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Interfacial reactions between a lead borosilicate glass containing CuO and an Al/Si alloy — evidence for galvanic cells

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Abstract

A PbO-rich borosilicate glass with the additions of CuO and Al_2O_3 has been developed as a thick-film, dielectric coating for a high Si content Al/Si alloy produced by the Osprey process (Al–70Si wt.%). Wetting behaviour and interfacial reactions were investigated using sessile drop experiments at temperatures between 520 and 583°C under air and argon atmosphere. The wetting behaviour of the glass was found to be a function of atmosphere and wetting angle decreased with increasing temperature and time. Coatings applied in air in the range 520–565°C showed $<1\%$ porosity, whereas those applied at 583°C in argon exhibited relatively high porosity ($\sim 8\%$) and both coating and un-wetted substrate surface supported large Al–Si spheres containing ~21 wt.% Si. Coatings heated in air at 520 and 540°C show good bonding with no interfacial reaction products. However, those samples heated in air at 565°C consistently show evidence of excessive interfacial reactions which are the components of a galvanic process, leading to the oxidation and dissolution of the Al regions (anodic) and the deposition of copper at the glass/Si interface (cathodic). From observations of the rate of copper deposition, the current density arising from the electron flow through the alloy has been calculated to be ~ 0.91 A m^{-2}. The galvanic process is suppressed at the periphery of the coating where oxygen diffused from the atmosphere enables interface oxidation. The onset of the galvanic process between 540 and 565°C occurs when dissolution rate exceeds oxidation rate, exposing the fresh Al anode to the glass melt. Under inert atmosphere (at 583°C), air oxidation is not possible and galvanic cell redox reactions generate an excessive copper interlayer as the system attempts to sustain the oxide layer at the Al anode. Crown Copyright © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Al/Si alloy; Bonding; Borosilicates; Glasses; Interfaces; PbO; Wetting

1. Introduction

There are many technological applications where the useful properties of a bulk material can only be exploited if the surface of that material is modified in some way. This may be to impart corrosion resistance, improve appearance, prevent electrical contact etc. A wide variety of coating/substrate combinations have been exploited and much work has been carried out to identify the requirements for a robust coating. The material of the coating must be chosen not only to provide the surface properties required but also to be compatible with the substrate and the thermal excursions experienced during the coating procedure and any subsequent usage. In the case of inorganic oxide coatings on metals, the major factors contributing to the formation of successful coatings are matching of thermal expansion coefficients (TCE) and production of a strong chemical bond between the coating and the substrate. The factors which control a successful bond between a metal substrate and a glass coating were first established by King et al.[1] and Pask and co-workers.[2–4] More recently, work in this area has been reviewed by Donald.[5] The main requirement for a good bond is the maintenance of continuous chemical bonding from the metal through to the glass (or ceramic). This is usually achieved by a thin metal oxide interlayer. If this interlayer is lost (by dissolution) then bonding is weak and so it is essential that the coating, adjacent to this interlayer, be saturated by the metal oxide or that there is some mechanism for continually forming the interlayer. Coating design is, therefore, particularly concerned with

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the chemistry of the coating/metal interface. There is considerable literature on the coating of individual metals and alloys but little work has been conducted regarding the coating of composites, especially where the components of the composites are very different in character. We have recently been studying dielectric glass coatings on Al/SiC composites with a view to their use as substrates for microelectronic device packaging and preliminary findings have been reported.[6] In the course of this work, we have also investigated a high Si content Al/Si alloy (Osprey 30Al/Si), which has a coarse microstructure consisting of interconnecting regions of nearly pure Si and Al. The problems associated with producing a successful glass coating on such a substrate are discussed here and evidence presented for the operation of a galvanic cell at elevated temperature.

2. Experimental procedure

2.1. Substrate preparation

The substrate used was an Al-70Si Osprey alloy formed by spray deposition.[7] This alloy contains 30 wt.% Al and 70 wt.% Si, with a room temperature microstructure consisting of discrete, interpenetrating zones of Al and Si (~73 vol.% Si). It has a thermal expansion coefficient (TCE) of 7.9 MK^{-1} (50–300°C) and softens at ~533°C. Squares of the material were cut with lateral dimension 20 mm and thickness ~2 mm. One face of each square was polished to a 1/4 micron finish.

2.2. Glass preparation

The composition used, 39.9 PbO, 25.5 B_2O_3, 19.8 SiO_2, 6.5 Al_2O_3 and 8.3 CuO (mol%), was chosen to have thermal coefficient of expansion (TCE) match to the alloy (observed values 8.4±.0.5 MK^{-1} and 7.9 MK^{-1} for the glass and alloy respectively, over the range 50–300°C) and softening point below the eutectic temperature of the alloy. A similar system containing Na_2O instead of CuO will be reported separately. Differential thermal analysis indicated the glass transition of the present composition to be 380±5°C and the onset of sintering to be 467±5°C. The glass was made by heating the stoichiometric quantities of Pb_3O_4, B_2O_3, SiO_2, Al_2O_3 and CuO in an alumina crucible, at 10°C min^{-1}, from 300 to 950°C. Once the melting temperature was reached, further batch powder could be added, at 15 min intervals (up to 150 g batch), and the resulting melt was held at temperature for a further 45 min. The crucible was then removed from the furnace and the melt swirled to aid homogeneity. The crucible was returned to the furnace, allowed to regain temperature and held there for a further 15 min before removal followed by melt-casting into pre-heated (250°C) steel moulds to produce blocks of glass. The blocks were annealed at 370°C for 3 h and then cooled to room temperature at 2°C min^{-1}. After annealing, blocks were cut from the glass with dimensions 3×3 mm×(5–6.5) mm. One minor surface of each block was polished to 1/4 micron finish using oil-based polishing media.

