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Glass-ceramic interactions and thick-film metallization of aluminium nitride

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A frit-bonded thick-film metallization for aluminium nitride (AlN) ceramic substrates has been developed. The glass system is thermodynamically stable with respect to AlN at the temperatures employed during thick-film processing. The model glass, a lithium borate, has comparable physical properties to that of the standard lead borosilicate glasses used in frit-bonded films designed for oxide ceramics. The wetting properties of the glass on AlN, in both air and nitrogen atmospheres, have been determined by use of a hot-stage microscope. The low-temperature oxidation of the AlN surface was found to be a significant factor in the glass spreading rate. The glass was formulated into a palladium–silver thick-film metallization and the performance of this material on three types of AlN substrate was determined. Examination of the film morphology and the fracture surfaces was carried out using scanning electron microscopy.

1. Introduction

Trends in electronic device manufacture and applications indicate that substrates having high thermal conductivities will become of increasing importance [1, 2]. The most commonly used substrate material, 96% aluminium oxide (Al_2O_3), having a thermal conductivity in the range 10–30 $W\,m^{-1}\,K^{-1}$, cannot meet forthcoming thermal requirements. Beryllium oxide (BeO) substrates possess a high thermal conductivity, 150–250 $W\,m^{-1}\,K^{-1}$, but due to the toxic nature of BeO powder the use of these substrates is severely restricted. Aluminium nitride (AlN) has produced a great deal of interest as an alternative substrate for high-power applications [3–6]. The thermal conductivity of presently available materials is as high as 170 $W\,m^{-1}\,K^{-1}$; theoretical predictions indicate a maximum thermal conductivity of 320 $W\,m^{-1}\,K^{-1}$ [7]. For utilization of AlN as a substrate material, a suitable metallization system is required. Thick-film technology is widely used to provide the metallization for mounting of the integrated circuit and to provide interconnection between circuit components. The most common method of achieving adhesion between the metallization and the substrate is frit bonding. This involves the addition of 2–10 wt % glass powder relative to the metal. During firing, the glass should wet the substrate and penetrate to some extent into the metal network. The development of an interlocking glass structure is desirable for good adhesion because it provides a mechanical interlock in addition to chemical bonding between phases [8]. To achieve the required microstructure at the conductor/substrate interface, it is necessary that the glass has the appropriate surface tension and viscosity values during the firing process and that the requirements for wetting of the surfaces are met with relation to the interfacial energies between solid, glass and vapour phases [9]. The firing range used in the processing of thick films is 800–900 °C. A number of references to the thick-film metallization of AlN have appeared in recent years [6, 10–14], the thick-film inks used in many cases have been those designed for oxide ceramics. The adhesion mechanisms have been reported to be mechanical [11] or reliant upon formation of a significant oxide layer on the AlN surface [10, 11]. The development of a thick-film conductor ink designed specifically for AlN has been reported [6]. The formulation contains a frit of composition $PbO–SiO_2–CaO–Al_2O_3–B_2O_3–ZnO$ and the firing-temperature range is 870–920 °C. From recent work [13, 15] it is unlikely that this glass system is compatible with AlN due to reaction between AlN and PbO at the firing temperature. Most electronic glasses either do not wet AlN or react, creating bubbles, blisters and leading to poor adhesion [12].

This study represents a systematic investigation of a model glass system which is thermodynamically compatible with AlN. The glass used was a lithium borate. The physical properties of alkali borates have been widely reported [16–21]. A glass composition was chosen which would have comparable rheological properties to a lead borosilicate. The glass was used to provide the adhesion mechanism in a palladium–silver thick-film ink for application on AlN. Palladium–silver (Pd–Ag) was chosen as the metals system because the adhesion of these materials can be easily

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determined and they represent a low-cost conductor system suitable for use in forming interconnections and solderable end terminations for lead attachment. The adhesion of the film to the substrate was determined using a 90° peel test and the fracture surfaces were examined by scanning electron microscopy (SEM). The microstructure of the fired films was studied because the degree of densification is important in determining aged adhesion [22]. Since tin/lead (Sn/Pb) solder alloys are used in the industry for lead attachment and the conductors are primarily precious metals, diffusion from the solder into the metallization can take place [23]. Accelerated thermal ageing tests of conductors at 150 °C are performed to determine long-term effects of this interaction. Data indicates that most of the loss of adhesion occurs within the first 12 h and is virtually complete by 48 h [24, 25]. The adhesion after one refire at the initial temperature was measured because generally even simple conductor networks require at least two firings, one to form the terminations and the second for either interconnection or formation of thick-film resistors. The variation of adhesion with firing temperature and glass content has also been measured.

