JOURNAL OF MATERIALS SCIENCE 12 (1977) 1088–1094

Thick film adherence fracture energy: influence of alumina substrates

P. F. BECHER, J. S. MURDAY
U.S. Naval Research Laboratory, Washington, D.C., USA

The adherence of a glass bonded Pt–Au thick film conductor to various alumina substrates is degraded by changes in the surface composition of and by the presence of (0 0 0 1) crystallographic texture in the substrate. Using the critical fracture energy (γ_{IC}) required to separate the thick film from the substrate, it was found that γ_{IC} was reduced from a maximum of 3.7 J m^{-2} using an as-received 96+ wt% alumina substrate to ~ 2 J m^{-2} using an as-received 99+ wt% alumina. In addition, the thick film adherence γ_{IC} using (0 0 0 1) sapphire substrates was less than that using (1 1 $\bar{2}$ 3) sapphire. The 96 wt% substate exhibited essentially a random crystallographic surface texture and a considerable amount of surface silicates. The as-received 99+ wt% Al_2O_3 substrate was charactarized by a high (0 0 0 1) surface texture and, while exhibiting a similar composition silicate layer as that of the as-received 96 wt% alumina, the total amount of the glass layer is greatly diminished. Fractographic analysis of the separated thick films and substrates showed that changes in the substrate crystallographic texture and the glass layer diminish the interpenetrating nature of the glass–metal interface and weaken the glass–substrate interface. Such changes in thick film microstructure lead to poorer thick film adherence.

1. Introduction

An earlier study has shown that fracture mechanics tests could be used to determine adherence in terms of the energy required to separate a thick film conductor from an alumina substrate [1]. The adherence fracture energy (γ_{IC}) of glass bonded Pt–Au conductors to alumina was shown to be degraded by thick film firing conditions, involving 10 min firings at peak temperatures above 860° C; and that such degradation is enhanced by longer peak firing times [1]. Optimum adherence occurred when the glass–metal interface had a strongly interpenetrating nature; then failure occurred in the glass layer bonding the conductor to the substrate. Overfiring leads to a diminished glass–metal interpenetration and thus allows fracture to occur along a smoother glass–metal interface where the bonding is weak [1]. While peel strengths of thick films exhibit similar temperature dependence [2], such γ_{IC} measurements, coupled with fractography, have made it possible to correlate adherence with those phases and microstructures that control adherence.

It is recognized that differences in the firing temperature/time profiles are not the sole source of a variable thick film adherence. For instance, these systems can be mechanically weakened by thermal shock [3] which is consistent with the bulk behaviour of the brittle constitutent phases present in these thick films. However, much of the adherence variation may well be due to subtle or not so subtle differences in materials and processing conditions. For example, previous investigators found that altering the glass phase in [4, 5] or decreasing the grain size of [5] the alumina reduced the adherence strength of a high temperature Mo–Mn metallization which did not use glass additions. Comparable studies of the thick film conductors are limited [6], this, combined with interest in thick film reliability, led to this study of the influence of alumina substrate characteristics on thick film adherence.

TABLE I Al_2O_3 substrate characteristics

Substrate	Grain size	Surface finish	Bulk composition (wt%)
Polycrystalline 96 wt%	Bimodal ~ 85% 6–8 μm ~15% 20–25 μm	As-fired ~ 27 μin. CLA	94 Al_2O_3, 4 SiO_2, 0.8 MgO, < 0.1 CaO
99+ wt%	Bimodal 90% 1–3 μm 10% 10–15 μm	As-fired ~ 10 μin. CLA	99 Al_2O_3, < 1 SiO_2, < 0.1 MgO, < 0.1 CaO
Sapphire (0 0 0 1) and (1 1 $\bar{2}$ 3)	Single crystal	Mechanically polished ≤ 1 μm in CLA	~ 100 Al_2O_3

2. Experimental

The 0.635 mm (0.025 in.) thick alumina substrates included AlSiMg 614 (96 wt% Al_2O_3), AlSiMg 772 (99+ wt% Al_2O_3) and sapphire single crystal substrates with 0° (0 0 0 1) and 60° (1 1 $\bar{2}$ 3) surfaces. Variations in substrate surface conditions included as fired surfaces for the 614 and 772 substrates, a group of 772 substrates leached in 20 vol% HF to remove any surface silicate phase, and mechanically polished (~$\frac{1}{4}$ μm final abrasive) surfaces for the sapphire substrates. Other characteristics of the substrates are shown in Table I.