2.3. Bonding procedure

Prior to bonding, the glass blocks and substrates were ultrasonically degreased in isopropanol for 5 min, washed in fresh isopropanol and then dried using an air jet. Cleaned specimens were stored in a vacuum desiccator until required. To produce a coated sample, a polished surface of a glass block was placed on top of a polished surface of the alloy substrate and the assembly heated, in a controlled atmosphere furnace from room temperature to the bonding temperature, at a rate of 160°C h^{-1}. The assembly was held at temperature for various periods of time and then cooled at 60°C h^{-1} to room temperature. Either static air or flowing argon atmospheres were used during the bonding process. Coatings in air were formed by heating for 24 h at 520 and 540°C and a series were also made at 565°C with hold times from 0.8 to 24 h. Some samples were also bonded, under argon, at 583°C, which is above the eutectic temperature of the Al–Si alloy. During bonding, the glass blocks softened, flowed and wetted the surface of the alloy and eventually formed a spherical cap of glass.

It should be noted that glass coatings would in practice be most likely applied as inks (powder mixed with an organic vehicle) by screen printing of layers ~100 μm thick and the bonding procedure would involve holds of typically 15–30 min at temperature. The use of glass blocks and extended heating periods in this work were specifically aimed at enhancing the interfacial reactions for study.

2.4. Coating characterisation

Coating surfaces were examined using optical microscopy, prior to sectioning for further characterisation. The sectioning was perpendicular to the glass/substrate interface and followed the diameter of the spherical cap. Oil-based lubricant was used with a diamond saw and the resulting section was mounted in conducting resin and polished, again using oil-based media, to 1/4 micron finish. The polished section was sputter coated with carbon to provide charge removal when viewed by scanning electron microscopy (SEM). A JEOL 6100 Scanning Electron Microscope was used for imaging, in secondary electron and backscattered electron modes. Porosity measurements were obtained through the analysis of backscatter images (×100) using quantitative stereology. Compositional analysis used energy dispersive X-ray analysis (EDX, Oxford Instruments Link Pentafet detector, model. No. 6641) at 20 kV. EDX provided both qualitative and semi-quantitative analysis of all elements except oxygen and boron. The distributions of constituent elements across the interface were determined using linescans of the K_α lines of Si and Al and the M_α line of Pb, with a sampling time of 400 s.

3. Results

3.1. Surface appearance

The coatings were dark green in colour and too absorbing to permit imaging of sub-surface features with reflected or transmitted light optical microscopy. All coatings, with the exception of the coatings bonded at 583°C, supported some surface dendritic crystal growth (Fig. 1), the extent of which increased with increasing hold-time and decreased with increasing hold temperature. Similar features were observed for coatings of the same glass on pure Si and pure Al, indicating that it is a feature of the glass rather than the result of the bonding process.

The results of SEM imaging and EDX analysis of the crystal growth are shown in Fig. 2. These suggest that the crystal phase is a copper oxide, although the presence of boron cannot be ruled out. There is insufficient material to analyse the phase by XRD but Mallick[8] has reported surface growth of tenorite (CuO) on a soda-lime silicate glass containing the addition of ~2 mol% CuO. Those coatings formed at 583°C did not show any surface dendrites but did support the occasional large, metallic bead which appeared to have floated to the surface of the molten glass during bonding. Some fine cracks were also observed in those coatings fired under argon, especially close to the perimeter of the glass cap.

3.2. Bulk and interfacial microstructures

Sectioning of the coated samples resulted in fracture along the coating/substrate interface for some of the assemblies heated at 583 or 565°C. Fig. 3 shows cross-sections of coatings heated in air for 24 h/520°C, 24 h/540°C and 3 h/565°C. The extent of wetting of the substrate by the glass increases with time and temperature and indicates reaction at the interface. The bulk microstructure shows a small amount of bubble formation, increasing with temperature but there is no bulk crystallisation. Nor is there any formation of lead-rich precipitates as is the case when CuO is not present in the glass. The low level of porosity (< 2 vol.%) is probably due to out-gassing of the alloy which is itself ~2% porous. The bubbles formed were located in an ~70–150 μm thick band, from 50 to 400 μm above the interface, depending on time and temperature, suggesting a process which is of finite duration.

Fig. 4 shows the large metallic bead formed on heating at 583°C. EDX analysis showed that the bead is composed of an Al–Si alloy containing ~21 wt.% Si. This contrasts with the eutectic composition of ~12 wt.% Si. The bead is formed from material which has bled from the exposed Al regions of the substrate and then coalesced. The density of the bead predicted from composition is ~2.62 g cm^{-3} and, comparing the glass density of ~5.27 g cm^{-3}, it is not surprising that the alloy bead has risen to the glass surface. In addition to the metallic bead, the coating also contains numerous large bubbles which are more uniformly distributed than seen at lower temperatures. These are most probably the result of gases released from pores in the substrate during the course of the alloy bleeding.

