Development of Glass-Free Metal Electrically Conductive Thick Films

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Air-firable glass-free metal electrically conductive thick film pastes of different compositions were developed by using a titanium alloy component, and tin and zinc metal substitutes for glass frit used in traditional thick film pastes. The effect of different components on the electrical resistivity and bonding between the thick film and the alumina substrate was investigated. Thick films with low electrical resistivity and good bonding to the alumina substrate were obtained by using silver, zinc, tin, and TiCu alloy powders in the pastes. The addition of zinc at a small proportion (<0.5 wt.%) to a thick film paste enhanced the adhesion between the thick film and the alumina substrate with negligible increase in the electrical resistivity. The use of titanium alloy powder instead of pure titanium powder is preferred. Better composition distribution, and consequently, better wetting and bonding are expected by using active metal particles of a smaller size.
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Introduction

Thick film conductive pastes play a critical role in interconnections in the electronic packaging industry. A thick film paste usually consists of three parts: (1) metal powders, (2) glass frit, and (3) vehicle which will be burnt out after air firing. The preferred microstructure after air firing encompasses a low porosity metal layer at the top, a thin glass frit layer between the substrate (usually alumina) and the metal layer, and a rough glass-metal interface. This is essential to obtaining a high adhesion strength, as reported by Enokido et al. [1], who studied the relation between microstructure and adhesion strength of silver thick films. Traditionally, noble metals such as silver and gold have formed the basis of the conductive components of thick film pastes due to their low electrical resistivity (1.6×10^{-6} Ω.cm and 2.3×10^{-6} Ω.cm for silver and gold, respectively (Garter [2]), stability in the presence of glass frit, and limited oxidation during air firing (Lasance et al. [3]).

Although glass is commonly used as a binder in conductive thick films, it is not conducting and the resulting thick film is high in porosity, which is of concern to the AC loss, hermiticity and reliability. Zhu and Chung [4] have reported a glass-free (all metal) thick film paste by using Ti (an alloying element in the metal particles) as an adhesion promoter. However, the formulation suffers from the need to fire in an inert atmosphere, due to the tendency for titanium to oxidize in air.

To develop a glass-free metal thick film paste, one needs to develop a substitute for glass frit. The function of the glass frit in the thick film mainly includes two aspects: enhancing the adhesion between the thick film and the substrate, and maintaining cohesion among the metallic particles. During air firing, the glass frit softens, melts, and then flows to the interface between the thick film and the substrate under the influence of gravity and capillary action, and finally, chemically bonds with the substrate, thereby enhancing the adhesion between thick film and substrate, and enhancing the cohesion among the metallic particles. Therefore, a substitute of glass frit must possess such properties as a low melting point, good wettability with both Al_2O_3 and the conductive metallic particles in the thick film, and excellent oxidation

resistance. In short, good bonding between the substrate and the thick film and strong cohesion among the metallic particles must be obtained by using a glass frit substitute.

How to attain good bonding between the thick film and the Al_2O_3 substrate, especially after firing in the air, is a critical issue. The bonding between metal and Al_2O_3 has been studied by numerous investigators. One common bonding mechanism for the metal thick film and the substrate is related to the presence of glass at the interface, as the glass bonds the metallic layer to the Al_2O_3 grains, as reported in the case of tungsten as the metal by Behrens and Heuer [5]. In addition, an interface reaction layer (reaction bonding) or diffusion of the metal into alumina (diffusion bonding) also results in good bonding. For example, the eutectic reaction of copper and copper oxide has been widely used to bond copper and alumina (Yoshino and Shibata [6]; O'Brien and Chaklader [7]). Reaction bonding between transient liquid-phase metal interlayers (tin-based filler metal and either amorphous $Cu_{50}Ti_{50}$ or NiCrB interlayers) and Al_2O_3 was investigated by Zhai et al. [8]. The diffusion of aluminum into alumina also resulted in good bonding when aluminum was vacuum deposited on alumina (Yoshino [9]). A method combining the processing advantages of liquid-state bonding methods (brazing) with the ability to use refractory metal interlayers normally associated with solid-state bonding methods (diffusion bonding) was explored to join ceramics by low temperature routes (Dalgleish et al. [10]). The joining of Al_2O_3 to a bulk metal is often conducted under high temperature, high pressure, and high vacuum conditions to attain good bonding. Active metallic elements such as titanium, zirconium, chromium, and manganese are often used to wet Al_2O_3 because of the inherent difficulty of Al_2O_3 to be wetted by many other metallic elements. However, the active metallic elements have a strong affinity with oxygen or nitrogen. For example, zirconium oxidation occurs at temperatures around 205°C, a temperature far below the temperature to burn out the vehicle (usually around 450°C). The strong affinity of the active metallic elements for oxygen is the reason why brazing, joining, and cofiring of Al_2O_3 by using active metals or alloys are usually carried out in a high-purity dry inert-atmosphere furnace or in a vacuum furnace. Commercial brazing alloys such as 49Ti-49Cu-2Be and Ag-Cu-Ti are often used to braze Al_2O_3 in vacuum. It is difficult to avoid the oxidation of active metal powder with a diameter about 3 μm; to be printable, the diameter of powders is usually less than 3 μm.