Auger spectroscopy was used to analyse both as-received substrates as well as substrates that had been fired to various peak firing temperatures and quenched in pure, flowing N_2 gas. Both X-ray diffraction and scanning electron microscopy (SEM) analysis were used to characterize the substrates while the SEM was employed to also examine the fracture surfaces formed by separating the thick film from the substrate during the fracture energy tests.

The glass bonded Pt–Au thick film composition* was printed (200 mesh screen) on the substrates, dried at 150° C in air for ~15 min, then fired in air using commercial firing profiles to various peak firing temperatures where they were held 10 to 12 min. A brass arm was subsequently attached using a 63 Sn–37 Pb solder dip to complete the fracture energy specimens.

The adherence fracture energy measurements employ the applied moment double cantilever technique [7] and specimen geometry and procedures have been previously described [1, 2]. All γ_{IC} measurements were made at 22° C, 40% r.h. with a deflection rate of 2×10^{-2} cm min^{-1}.

3. Results

3.1. Auger electron spectroscopy and X-ray diffraction analysis

Auger electron spectroscopy measures the elemental composition of surface layer 10 to 40 Å thick. Auger analysis of the various substrates show that a comparable silicate layer is present on both the as-received 96 and 99+ wt% substrates, Table II. The comparison of the intensities of the high and low energy Auger lines establishes that the glass if predominately as a layer of variable thickness on both substrates. Sputter profiles show the glass layer to be much thinner, on the average, for the 99+ wt% versus the 96 wt% alumina. The sapphire substrates are essentially free of surface contaminates as are the leached 99+ wt% substrates (Table II).

We are really interested in what glass phases are present on the substrate surface at the firing temperature since such phases are the ones important in forming the interface between thick film and

TABLE II Surface analysis of substrates for silica

Substrate	Temperature (°C)	Relative wt% SiO_2
Sapphire (0 0 0 1) and (1 1 $\bar{2}$ 3)	as-received	≤ 1
	850	≤ 1
96 wt%	as-received	~ 23
	850, 950, 1050	~ 23
99+ wt%	as-received	~ 25
	850	~ 18
	950	~ 13
	1050	~ 10
99+ wt% leached	as-leached	< 1
	850	~ 2
	950	~ 3
	1050	~ 4

---

* Mixture of glass frit (primary borosilicate + Bi_2O_3 + CdO), organic vehicle and Pt(~ 0.5 μm) and Au (~ 2 μm) powders.

substrate. The relative surface glass compositions for samples quenched from various temperatures are listed in Table II. The surface glass composition remains unperturbed for the 96 wt% alumina while the glass appears to be absorbed into the alumina with increasing firing temperatures for the as-received 99+ wt% alumina. The leached 99+ wt% substrates indicate some possible increase in surface silicate content with increasing temperature. As expected there is no change in the essentially zero surface silicate content of the sapphire substrates.

X-ray diffraction studies of the polycrystalline substrates using the analysis discussed by Nakada and Schock [8] revealed a strong crystallographic texture involving the (0 0 0 1) of the grains lying parallel to the 99+ wt% substrate surface (Fig. 1). Incremental removal of various thicknesses from the surface decreased the magnitude of the (0 0 0 1) texture by a factor of ~2 near the mid-plane of the substrate. The surface texture for the 99+ wt% alumina is concentrated about the (0 0 0 1) orientation. The increased relative intensity of certain other planes [e.g. (0 1 . 1 0) and (0 2 . 1 0) are due to the (0 0 0 1) texture [9]. By comparison to the 99+ wt% substrate, the 96 wt% alumina substrate exhibits a much weaker (0 0 0 1) surface texture, both in the magnitude of the (0 0 0 1) intensity and the relative increase in the intensities of other crystal planes (Fig. 1). The 96 wt% alumina data represents a substantial reduction in texture, particularly involving the (0 0 0 1) orientation, which is nearly eliminated at the mid-plane thickness of the 96 wt % substrate.