The coatings formed at 520 and 540°C in air were well bonded, with no precipitates at the interface. Fig. 5 shows an example of an interface and illustrates the typical alloy microstructure of interconnecting regions

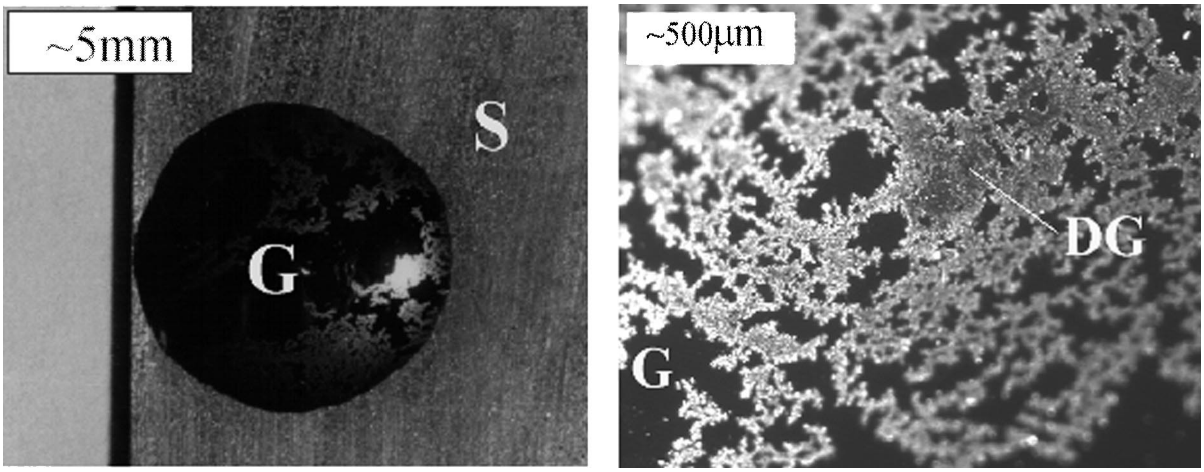


Fig. 1. Optical micrographs of the spherical cap formed by flow of the glass G and wetting of the composite surface S. These show the dendritic growth of a crystal phase DG on the curved surface. Sample formed at 565°C in air for 24 h.

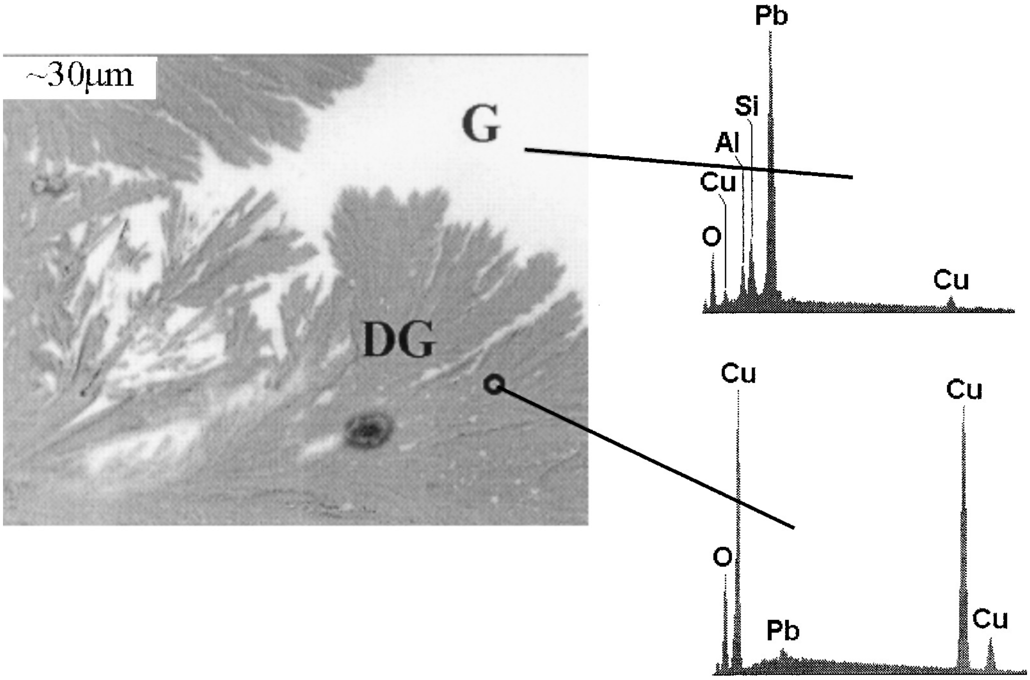


Fig. 2. Scanning electron micrograph of the dendritic surface growth. EDX analyses of the glassy region G and the crystalline region DG indicate that the crystal phase is a copper oxide.

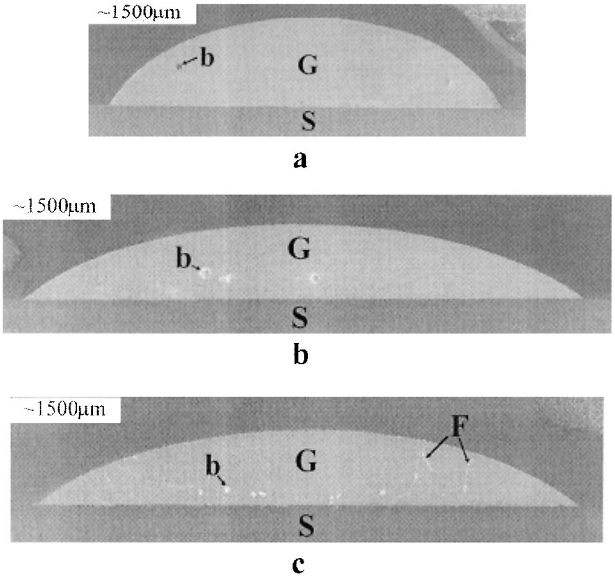


Fig. 3. Spherical caps of glass G on substrate S showing the effect of time and temperature on coating spreading. b indicates the presence of bubbles in the coating and F indicates fractures. (a) 24 h at 520°C, (b) 24 h at 540°C and (c) 3 h at 565°C.

of aluminium and silicon. The bright regions within the alloy are an iron aluminium silicide phase. Zhou et al.[9] identified a similar phase as δ-Al_4FeSi_2, present in their Al-20Si-5Fe Osprey alloy. The EDX linescans in Fig. 4 show a continuous interface, the main features of which are some limited aluminium and silicon diffusion from the alloy into the glass. For those coatings which detached during cross-sectioning, the fractures followed the interface and the two surfaces created were found to support a reddish-brown layer, which had formed during bonding. The coating fired for 3 h survived the cross-sectioning process and a scanning electron micrograph of the resulting interface is shown in Fig. 6. The extent of the damage at the interface may have been increased by the cutting and polishing processes. Fig. 7 shows a higher magnification section of the interface (rotated by 90° relative to Fig. 6) adjacent to a silicon region and the accompanying EDX line scan shows the presence of copper rich features at the interface. No such features are found at the glass/aluminium interface. In Fig 6, it can be seen that the crack propagates along the glass/silicon interface but then deviates into the glass when an aluminium region is reached. The glass has in fact penetrated into previously aluminium regions, often to a significant effect. In some cases this has revealed a sub-surface pore (Fig. 8) and the escaping gas has formed a bubble in the neighbouring glass region.