One way to decrease the oxidation of the active metallic elements during heat treatment is to use a high energy beam heating method, such as laser cladding and electron beam brazing, to decrease the contacting time of the active metallic elements with oxygen, hydrogen or nitrogen. However, the heating technique is inconvenient and costly for the electronic packaging industry. Decreasing the firing temperature also seems to be not useful, because the oxidation temperature of the active metallic elements is lower than the temperature needed to burn out the vehicle.

It is difficult or impossible to get an oxide free thick film if active metals have to be used to wet and join Al_2O_3. However, the active metal oxides may have little influence on the electrical conductivity of the thick film if the oxides concentrate in a thin layer adjacent to the substrate. According to the work of Liang et al. [11], the effects of different oxide additives on the sheet resistance of tungsten thick film conductor are different. Some oxides do not form a glass phase during firing and remain on the surface of metal particles, resulting in an increase of the tungsten thick-film sheet resistance; other oxides mainly concentrate at the interface between the thick film and the substrate and have essentially no influence on the tungsten thick-film resistance. The oxides of active metallic elements can be found at the interface even if the processing of the thick film is conducted under high vacuum. Therefore, some investigators used active metal oxides as parts of the binder, particularly since good bonding between the substrate and the film can be obtained by using the metal oxides (Lee et al. [12], Kuromitsu et al. [13]). For instance, the effect of the addition of cupric oxide on the adhesion strength between a copper thick film and alumina substrate was investigated by Lee et al. [12]. It was found that the adhesion strength was improved by controlling the cupric oxide content. Thus, a thick film with good bonding to the substrate and with excellent electrical conductivity may be obtained if the oxide of a certain active metal can be induced to concentrate at the interface.

Active metal alloy powders can be directly added to thick film pastes Okamoto [14]. The active elements may segregate to the alumina substrate and play a role in joining to the substrate. One problem is that the active elements may be partly or completely oxidized before reaching the interface. This will make it difficult to get an oxide free layer. Moreover, the driving force for the Ti diffusion toward the interface, as needed for adhesion, will be lost. Related research work (Carim and Loehmann [15]; Adlaβnig et al. [16]; Reicher et al. [17]) indicates that a high adhesion strength can be attained by the development of Ti enriched layers at the interface between metallization and ceramic AlN if the process was conducted in vacuum.

The purpose of this work is to develop air-firable glass-free thick film pastes by using active metal alloy components and metal substitutes for glass frit used in traditional thick film pastes.

Experimental Methods

Materials.   The metal and alloy powders used in the pastes are silver (Ag), copper (Cu), aluminum (Al), zinc (Zn) and tin (Sn), Ti 25Cu, and Ti 14Al 21 Nb alloy. The organic vehicle consists 60 wt.% ethyl cellulose and 40 wt.% di(ethylene glycol) butyl ether. The ratio of metal powders to the organic vehicle in the paste is 4:1. The typical composition of metal powders in the thick film pastes investigated here are listed in Table 1. The standard commercial alumina substrate (50.8×50.8×0.6 mm) was used. It contained 96% Al_2O_3 and was made by 3M Corporation, St. Paul, MN.