2. Experimental procedure

2.1. Materials

The AlN ceramic substrates used were selected from commercially available materials. They included two grey materials (Toshiba, Heraeus) and one translucent material (Tokuyama Soda "Shapal"). The materials had all been produced by pressureless sintering using oxide sintering aids. The properties of the substrates and their microstructure have been reported previously.

The lithium borate glass was produced by melting high-purity boric oxide and lithium carbonate in a platinum crucible at 1100 °C for 15 min. The short melting times were used to minimize possible volatilization of either boric oxide or lithium oxide. The melt was air quenched to room temperature. The glass was reduced to yield a particle size distribution 90% $< 9\ \mu$m. Ethanol was used as the milling medium rather than water to prevent possible corrosion of the glass.

2.2. Evaluation of glass-ceramic interactions

The contact angle of the glass on the substrate was determined by use of a hot-stage microscope. The technique has been reported in detail elsewhere [27]. Briefly, a small bead of the glass was placed on the desired substrate. The image of the glass could be recorded photographically at any required time or temperature interval. The atmosphere within the quartz furnace chamber could be controlled as required. Air and high-purity nitrogen were used in this study.

In order to examine the reaction between the glass and AlN, the milled glass was mixed into an organic vehicle/solvent system and screen printed on to the substrate. The glass film was dried at 120 °C then fired at the desired temperature in a belt furnace capable of providing reproducible time/temperature profiles. The sintered glass-coated substrate was then scribed on the reverse and fractured after rapid extraction from a liquid nitrogen bath. The cross-section was examined by SEM.

2.3. Thick-film coating and adhesion testing

The lithium borate glass prepared as described above was mixed into a Pd–Ag ink using a previously prepared metal/organic formulation. To ensure homogeneity the glass was blended into the metal ink system using a three-roll mill. The metal ratio was Pd:Ag 1:3. The ink was screen printed on to the AlN substrates using a standard test pattern to produce areas 2 mm × 2 mm suitable for adhesion testing. The ink was dried at 120 °C in a fan-assisted oven, then fired at various peak firing temperatures for dwell times of 8–10 min. The fired film thickness was 12–14 μm. The adhesion was determined using a standard 90° peel test [24, 28]. Pretinned copper wires were soldered using 62Sn/36Pb/2Ag solder alloy and a medium active flux at 230–235 °C to the 2 mm square pads. The component is placed in a solder pot with wires at right angles to the solder surface. The component remains in the solder for a time sufficient to ensure complete wetting of the test pads, usually 10 s. After removal from the solder, the component is allowed to cool for 15 min and then rinsed with a suitable solvent to remove flux residues. After a minimum of 16 h at room temperature, during this time the solder system will have approached a sufficient degree of structural equilibrium to permit best reproducibility during the testing [29], the wires were bent at 90° to the substrate and the adhesion determined (Unitek Micropull 1). For aged adhesion the soldered and defluxed components are stored in a static air oven. After removal from the oven they were left 16 h before measuring the adhesion.

3. Results and discussion

3.1. Wetting and interface reactions

The contact angle of the glass on Heraeus AlN and 99.5 wt % Al_2O_3 substrates is shown in Fig. 1. The Al_2O_3 substrate was chosen to provide a substrate whose surface should be invariant in air or nitrogen, so any atmosphere effect on the contact angle could be determined. Complete flowing of the glass occurs at temperatures around 900 °C on Al_2O_3 and on AlN in air. For the glass on AlN in nitrogen, instantaneous spreading was not observed at any temperature. A time-dependent contact angle was, however, found (Fig. 2).