Fig. 9a and b shows optical micrographs of the two surfaces formed by fracture at the glass/alloy interface, with (a) being the glass side of the fracture and (b) the alloy. The shiny areas G in 9(a) are the original glass in the form of green, sunken features on the glass surface. These correspond to the raised (now red) glassy features G observed in 9(b) on the alloy surface, i.e. in some regions the glass has remained attached to the alloy and

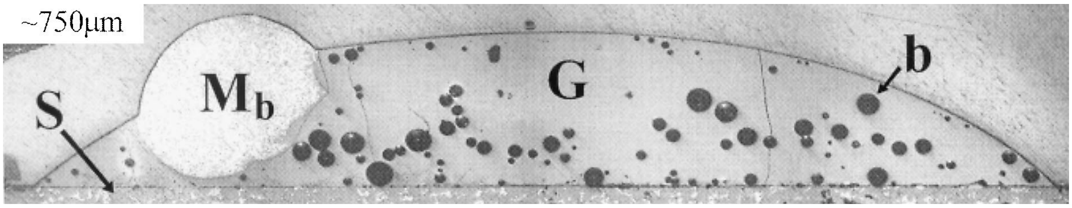


Fig. 4. Optical micrograph of the coating formed by heating at 583°C under argon for 1 h. G — glass coating, S — alloy substrate, b — bubble, M_b — metallic bead.

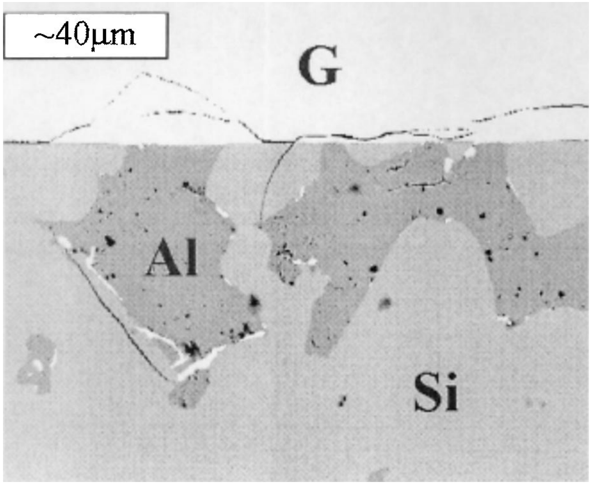


Fig. 5. Backscatter image of coating/substrate interface of sample heated at 540°C for 24 h in air. The fractures in the glass G may be the result of local TCE mis-match or may be introduced during sectioning and polishing.

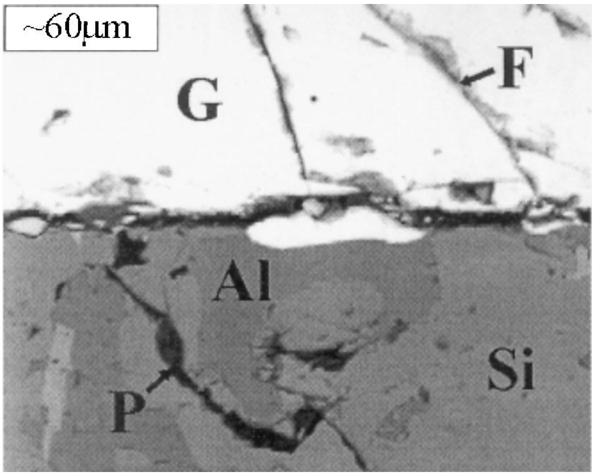


Fig. 6. Backscatter electron micrograph of coating/substrate interface of sample heated for 3 h at 565°C in air. A fracture has propagated along the interface with the silicon (Si) regions but travels through the glass adjacent to the aluminium (Al) regions. A pore (P) in the alloy and a fracture (F) in the glass (G) are indicated.

has also changed colour. Approximately 27–35% of the area is covered by glass. From the alloy composition, ~33% of the area should be Al phase. Fig. 10a shows an SEM micrograph of the fracture surface of the alloy and Fig. 10c an enlargement of the area containing the red phase. EDX analyses of the glassy region (Fig. 10b) and the region of red particles (Fig. 10d and e) are included. The analysis from the glassy phase is nearly identical to that obtainable from the bulk glass except that the peak due to copper is approximately twice as large. The analysis from the area of red deposit shows peaks from copper, silicon and oxygen. These fracture surfaces therefore confirm what is observed in the cross-section micrographs, that whilst glass remains adherent to the Al regions of the alloy, an interfacial layer, most probably copper metal, is deposited on the Si regions. The size of the copper particles increased with hold-time, from ~1.4 μm (1 h/565°C) to ~7 μm (24 h/565°C). X-ray diffraction of the substrate fracture surface is dominated by peaks from silicon. The peaks from aluminium are only a few percentage of what they would normally be by comparison with the silicon in the alloy — a result of the continued coverage of the aluminium regions by glass. In addition to these phases, there are small peaks from the iron aluminium silicide phase and from copper metal. There is no evidence of any copper oxide, copper silicate or borate phase, leading us to conclude that the deposit on the silicon regions is copper metal.