The silver powder, with a size less than 3 μm, was purchased from AMES Goldsmith Corp., Glens Falls, NY. Copper and tin powders, with a size of about 1 μm, were supplied by SCM Metal Products, Inc., Cleveland, OH. Ti 25Cu alloy powder was obtained from Aldrich Chemical Company, Inc., Milwaukee, WI. Its size was about 6–12 μm. Titanium (with a size of −8 mesh) and Ti 14Al 21Nb (with a size range from −35−+80 mesh) powders were supplied by Robert Farley Starmet Corp., Concord, MA.

Table 1   Compositions of thick films

Designation	Composition (by weight)
A	97.91% Ag 0.75% Ti 0.25% Cu 1.09% Sn
B	98.00% Ag 0.38% Ti 0.13% Cu 1.49% Sn
C	97.14% Ag 0.38% Ti 1.20% Cu 1.28% Sn
D	85.06% Ag 0.60% Ti 13.40% Cu 0.94% Sn
E	96.66% Ag 0.38% Ti 1.20% Cu 1.28% Sn 0.48% Zn
F	95.00% (50.0% Ti+50.0% Al) 5.00% flux
G	Pure Ti powder
H	75.0% Ag 20.0% Cu 1.0% Zn 1.0% Sn 3.0% (Ti 14Al 21Nb)
I	95.00% (75.0% Ag 20.0% Cu 1.0% Zn 1.0% Sn 3.0% (Ti 14Al 21Nb) 5.00% flux
J	91.00% Ag 5.89% Ti 1.97% Cu 0.59% Sn 0.55% Zn
K	95.00% (91.00% Ag 5.89% Ti 1.97% Cu 0.59% Sn 0.55% Zn) 5.00% flux

Zinc powder (98.7%), with a size of about 1 μm, was purchased from Fisher Scientific Company, Fair lawn, NJ. Aluminum powder, with a size of about 2 μm, was supplied by Silberline Manufacturing Co., Inc., Tamaqua, PA. Ethyl cellulose (98%) was supplied by Dow Chemical Company, Midland, MI. Di(ethylene glycol) butyl ether (>99%) was purchased from Aldrich Chemical Company, Inc., Milwaukee, MI. Flux (AMCO 446) was supplied by American Solder & Flux Co., Inc., Paoli, PA.

Sample Preparation and Air Firing Process.   The pastes were applied on alumina substrates manually, not by screen printing, due to the large particle size of pure titanium, Ti 14Al 21Nb and Ti 25Cu alloy powders. The air firing process was conducted at 850°C for 30 min, with a heating rate of 5°C/min.

Electrical Resistivity Testing.   The volume electrical resistivity of the air fired thick films (corresponding to compositions A-E, I, J, and K) was measured using the four-probe method. The four electrical contacts were made by conductive silver paint. The outer (current) probes were 48.5 mm apart; the inner (voltage) probes were 41.5 mm apart.

Scratch Testing.   Scratching testing (Zhu and Chung [4]) of the thick films (corresponding to compositions C and E) was conducted on a 502 shear/scratch tester, made by Teledyne Taber, North Tonawanda, NY. The specimen was mounted on a horizontally rotatable plate. The scratching tool was attached to a finely balanced scale beam calibrated in grams. A diamond scratching tool in the form of an awl was used. The load was 500 g.

Microstructure.   The surface quality and the composition distribution of the air fired thick films, the fractured cross-sections of the fractured thick films, and the scratch morphology (corresponding to compositions C and E) were examined under a Hitachi S-4000 scanning electron microscope (SEM). X-ray spectroscopy was conducted using the SEM to analyze the elemental composition in selected regions of the microstructure.

Results and Discussion

Electrical Resistivity.   Table 2 shows the volume electrical resistivity of air fired thick films of different compositions and the visually assessed quality of wetting and bonding. Quantitative analysis of the bonding strength between the thick film and the Al_2O_3 substrate will be addressed in another paper.

