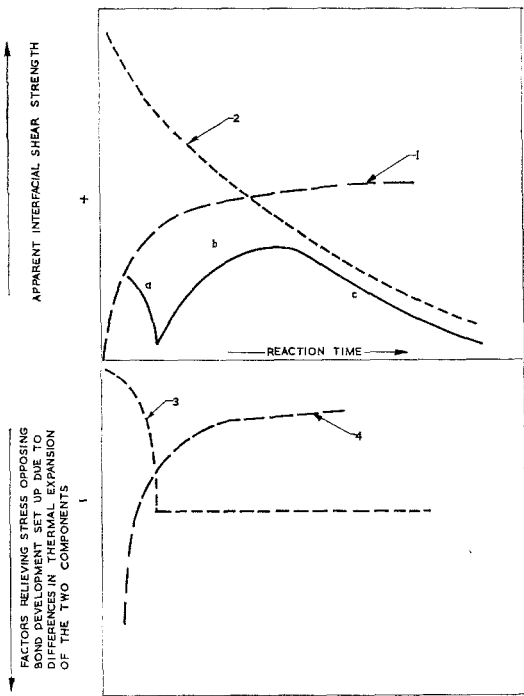


Figure 6 Schematic representation of the factors affecting the interfacial shear strength.

effect of this range of grain sizes has an important bearing on interfacial shear strength.

By combining curves (3) and (4) to give conditions of maximum interfacial stress relief and subtracting this effect from a combination of curves (1) and (2), then a curve results which, in form, agrees with the actual interfacial shear strength versus pressing time curves for temperatures of 1100, 1200 and 1300° C.

### 3.2. The Nature of the Bond

Although it is accepted that a chemical bond is required in the nickel/alumina whisker system between the two components, the nature of this bond has not been fully determined. Electron diffraction work in this study has indicated the presence of  $NiAl_2O_4$  in some cases where no bonding has resulted and not in others where bonds have been developed. However, it is considered that where bonds are formed, the shearing action in separating the interface for examination precludes sensitive electron diffraction study and contrasts with the no bond condition which produces an ideal specimen for glancing angle diffraction. A number of unidentified rings have arisen on diffraction patterns taken of reaction products at the nickel/alumina inter-

face. Lejus [6], in a study of the  $NiO-Al_2O_3$  reaction, has shown that the "a" spacing in the resulting  $NiAl_2O_4$  can be reduced by the solubility of  $Al_2O_3$  into the spinel at temperatures  $> 1000^\circ C$ . It is thought that the unidentified reaction products in this present work may be accounted for in terms of the solubility of  $Al_2O_3$  in the spinel which, in turn, alters the "a" spacing of the spinel.

The effect of the hot pressing variables on the production of the nickel- $Al_2O_3$  bond have been studied in detail and commented on previously. By holding bonded specimens for up to 1000 h at  $1100^\circ C$  very little change in the measured room temperature bond strength occurred (fig. 7), although the mode of fracture changed in such a manner as to indicate a marked weakening of the sapphire with increasing reaction time. After 1000 h in argon, the interface showed a blue coloration indicative of the formation of the spinel,  $NiAl_2O_4$ .

### 4. Conclusions

(1) Nickel powders of differing manufacturing

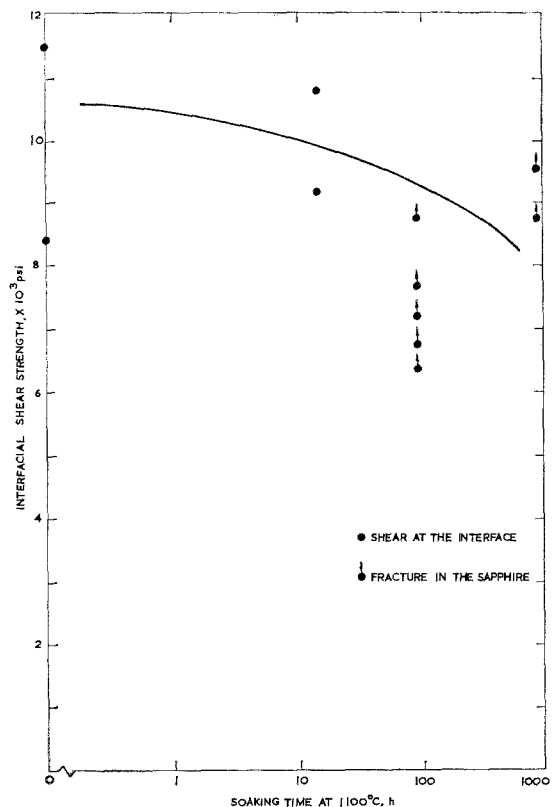


Figure 7 Shear strength of the nickel/alumina interface as a function of holding time at  $1100^\circ C$ .