3.2. Effect of substrate on the average γ_{IC} for thick film–substrate separation

The fracture energy results shows that for firing temperatures above 750° C the adherence of the glass bonded Pt–Au conductor is reduced using the as-received 99+ wt% alumina substrate as compared to the as-received 96 wt% alumina (Fig. 2). At the optimum firing temperature of 850° C, γ_{IC} is lowered from 3.7 J m^{-2} with the 96 wt% alumina to 2.0 J m^{-2} with the 99+ wt% alumina. Further, γ_{IC} drops to $\leqslant 0.7$ J m^{-2} after 10 min firings at 1050° C with the purer alumina while such values were not obtained with the 96 wt% substrate until firings of ~30 min at 1100° C [1].

When the 99+ wt% alumina substrates were leached to remove surface silicates, the γ_{IC} values for 10 min firings at 850° C were reduced to 1.2 J m^{-2}. In order to further examine the effects of the surface glass, pure sapphire substrates with polished (0 0 0 1) surfaces were employed; these resulted in thick film adherence γ_{IC} values comparable to as-received 99+ wt% alumina (Table III). However, if a polished $(1 1 \bar{2} 3)$ surface sapphire is used, the γ_{IC} for thick film separation

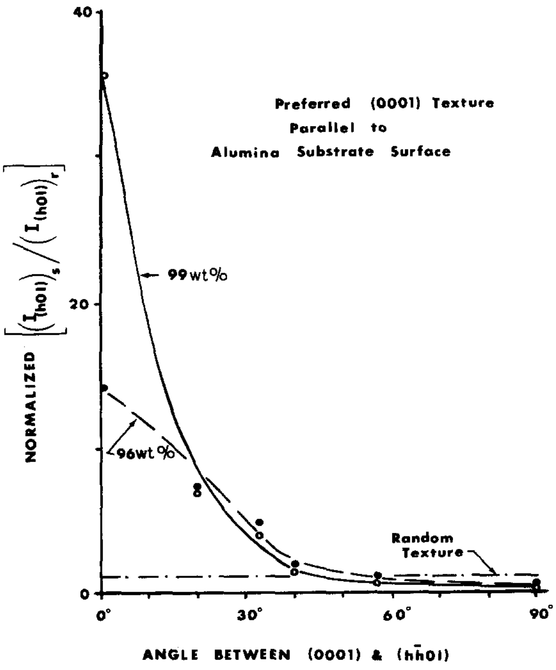

Figure 1 Relative X-ray intensities for various crystal planes in alumina substrates. Normalized ratios were calculated from the intensities of $(h \bar{h} 0 l)$ divided by that of the $(1 1 \bar{2} 3)$ in substrate surface plane versus random powder [8]. When the normalized intensity ratios are high there is a greater tendency for plane to be oriented parallel to substrate surface.

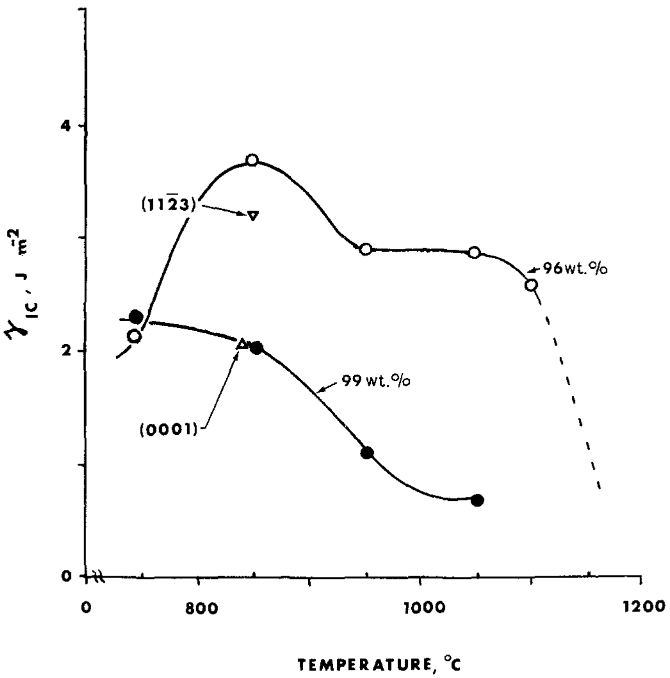

Figure 2 Adherence γ_{IC} for glass-bonded Pt–Au thick film on alumina substrates versus peak firing temperature. Samples were printed, dried and fired in air, heated and cooled under equivalent conditions with the exception of peak firing temperature. All samples held at temperature for 10 min.

is raised to near the level obtained with the 96 wt % alumina (Table III).