From this table, the findings can be summarized as follows.

1 Decreasing the amount of Ti decreased the electrical resistivity of the thick films due to the high electrical resistivity of titanium, as shown by comparing compositions A and B. Thus, a good electrically conductive thick film needs a small proportion of Ti in the composition. However, too small an amount of Ti in the composition of thick films resulted poor wetting and bonding between the thick film and the substrate, though this case is not
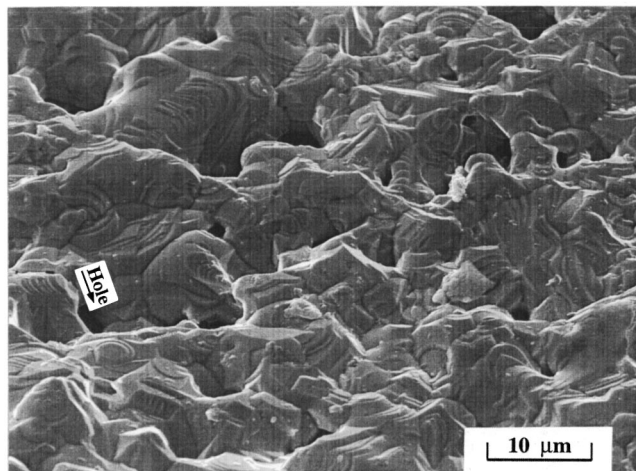
Table 2 The electrical resistivity of air-fired thick films with different compositions

Composition	Electrical resistivity (Ω.cm)	Thickness (μm)	Wetting and bonding
A	8.25×10^{-6}	32 ± 3	Good
B	5.35×10^{-6}	18 ± 2	Good
C	3.37×10^{-6}	16 ± 2	Good
D	1.11×10^{-5}	30 ± 3	Good
E	4.31×10^{-6}	16 ± 2	Good
F	/	/	No wetting
G	/	/	No wetting
H	/	/	No wetting
I	3.49×10^{-4}	18 ± 2	Good
J	7.25×10^{-5}	17 ± 2	Good
K	10.45×10^{-5}	16 ± 2	Good
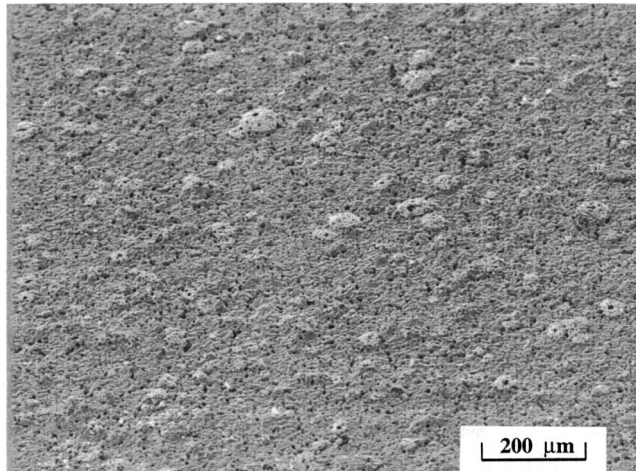
**Fig. 1 Typical surface SEM micrograph of the air-fired thick film**

Fig. 2 Microstructure of silver in the thick film

shown in Table 1. It was found that Ti in the amount of 0.3–0.4 wt.% resulted in both low electrical resistivity and good bonding.

2 Increasing the proportion of Cu to a certain value decreased the electrical resistivity of the thick film (as shown by comparing compositions B and C) due to the increased density of the thick film caused by the different sizes of the Ag and Cu powders, as indicated by SEM surface examination of air fired thick films. Further increase of the proportion of Cu increased the electrical resistivity because of the oxidation of copper powder, as shown by comparing compositions B, C, and D.

3 Slight addition of Zn powder had little effect on electrical resistivity (comparing compositions C and E), if the effect of the decreased proportion of Ag in composition E on the electrical resistivity is also considered.