Fig. 11 shows the fractured interface of the sample prepared at the 583°C. This sample has been at temperature for 1 h only but a copper deposit can readily be seen at the interface. It is noticeable that the fracture appears to be flanked by regions of high oxygen content which may be oxide on the silicon.

The coverage of the fracture surface by this interlayer is dependent upon the atmosphere used during the coating process. If fired in air, then the periphery of the coated region does not support an interlayer — there is no copper deposit on the silicon in this region and the glass coating is well adherent to the surface. Fig. 12 shows an alloy surface on which a segment of the peripheral coating remains. Also noticeable, was that the red colouration of the fracture surface increased from the perimeter to the centre of the coated area. If the coating procedure is performed in an atmosphere of argon, the interlayer is formed over the entire coated surface and the red colouration of the surface is more intense, compared with coatings produced in air for identical time and temperature.

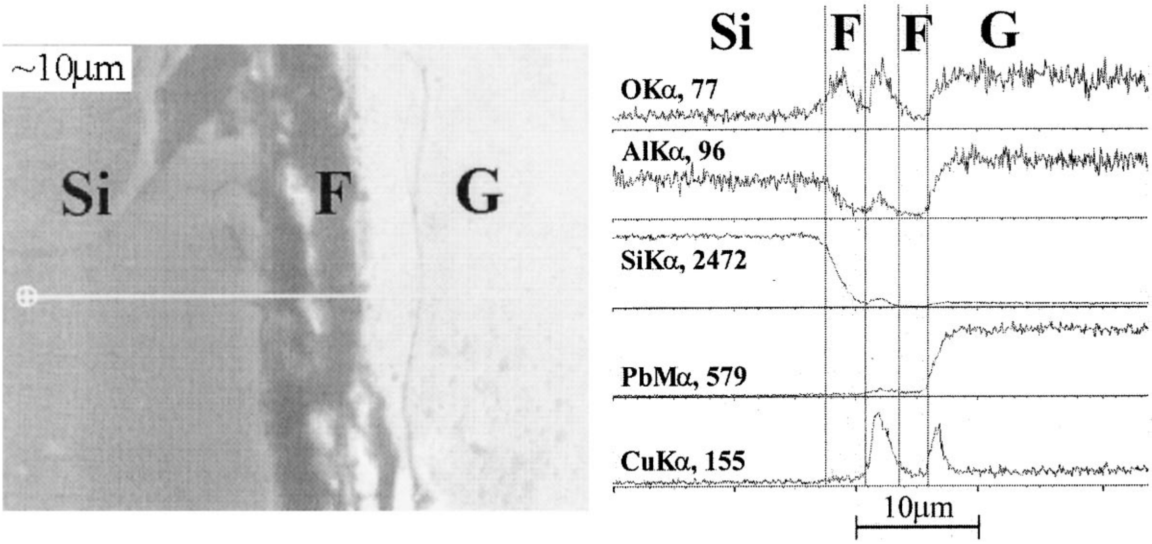


Fig. 7. Electron micrograph showing interface between a silicon (Si) region of the substrate and the glass coating (G). The EDX scans show that the fracture (F) along the interface follows the copper-rich interfacial deposit. Coating formed at 565°C for 3 h in air.

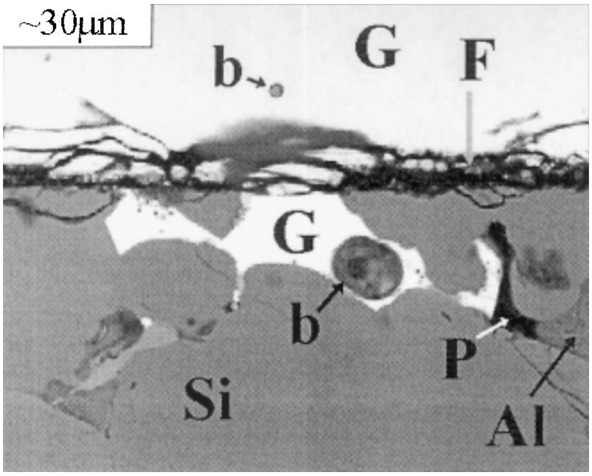


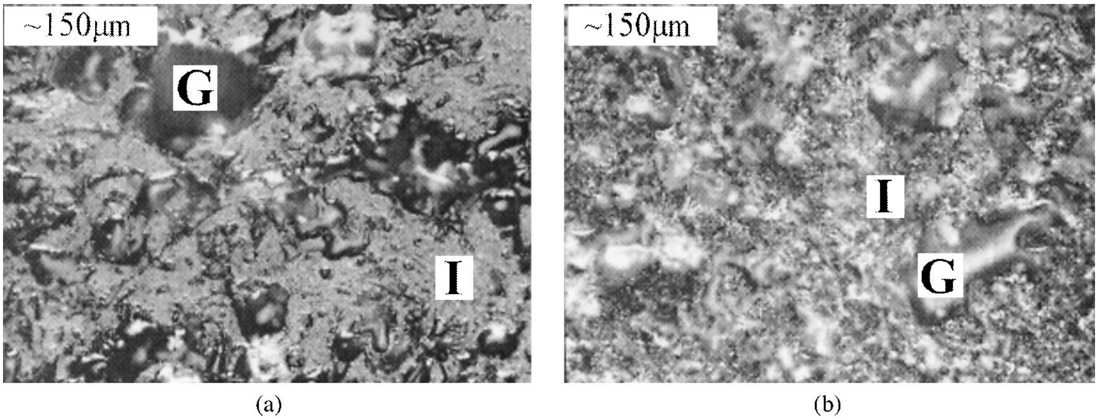
Fig. 8. Backscatter electron micrograph of the interface between the glass coating (G) and the substrate showing extensive dissolution of aluminium (Al), penetration of the glass into what was the Al region and escape of a gas bubble (b) from what was an internal pore (P) in the alloy. Another bubble is shown in the glass above the interface, having escaped from another revealed pore.