The effect of atmosphere obviously has a profound effect on the glass spreading rate. The oxide of aluminium is thermodynamically favoured over the nitride at all temperatures in air. AlN powders have been found to start oxidizing at temperatures above 700 °C in air [30]. In a fully dense material produced by pressureless sintering, oxidation in air was reported to start at about 900 °C and the rate of oxidation being

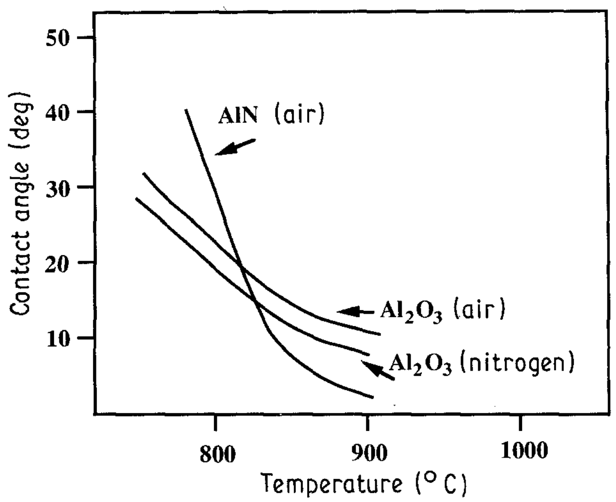


Figure 1 Variation of contact angle with temperature for lithium borate glass on aluminium nitride and aluminium oxide.

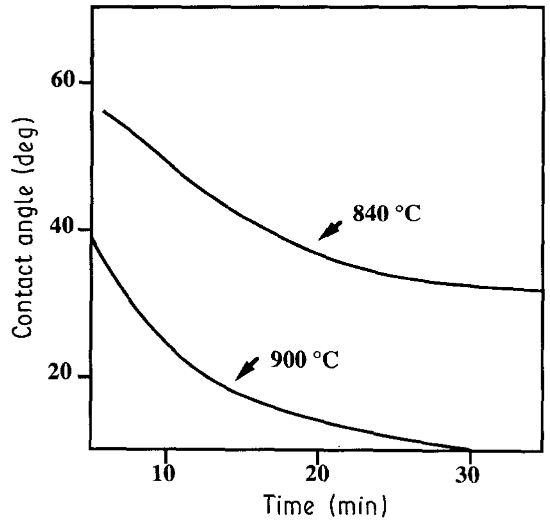


Figure 2 Time-dependent contact angle of lithium borate glass on aluminium nitride in nitrogen.

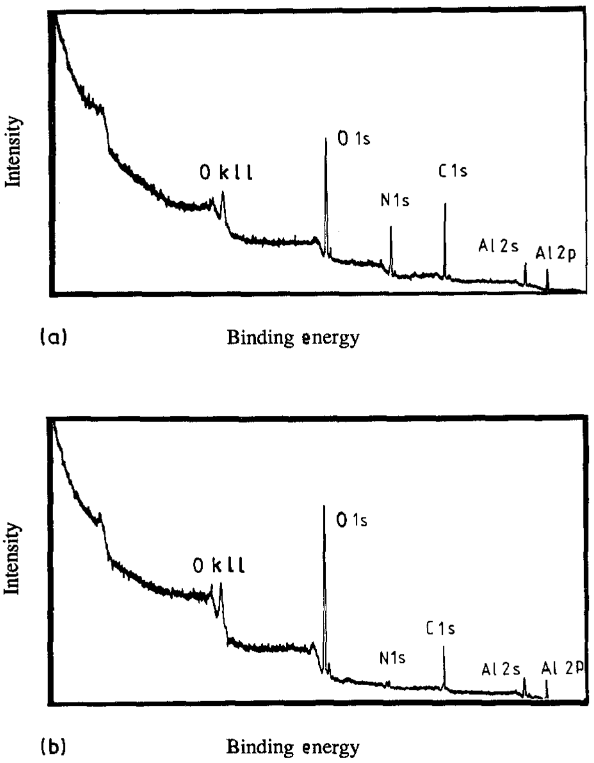


Figure 3 ESCA Spectra for (a) as-received Heraeus aluminium nitride (b) heat-treated Heraeus aluminium nitride.