history and purity have differing bonding characteristics with  $\alpha\text{-Al}_2\text{O}_3$  single crystal plaques.

(2) For type A nickel powder, chosen for its ease of bonding with  $\alpha\text{-Al}_2\text{O}_3$ , the apparent bond strength in shear varies from 2 to  $11 \times 10^3$  lbf. in<sup>-2</sup> [13.8 to 75.8 MN. m<sup>-2</sup>] depending on bonding atmosphere, pressing temperature, pressing pressure and pressing time. The optimum bond strengths possible are well in excess of the minimum requirements (from the aspect ratio view point) for the fibre reinforcement of nickel by  $\text{Al}_2\text{O}_3$  whiskers.

(3) In some cases the spinel,  $\text{NiAl}_2\text{O}_4$  has been identified as a reaction product at the interface whilst in other cases a number of unidentified diffraction patterns have arisen due possibly to dissolution of alumina in the spinel.

(4) Long term heat soakings (up to 1000 h) at 1100° C in argon of bonds between A type nickel powder and  $\alpha\text{-Al}_2\text{O}_3$  have not caused a gross deterioration of the bond strength. The mode of fracture has, however, changed in these experiments from a truly interfacial fracture after < 10 h heat treatment to irregular fracture through the sapphire after 1000 h at temperature.

This latter fracture type is associated with a blue coloration at the interface indicative of a thick film of  $\text{NiAl}_2\text{O}_4$ .

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## Appendix

ASTM " $\alpha$ " spacings		Type (i) bond		Type (ii) bond		Type (iii) bonds	
Ni	Al <sub>2</sub> O <sub>3</sub> NiAl <sub>2</sub> O <sub>4</sub>	Al <sub>2</sub> O <sub>3</sub> surface	Ni surface	Al <sub>2</sub> O <sub>3</sub> surface	Ni surface	Example (1)	Example (2)
	4.65						3.50
	3.479						
	2.846	2.84	2.78			2.95	
	2.552			2.59(Al <sub>2</sub> O <sub>3</sub> )	2.60(Al <sub>2</sub> O <sub>3</sub> )		
	2.427	2.43	2.42				
	2.379		2.32	2.44(Al <sub>2</sub> O <sub>3</sub> )	2.42(Al <sub>2</sub> O <sub>3</sub> )	2.30	
	2.165						2.15
	2.085			2.07(Al <sub>2</sub> O <sub>3</sub> )	2.08(Al <sub>2</sub> O <sub>3</sub> )		
2.04							
	2.013	2.00	1.99			1.975	2.02
	1.965		1.87				
1.77					1.79 (Ni)		
	1.740			1.73(Al <sub>2</sub> O <sub>3</sub> )			
	1.642					1.61	1.60
	1.601			1.62(Al <sub>2</sub> O <sub>3</sub> )	1.60(Al <sub>2</sub> O <sub>3</sub> )		
	1.549	1.55	1.49			1.525	
	1.546						
	1.514						
	1.510						
	1.423	1.42	1.39				
	1.404			1.40(Al <sub>2</sub> O <sub>3</sub> )	1.39(Al <sub>2</sub> O <sub>3</sub> )		
	1.374						
	1.360						
	1.337						
	1.274					1.295	
1.25				1.26(Ni)	1.26(Ni)		
	1.239						
	1.234						
	1.227						1.25
	1.213						1.22
	1.190						
	1.161		1.16				1.16
	1.160						1.14
	1.075						
1.070				1.06(Ni)	1.07(Ni)		
	1.048						1.04
1.020							
	1.006						
0.990							
	0.929						
	0.900		0.90				
	0.821		0.89				
0.810					0.810(Ni)		
0.790							
0.720							
0.680							
0.630							
0.600							
0.590							