3.3. Fractography of separated thick film–substrate surfaces

Examination of stereo SEM photographs revealed several changes in fracture surfaces when 99+ wt % substrates were used as compared to previous findings with 96 wt % substrates [1]. In samples fired at 850° C, failure occurred along the glass-metal interface involving fracture of glass fibrals which penetrated across the interface into the metal (comparable to those obtained with the thick film fired on 96 wt % substrates at 950° C, Fig. 5, [1]). Some evidence of failure along the glass–alumina interface was also found. The thick film glass addition does not then penetrate as well into the metal conductor layer using the 99+ wt % substrate as compared with the 96 wt %. Further, the thick film glass is taken into the crevices between the grains of the 99+ wt % alumina and "uplifting" of grains suggests glass is absorbed into the surface grain boundaries. Also crystal products are formed in the glass on the 99+ wt % Al_2O_3 at $\geqslant$850° C, which was not prevalent until firing temperatures exceed 1050° C when the 96 wt % alumina was used [1, 10]. Firing at 950° C leads to a similar fracture path as the 850° C firing while

TABLE III Adherence γ_{IC} values for separation of glass-bonded Pt–Au thick film from alumina substrates

Substrate	Peak firing temperature (° C)*	γ_{IC} (J m^{-2})	δ†	No. of specimen
96 wt %	750	2.1	±1.1	11
	850	3.7	±1.6	21
	950	2.9	±0.5	4
	1050	2.9	±1.3	3
99+ wt %	750	2.3	±1.2	10
	850	2.0	±0.7	9
	950	1.1	±0.3	7
	1050	0.7	±0.2	7
99+ wt % leached	850	1.2	±0.8	14
Sapphire polished				
(0 0 0 1)	850	2.0	±1.0	8
(1 1 $\bar{2}$ 3)	850	3.2	±1.2	6

*Held at temperature 10 min, air firings.
†δ is the standard deviation.

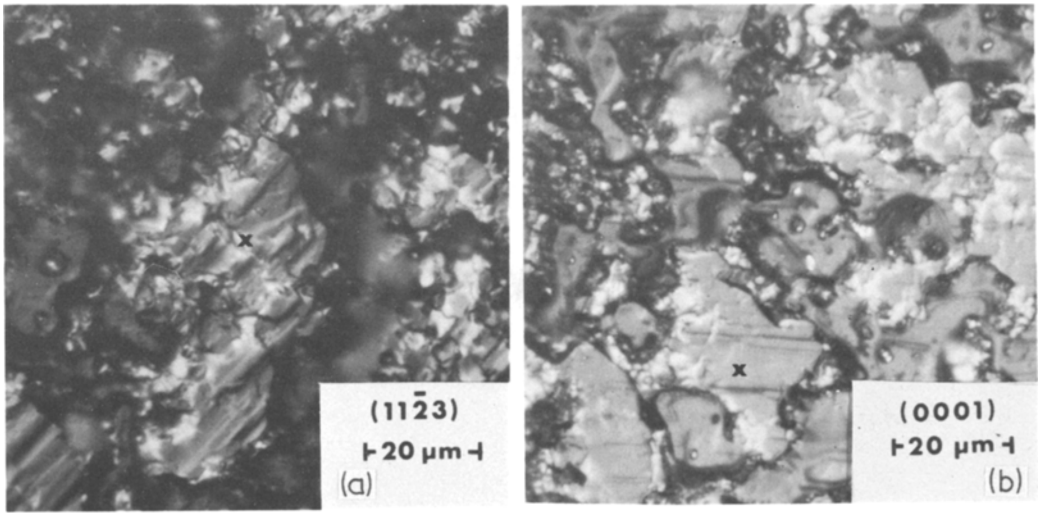

Figure 3 Thick film–substrate fraction surfaces obtained with sapphire substrates. Substrate half of fracture surface shows greater attack of 60° (1 1 $\bar{2}$ 3) (a), versus 0° (0 0 0 1) (b), sapphire surface by thick film glass (note areas marked x).