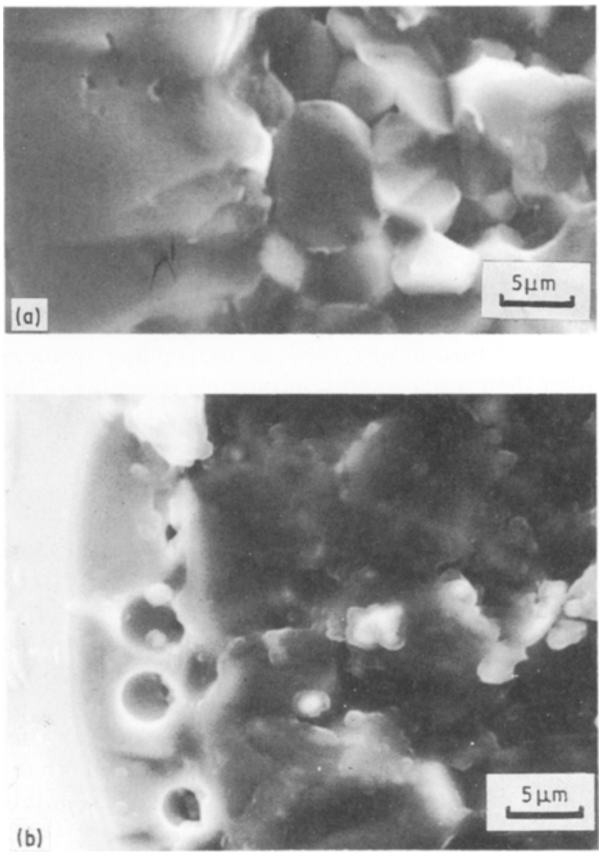


Figure 4 (a) Interface between lithium borate glass and aluminium nitride after firing at 900 °C/10 min in nitrogen; (b) interface between lead borosilicate glass and aluminium nitride after firing at 670 °C/10 min in nitrogen.

slow up to 1450 °C [8]. The oxidation of the Heraeus material was found to be significant after 10 min at 850 °C. The surface composition was determined by use of electron spectroscopy for chemical analysis (ESCA). The spectra for the as-received and oxidized materials are shown in Fig. 3a and b, respectively. The formation of this oxide phase at low temperatures has an effect on the wetting properties of the glass.

The balance of the interfacial free energies for a liquid on a solid surface is given by the Young–Dupré equation

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos\theta \tag{1}$$

where γ is the interfacial energy, sv for solid/vapour, sl for solid/liquid and lv for liquid/vapour. The mechanism for spreading involves a reaction between the liquid and solid [31]. In the absence of a reaction the driving force for wetting will never exceed the liquid/vapour interfacial energy (γ_{lv}) and spreading or extension of the liquid drop will not occur. When a reaction occurs, the free energy of reaction (G_R) per unit interfacial area (A) and unit time ($+$) enhances the driving force for wetting, as indicated in the inequality below, only if the solid is an active participant [31].

$$\gamma_{sv} - \left(\gamma_{sl} + \frac{-\mathrm{d}G_{R}}{\mathrm{d}A\mathrm{d}t}\right) \rightarrow \gamma_{lv}\cos\theta \qquad (2)$$

The rate of reaction involving the glass and the oxidized surface is faster than the corresponding reaction between the glass and the unoxidized surface. The dissolution rate, therefore, of Al–O in the glass is faster than Al–N. The Tokuyama Soda ceramic behaved in an identical manner to the Heraeus material. The behaviour of the Toshiba ceramic was different, with instantaneous spreading occurring at around 900 °C in both air and nitrogen. This effect could be correlated to the fact that the Toshiba AlN has a thick oxide layer covering the surface [32].

The thermodynamic aspects of glass–AlN reactions have been reported [15]. The lithium borate glass satisfies the requirements for thermodynamic stability in contact with AlN. The interface between glass and ceramic is shown in Fig. 4a. The glass has wet the ceramic surface and there is no evidence of any deleterious reaction. The interface between a lead borosilicate glass and AlN is shown in Fig. 4b for comparison. The evidence of reaction and gaseous evolution is clearly visible.

3.2. Thick-film metallization of AlN

The lithium borate glass showed good wettability to AlN when fired in air. No deleterious reaction or dewetting was observed. To determine the suitability of this glass for use as an adhesion promoter in thick film inks for AlN, the glass was formulated into a Pd–Ag thick-film ink. The initial formulation was made using a glass content of 7.5 wt %. The surface of the films for firing temperatures from 800–900 °C are shown in Fig. 5a–d. Increasing the firing temperature increases the density of the fired film as would be expected. An increase in glass content from 2.5–10 wt % (Fig. 6a–c), at the same firing temperature increases the film density only slightly.