4. Discussion

The coatings formed at 520 and 540°C in air are typical of good glass-to-metal (or in this case composite) bonding. There is sufficient diffusion from the substrate into the glass to provide the continuity of chemical bonding across the interface but there is no indication of excessive dissolution and diffusion which would result in either unacceptable levels of corrosion or in loss of the transitional oxide layer and hence loss of bonding. The sample shown in Fig. 5 has been heated for 24 h, which is far longer than typical coating practice, where time at maximum temperature is usually much less than 1 h. More typical thick film coatings would show less diffusion but still be well bonded. The rate of dissolution of the interfacial oxides (Al_2O_3 and SiO_2) is sufficiently slow that re-oxidation of the surface can be achieved (directly or indirectly) by atmospheric oxygen, even though the coating is thick. There is therefore no evidence for reduction of any of the glass species at this temperature.

The samples prepared at 565°C show extensive interfacial reactions. The recessing of the Al regions at 565°C implies the onset of some corrosion mechanism, namely rapid oxidation of Al to Al^{3+} followed by its dissolution into the glass. On moving from the periphery towards the centre of the interface, atmospheric oxygen cannot be transported sufficiently rapidly to the interface to fuel this corrosion and therefore some species from the glass must be reduced. Thermodynamically, the most likely glass component to be reduced is CuO. If oxidation were achieved solely by the *local* reduction of the Cu^{2+} in the glass, then it would be expected that the Cu^{+} or Cu^{0} produced would be present at the aluminium interface. However, the copper particles are found exclusively at the interfaces with the *silicon* regions. If the aluminium and silicon are considered as providing regions of different electrochemical potential, then there is the possibility of creating a series of local Galvanic cells. Standard electrode potentials are not known for metals in contact with molten glass, however, observation shows that the Al regions act as anodes, giving the following electrode reaction:

$$Al_{alloy} \rightarrow Al^{3+}_{glass} + 3e^{-} \qquad (1a)$$



(a) (b)

Fig. 9. Optical micrographs of the substrate and coating surfaces revealed by fracture along the interface. (a) Glass surface — areas I are red and were in direct contact with silicon and support most of the interfacial copper deposit; areas G are green and are fractures through the bulk glass: (b) substrate surface — areas I are grey with red particles and are the silicon regions of the substrate; areas G are red, being glass containing cuprous ions, overlying the aluminium areas. The sample had been heated at 583°C for 24 h.