1050° C firings result in failure along the smooth glass–metal interface (see Fig. 4 of [1]). The 750° C fired samples employing both 96 and 99+ wt % substrates involve failure in the glass, at the glass–alumina interface and some at the glass–metal interface. The appearance of non-sintered metal clusters and only partially "melted" glass particles are indicative of an underfired microstructure.

The fracture surfaces of (0 0 0 1) and (1 1 $\bar{2}$3) sapphire substrates for thick film firing temperature of 850° C (Fig. 3) show there is greater roughening of the substrate surface with the (1 1 $\bar{2}$ 3) surface. Also, there is substantial glass–alumina interface failure with the (0 0 0 1) sapphire and not with the (1 1 $\bar{2}$ 3) substrate where failure occurs primarily in the glass layer. The fracture surfaces obtained with the use of both the (0 0 0 1) and (1 1 $\bar{2}$ 3) substrates show crystal formation in the thick film glass layer. Such crystals lie on the fracture surface when the crack propogates in the glass suggesting that they may contribute to the fracture process.

4. Discussion

The adherence γ_{IC} for thick film substrate separation shows a substantial reduction with the purer, finer grained 99+ wt % substrate. The reason for this appears two-fold. First, there is the decrease or removal of the silicate layer on the substrate. The fractography studies show this results in reducing the interpenetration of the frit glass layer–metal conductor interface. The glass layer presumably enters into the surface crevices of and possibly the grain boundaries of the alumina reducing the amount of thick film glass available for penetration into the metal. This soaking of silicates into the alumina is also indicated by the decrease in surface silicate content of the as-received 99+ wt % alumina with increasing firing temperature. The additional loss in adherence when the purer substrate is leached to remove the substrate surface silicates prior to bonding the thick film gives further evidence that the presence of surface glass on the as-received substrate is needed for good adherence. It is expected that better wetting occurs between the glass and the substrate than glass and metal [1] thus the surface energy acts as a driving force to pull the glass from the metal onto, and possibly into, the substrate surface.

However, the glass alone does not appear to account for the total difference in adherence. If depletion of the glass layer were all that led to the reduction in γ_{IC} with 99+ wt % alumina, then the γ_{IC} values using the purer (0 0 0 1) and (1 1 $\bar{2}$ 3) sapphire substrates should not be equal to or greater than those obtained with the 99+ wt % alumina.

One factor that was discounted as having a significant effect is that of the original surface roughness or surface area of the substrate. The fact that the thick film adherence to polished sapphire substrates is as good as or better than the smoothest polycrystalline substrate (i.e. the 99+ wt% alumina) indicates that substrate surface roughness is, at best, a second order factor in the present adherence observations. Therefore, some other substrate feature, in addition to surface silicates, appears to influence the thick film adherence.

The fractography of both the (0 0 0 1) sapphire and the 99+ wt% alumina show that fracture, in part, occurs along the glass–alumina interface. Also, crystals are formed in the glass and are associated with fracture for the 99+ wt% alumina and both sapphire substrates. These observations coupled with the strong (0 0 0 1) texture of the 99+ wt% substrate indicate that the adherence is partially reduced by a weaker glass–alumina interface when the glass wets the (0 0 0 1) surfaces. This is supported by the higher adherence γ_{IC} values and the lack of alumina–glass interface failure obtained with the $(1\,1\,\bar{2}\,3)$ sapphire substrates. The difference between the two sapphire substrates can be understood in terms of their surface energies. While no surface energy data as a function of surface orientation exists for sapphire, the denser ion packing of the (0 0 0 1) versus the $(1\,1\,\bar{2}\,3)$ surface would be expected to result in a lower surface energy for the (0 0 0 1). The lower the surface energy of the surface would result in less driving force for glass wetting and/or reaction with the substrate. The rougher surface of the $(1\,1\,\bar{2}\,3)$ surface in contact with glass after firing is indicative of greater glass–Al_2O_3 reaction and supports an orientation-dependent surface energy for sapphire. These results and the tendency for Al_2O_3–glass fracture using a (0 0 0 1) substrate are consistent with a degradation in thick film adherence caused not only by changes in substrate surface silicates but by the presence of a (0 0 0 1) surface texture in polycrystalline alumina substrates.