The addition of glass to thick film materials is important for providing adhesion to the substrate and the glass also improves film densification [27, 34]. The degree of densification is important in determining the electrical resistivity of the fired film. Increased film density lowers the electrical resistivity as the degree of contact between particles is increased. The electrical resistivity of the films prepared in this study with glass content 7.5 wt % ranged from 28–25 mΩ/□ as the firing temperature is varied from 800–900 °C. These values are within the range expected for this metal alloy ratio. The initial adhesion of the AgPd films with

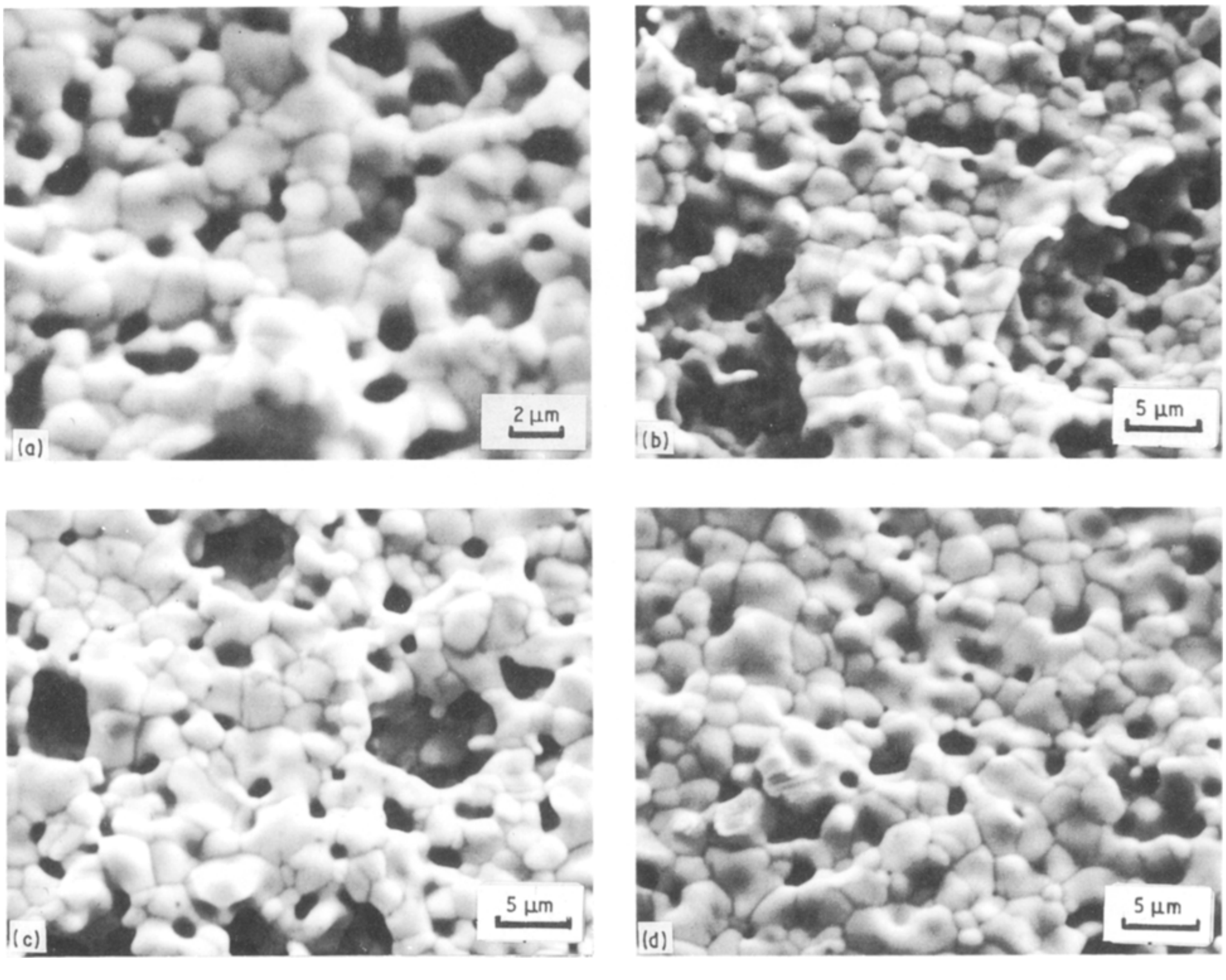
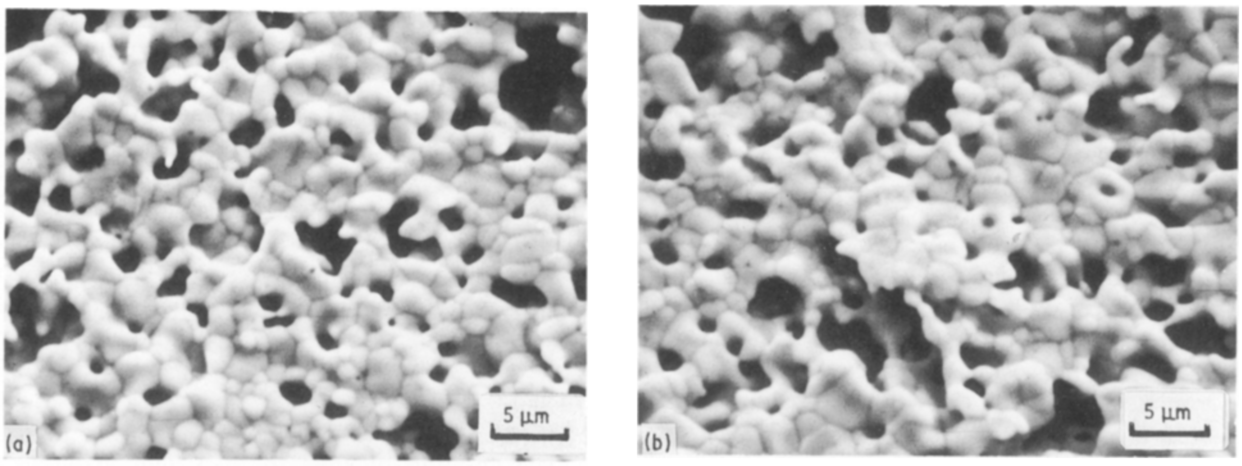