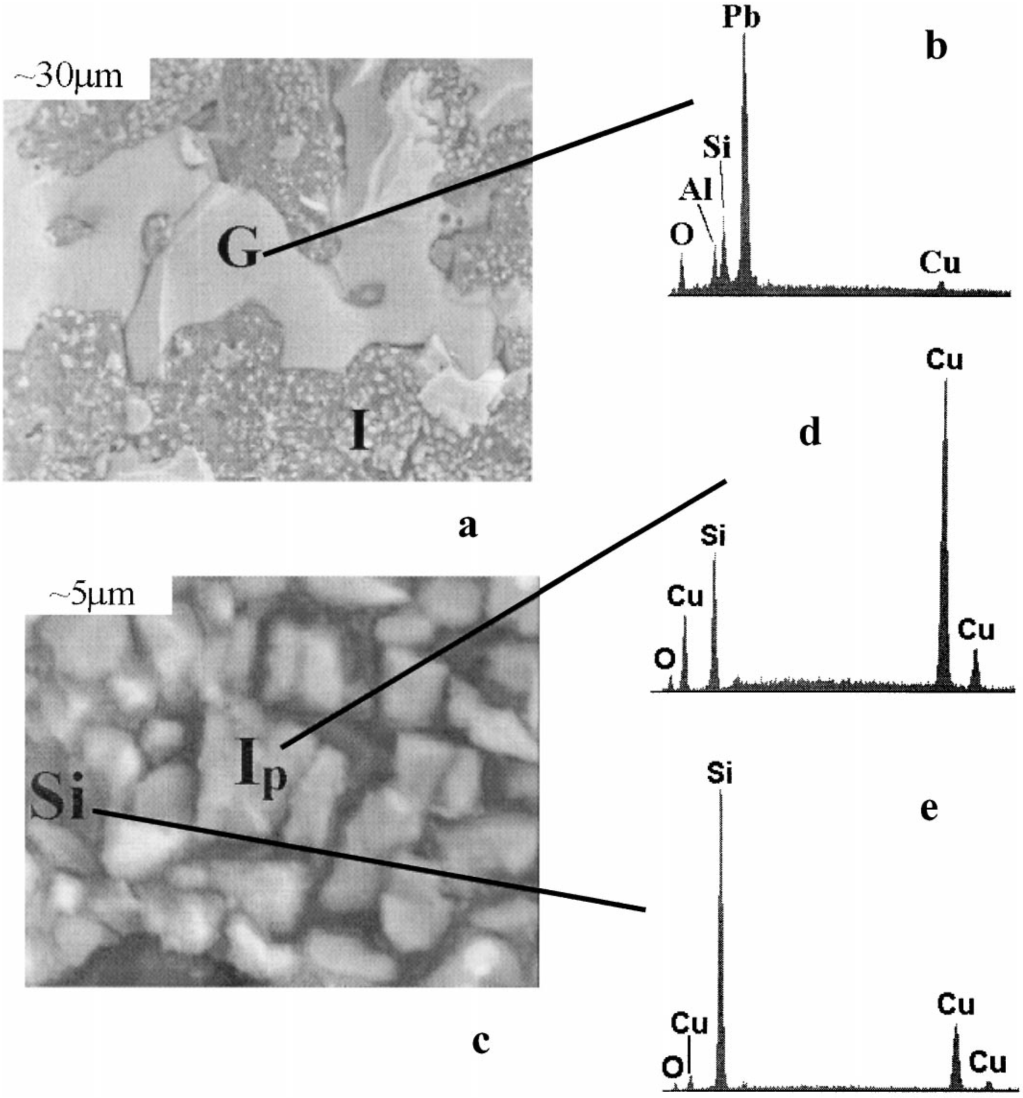


Fig. 10. (a) Electron micrograph of substrate surface after fracture along coating/substrate interface. G is an area of glass overlying an aluminium region. The EDX trace (b) is identical to that from the bulk glass. (c) Electron micrograph at higher magnification of area I, containing copper particles on a silicon region of the substrate, as shown by the EDX traces (d) and (e). The sample had been heated at 565°C for 1 h in air.

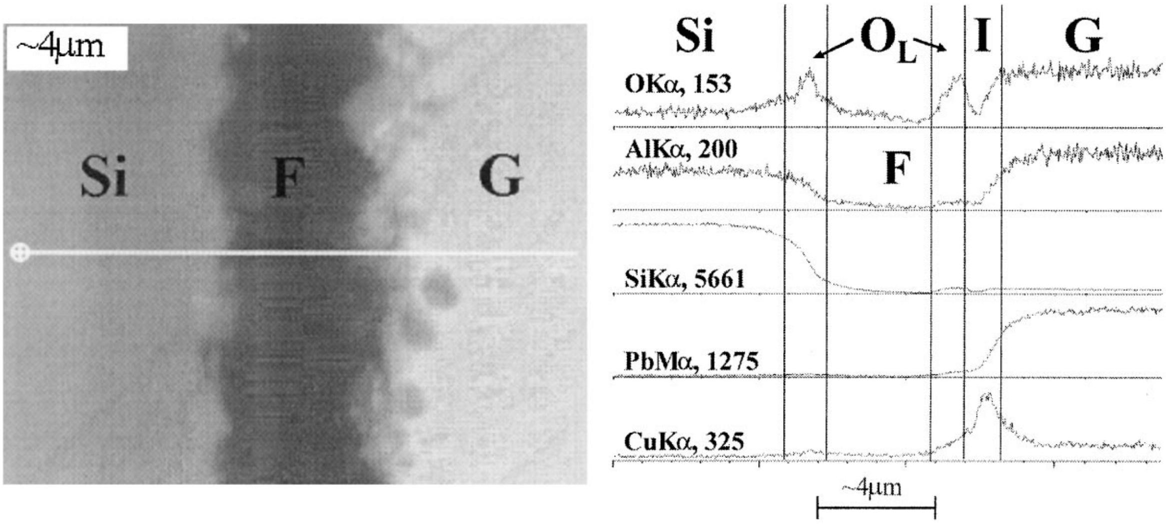


Fig. 11. Electron micrograph showing a silicon region of the substrate formed by heating at 583°C for 1 h under argon. Si — silicon, F — fracture, G — glass. The EDX linescans show a region of copper (I) adherent to the glass and regions which are oxygen-rich (O_L).

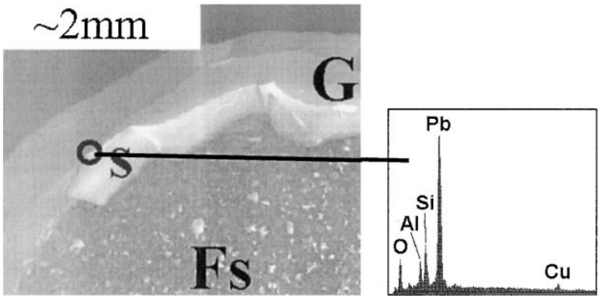


Fig. 12. Electron micrograph of sample fired for 1 h in air at 565°C. S — substrate, G — glass, Fs — fracture surface. This coating delaminated on sectioning.

This may proceed via intermediate formation and dissolution of the oxide

$$2Al_{alloy} + 3O^{2-}_{glass} \rightarrow Al_2O_{3\ interface} + 6e^-_{Al} \qquad (1b)$$

$$Al_2O_{3\ interface} \rightarrow 2Al^{3+}_{glass} + 3O^{2-}_{glass} \qquad (1c)$$

At the silicon regions, cathodic reaction occurs resulting in the formation of Cu^0 or possibly Cu^+:

$$Cu^{2+}_{glass} + 2e^-_{Si} \rightarrow Cu^0_{interface} \qquad (2a)$$

or

$$Cu^{2+}_{glass} + e^-_{Si} \rightarrow Cu^+_{glass} \qquad (2b)$$

which may undergo further reduction

$$Cu^+_{glass} + e^-_{Si} \rightarrow Cu^0_{interface} \qquad (2c)$$

Hence, the overall reaction is

$$2Al_{alloy} + 3Cu^{2+}_{glass} \rightarrow 2Al^{3+}_{glass} + 3Cu^0_{Si\ interface}\ \text{etc} \qquad (3)$$

The circuit is completed by transfer of electrons through the alloy from aluminium regions to silicon regions (Fig. 13) and by counter diffusion of O^{2-} ions from the glass adjacent to the silicon regions to the glass adjacent to the aluminium regions.

In addition to the red particles at the silicon interface, regions of the glass also appear to be red in the vicinity of the interface. This red coloration of the glass may arise from the formation of colloids of Cu^0 or Cu_2O, following the production of these species via reactions 2(a–c).[10] Where the crack has propagated through the glass, adjacent to the aluminium regions, it seems to have followed the boundary between the green, bulk glass and the red interfacial glass, which is much thinner over the Al regions than over Si.