The scatter in the γ_{IC} values obtained for various firing conditions and substrates is consistent with the heterogeneous nature of the thick film microstructure. Unlike bulk single phase materials, the thick film microstructure is a gross mixture of metal, glass and voids. The proportions of which vary locally in the thick film. The crack does not always see one phase or another but various mixtures of the phases. Thus, for example, the crack front does not always encounter a smooth glass–metal interface in the overfired condition as a void may be present or locally a greater degree of glass–metal interpenetration may occur. Such a local variation in microstructure at the crack front would result in variations in γ_{IC} just as overall microstructural changes brought about by changes in firing conditions alter the average γ_{IC} values.

A comment on the presence of crystal phases in the thick film glass layer is warranted. Normally, glass-bonded thick film compositions would be formulated to obtain matching of thermal expansion coefficients such that compressive strains are in the glass layer on cooling from firing temperatures. Obviously tensile strains in the glass would degrade the adherence; the formation of crystals within the glass can lead to a similar weakening. Second-phase particles in a brittle matrix may effect both the tensile strength and the fracture energy of a brittle composite depending on the size and amount of second phase and the difference in thermal expansion between matrix and second-phase particle [11–13]. The present results indicate that the adherence γ_{IC} for the Pt–Au conductor is not influenced significantly by the formation of crystal phases in the thick film glass. However, this does not say that the tensile (or peel) strength is not reduced or what would occur in the case of other thick film compositions.

The present observations point out that variations in the surface chemistry and crystallographic texture of the alumina substrate can reduce the adherence of a glass-bonded thick film conductor. Although two different grades of polycrystalline alumina substrates were used, similar differences might be expected from different lots or manufacturers of the same grade of substrate. For example, variations in ceramic processing have been observed to lead to differences in the crystallographic texture of high alumina substrates [7, 9]. Further, the removal of silicates from the surface of high alumina can diminish the adherence of *thin* films [14] thus substrate characteristics should be critical in the adherence of hybrid circuitry. Such differences in substrate characteristics together with fluctuations in firing temperature then result in changes in thick film microstructures which leads to variable thick film adherence.

Acknowledgement

It is a pleasure to acknowledge the very able assistance of our NRL co-workers E. L. Shafrin with the Auger analysis, C. Cm. Wu with the X-ray analysis, S. M. Morey with scanning electron microscopy, L. A. Mann with the sample preparation, T. Donahue and R. Munson with the γ_{IC} tests. This study was supported by the Naval Air Systems Command with J. W. Willis as contract monitor.

References

1. P. F. BECHER and W. L. NEWELL, *J. Mater. Sci.* **12** (1977) 90.
2. P. F. BECHER, W. D. BASCOM, J. L. BITNER and J. S. MURDAY, Proceedings of the International Microelectronics Symposium International Society for Hybrid Microelectronics, Montgomery, Alabama (1975) pp. 279–286.
3. C. J. PECKINPAUGH and R. TUGGLE, Proceedings of the International Microelectronics Symposium International Society for Microelectronics (Park Ridge, Ill. 1968) pp. 417–421.
4. S. S. COLE and F. J. HYNES, *Bull. Amer. Ceram. Soc.* **37** (1958) 135.
5. J. R. FLOYD, *ibid* **42** (1963) 65.
6. T. T. HITCH, E. J. CONLON and W. I. ROGERS, in [2] pp. 287–295.
7. S. W. FREIMAN, D. R. MULVILLE and P. W. MAST, *J. Mater. Sci.* **8** (1973) 1527.
8. Y. NAKADA and T. L. SCHOCK, *J. Amer. Ceram. Soc.* **58** (1975) 409.
9. F. V. DIMARCELLO, P. L. KEY and J. C. WILLIAMS, *J. Amer. Ceram. Soc.* **55** (1972) 509.
10. P. F. BECHER, W. L. NEWELL and R. W. RICE, Progress Report, NAVAIR, AIRTASK A310310B/4R2103-001, NRL, Washington, D.C., January 1975.
11. D. R. BISWAS and R. M. FULRATH, *J. Amer. Ceram. Soc.* **58** (1975) 526.
12. N. CLAUSSEN *ibid* **59** (1976) 49.
13. S. W. FREIMAN and L. L. HENCE, *ibid* **55** (1972) 86.
14. R. C. SUNDAHL, *J. Vac. Sci. Technol.* **9** (1971) 181.

Received 18 October and accepted 28 October.