Figure 5 Surface of AgPd film on aluminium nitride after firing at (a) 800 °C/8.5 min (b) 825 °C/8.5 min, (c) 875 °C/8.5 min and (d) 900 °C/8.5 min, in air, glass contents 7.5 wt %.



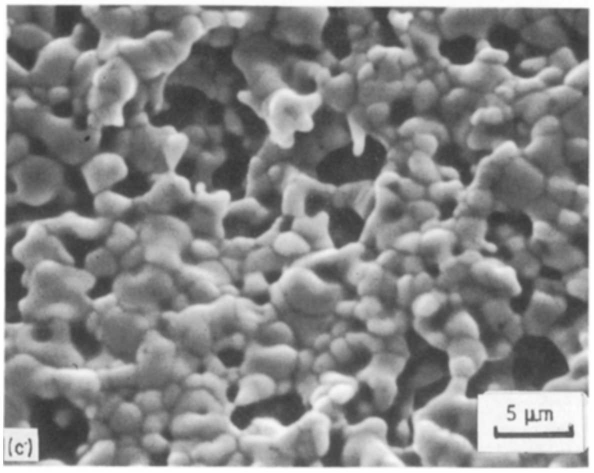


Figure 6 Surface of AgPd film on aluminium nitride after firing at (a) 825 °C/8.5 min in air, glass content 2.5 wt %, (b) 825 °C/8.5 min in air, glass content 5 wt %, (c) 825 °C/8.5 min in air, glass content 10 wt %.

7.5 wt % glass to Heraeus AlN substrates is shown as a function of firing temperature in Table I, maximum adhesion is obtained at 800–825 °C. The adhesion as a function of glass content is shown in Table II, for a firing temperature of 825 °C. The adhesion values quoted represent a mean of ten adhesion measurements for each change in experimental variable.