This Galvanic cell behaviour is not observed at 520 or 540°C, therefore, at some temperature between 540 and 565°C, the cells become active. One possible explanation for this is that, for the cell to operate, the oxide layer on the Al must first be dissolved into the glass and this may require temperatures in this region for the process to occur within a reasonable period of time. Another possibility may be related to the transport of electrons through the solid, where the barrier to free transfer of electrons between metal Al and semiconductor Si may be too high unless a certain temperature is achieved. The nature of the barrier will depend on the doping of the silicon, particularly in the grain boundary region between Al and Si. An estimate can be made of the current density produced by the Galvanic process by

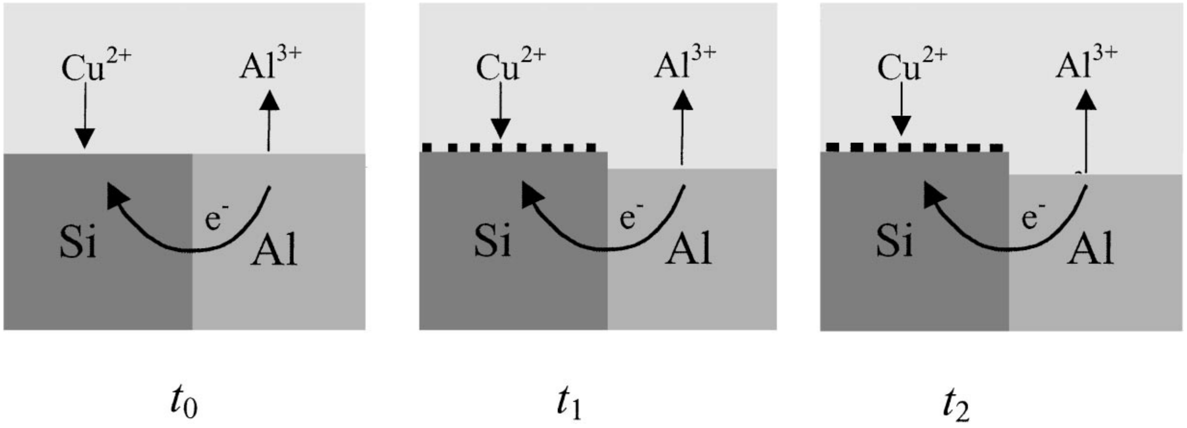


Fig. 13. Schematic of the galvanic process, showing dissolution with time of the Al regions as a result of the electrode reaction $Al \rightarrow Al^{3+} + 3\ e^-$ and deposition of copper at the silicon region as a result of the reaction $Cu^{2+} + 2\ e^- \rightarrow Cu$.

measuring the size and number density of the deposits on the silicon areas, assuming that they are pure copper. The amount of copper deposited over the whole surface (~1 cm^2 of silicon) is ~108 μg after 1 h at 565°C. This ignores any colloidal Cu which may be present in the glass and assumes that the current density is uniform over the period of heating. These figures then give a value for current density of 0.91 A m^{-2}. This is approximately a factor of 10^3 smaller than say the leakage currents typically observed in metal-oxide-semiconductor, field-effect transistor (MOSFET) devices and therefore unlikely to be blocked at an Al/Si junction. We have no knowledge of the doping level in the silicon regions in these samples, although it would most likely be p-type. Nevertheless, the possible potential barriers between the Al and Si regions would not prevent a Galvanic process which requires such small current densities to proceed, irrespective of temperature. This therefore indicates that it is the temperature dependence of the dissolution of the oxide film on the Al regions which controls the onset of the cell. This oxide could be either the original native oxide film or a passivating film formed by the Galvanic process at lower temperatures.

The dependence of the distribution of the interlayer on atmosphere can be explained by the shape of the glass coating. Because this has been produced from a glass block, the final coating has the form of a spherical cap which is significantly thicker in the centre than at the edges. In the thinner layers at the periphery, oxygen can diffuse to the interface to participate in the reactions

$$4Al + 3O_2 \rightarrow 4Al^{3+} + 6O^{2-} \tag{4}$$

In the thicker regions of the coating, oxygen access is insufficient to maintain the oxidation of the aluminium. Copper reduction now commences and, at a certain thickness, becomes the dominant process. In the absence of air, i.e. in an argon atmosphere, the CuO redox reaction takes over completely.

5. Conclusions

When an Al/Si composite material is exposed to molten lead borosilicate glass containing reducible Cu^{2+}, different potentials are established at the interface with each component phase. At elevated temperatures (commencing somewhere between 540 and 565°C) this leads to reduction of the Cu^{2+} to Cu^0 (and possibly Cu^+) at the interface with the silicon phase, followed by precipitation of copper metal particles on the silicon surface. The complementary oxidation process occurs at the interface with the aluminium phase, resulting in the formation and subsequent dissolution of Al^{3+} ions. Whilst the dissolution of aluminium regions can enhance bonding by the formation of mechanical keying, the dissolution of the oxide layer on the Al and the deposition of a weak interfacial layer of Cu on the Si regions ultimately cause the coatings to fail. The thermal exposures given to the samples studied here are far greater than would be used in the formation of coatings. Thus what is a cause of coating delamination in samples treated for several hours can be the source of good bond formation at short times or low temperatures. In this case, the survival of the oxide film on the aluminium regions is the critical factor. In addition, thick film coatings are typically ~100 μm and, at this thickness, atmospheric oxidation may be sufficient to suppress the galvanic cell behaviour. The behaviour of such composite/glass systems under typical thick film coating regimes will be the subject of future studies.

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