The fracture surfaces after the adhesion test had been performed are shown in Fig. 7a and b, for a firing temperature of 825 °C and glass content 7.5 wt %. The upper figure shows the fracture surface on the substrate side exhibiting a rough topography. The lower figure shows the conductor side fracture surface. The substrate side shows evidence of remaining metal and the glass phase. From Fig. 7b the metal network can be seen with no evidence of the glass; the failure has occurred within the metallization pad. The film microstructure will consist of an open metal network leading to a glassy matrix containing the metal network

TABLE I Film adhesion versus firing temperature

Firing temperature (°C)	Adhesion (N)
800	25.80 ± 3.47
825	25.36 ± 1.82
850	19.57 ± 1.82
875	21.57 ± 3.56
900	21.13 ± 4.89

TABLE II Film adhesion versus glass content

Glass content (wt %)	Adhesion (N)
10	21.80 ± 0.98
5	18.91 ± 3.25
2.5	6.23 ± 3.25

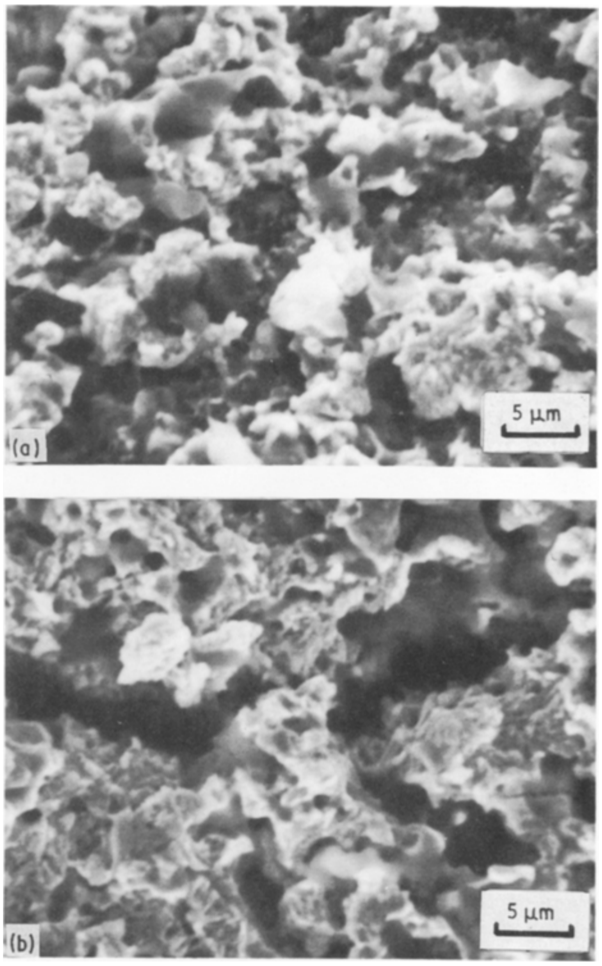


Figure 7 (a) Substrate-side fracture surface between Heraeus aluminium nitride and AgPd thick film. Firing temperature 825 °C, initial adhesion. (b) Soldered pad-side fracture surface between Heraeus aluminium nitride and AgPd thick film. Firing temperature 825 °C, initial adhesion.

and finally a glass layer bonded to the substrate. The glass layer forms at the ceramic/metal interface due to glass migration towards the substrate. The contact angle for many glasses is lower on ceramics than on metals [34, 35]. As a result of the lower contact angle of the glass on the substrate the glass would tend to migrate towards the substrate in order to lower its surface energy.

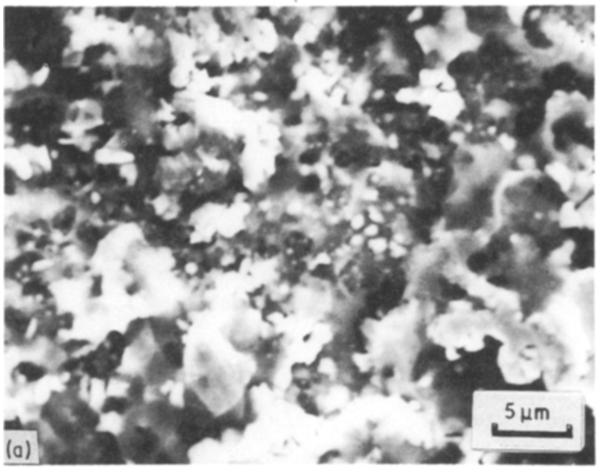
The adhesion gradually decreases as temperature increases. At higher firing temperatures the glass viscosity will be reduced and flow-out of the glass to the substrate/metal interface can occur. This flow-out has been noted at the edge of the metallization pad and is described as glass "bleed-out". This phenomenon is usually cured in commercial thick-film inks by either using a reduced firing temperature or by adding to the formulation an oxide (e.g. Al_2O_3) which is soluble in the glass and increases the viscosity when dissolved during the firing process.

High adhesion is not achieved until 5 wt % glass is added. Sufficient glass is required to wet the substrate and also to aid densification of the metal network. The adhesion of the ink was determined on the other two AlN substrate materials. The values are reported for a firing temperature of 825 °C with a dwell time at peak temperature of 8.5 min. The results are shown in Table III. The refire adhesion and also the thermal aged adhesion are given. In all cases the initial adhesion and refire adhesion are high. The failure mechanisms are similar to that observed in the Heraeus material; failure occurred within the metal network, leaving a glass/metal residue on the substrate side and a metal structure on the conductor side.

The adhesion of the films after ageing was reduced for all film/substrate combinations. The most dramatic decrease was for films sintered on to the Tokuyama Soda AlN. Fracture surfaces after the adhesion test had been performed are shown in Fig. 8a and b for the Tokuyama Soda material. Generally, failure has occurred closer to the substrate film interface as evident by the thin layer of metallization remaining. Penetration of the solder into the film has occurred during ageing which can lead to lower adhesion. Permeation of solder is possible because the films are not fully dense. Generally films with Ag:Pd ratios of > 3:1 have poor aged adhesion characteristics, due to their excellent wettability by molten solder. Improvements in aged adhesion are often found by addition of a third metal to the alloy system (e.g. Pt). This addition leads to an increase in film density.

TABLE III Adhesion of Ag/Pd 7.5 wt % glass thick films to AlN substrates (firing profile 825 °C/8.5 min)

Substrate	Number of firings	Adhesion (N)	Adhesion (N) after 48 h at 150 °C
Toshiba	1	22.24 ± 2.80	19.48 ± 3.69
Toshiba	2	24.02 ± 3.29	18.02 ± 2.67
Tokuyama Soda	1	24.91 ± 2.58	4.00 ± 1.51
Tokuyama Soda	2	23.35 ± 3.51	4.23 ± 1.47
Heraeus	1	25.36 ± 1.82	17.13 ± 2.45
Heraeus	2	20.46 ± 1.29	11.12 ± 2.71



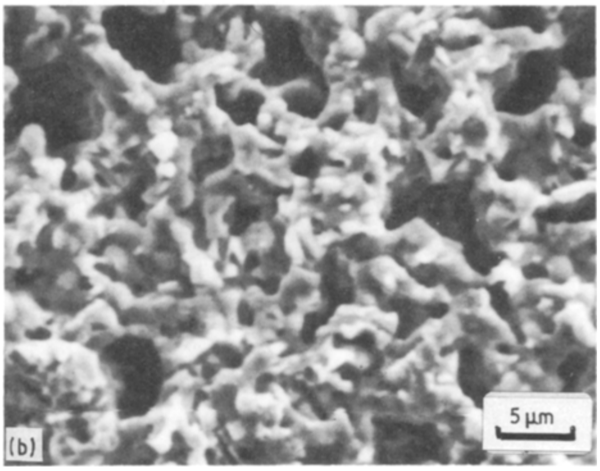


Figure 8 (a) Substrate-side fracture surface between Tokuyama Soda aluminium nitride and AgPd thick film. Firing temperature 825 °C, 48 h aged adhesion. (b) Soldered pad-side fracture surface between Tokuyama Soda aluminium nitride and AgPd thick film. Firing temperature 825 °C, 48 h aged adhesion.

This work has led to the development of a compatible glass system and the subsequent basis for the formation of a metallization system for AlN. The glass system represents a model system and modifications in formulation may well be required to develop a commercial frit system. Areas where improvements may be required are chemical durability and electrical resistivity.

4. Conclusion

The interfacial reactions between a thermodynamically compatible glass and AlN have been investigated. The glass flows on the ceramic although the spreading rate is dependent largely upon the phases present on the substrate surface during the firing process. The lithium borate glass studied was successfully used as an adhesion promoter in a PdAg thick-film metallization that showed very promising performance on AlN.

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