4 No wetting was obtained in compositions F, G, and H, due to the strong oxidation of pure Ti powder or Ti alloy powder and the consequent non-reactivity between Ti and the Al_2O_3 substrate. The addition of a flux to pure titanium powder (composition F) still did not attain wetting to the substrate. This indicates that the addition of the flux could not effectively limit the oxidation of pure titanium. However, the addition of a flux to the Ti 14Al 21Nb alloy powder thick film composition (comparing compositions H and I) resulted in good bonding, although the resistivity of the thick film was high due to the use of a flux. This indicates that it is preferred to use Ti alloy powder instead of pure Ti powder in the development of thick film compositions. In addition, a metal substitute of the flux should be used in the composition development to decrease the electrical resistivity. The metal substitutes here were Sn and Zn, as described in compositions A to E. The idea of using Sn and Zn is that molten Sn at a low temperature around 232°C (Lyman [18]) flows and covers the surface of Ti alloy and Zn powders and limits the oxidation of Ti alloy and Zn powders. Melting of Zn at a higher temperature (420°C) will further protect Ti alloy powders from oxidizing. In addition, according to Madakson [19], the oxidation of Ti could be reduced by the formation of SnO_2 resulting from the presence of Sn.
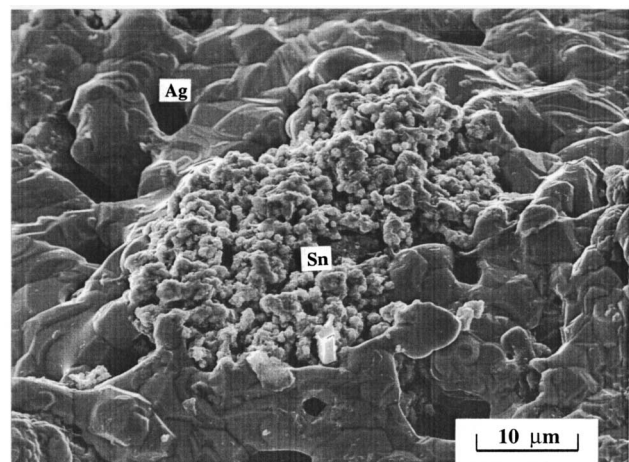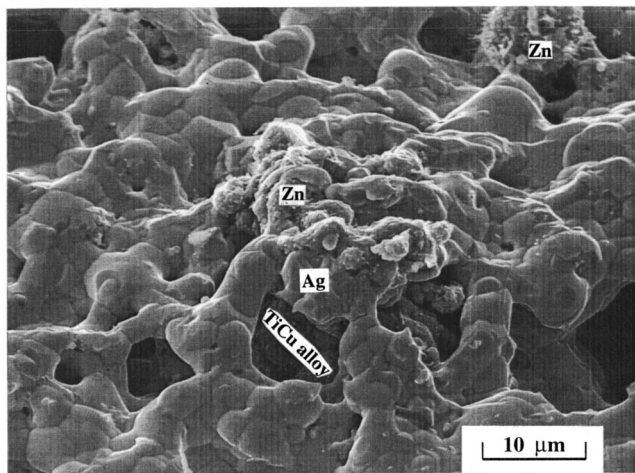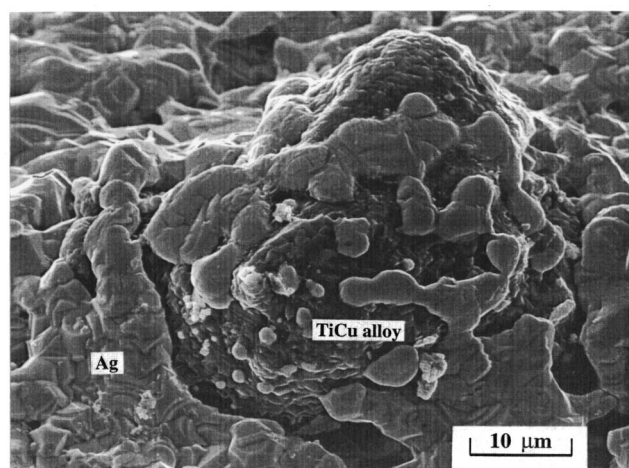

(a)
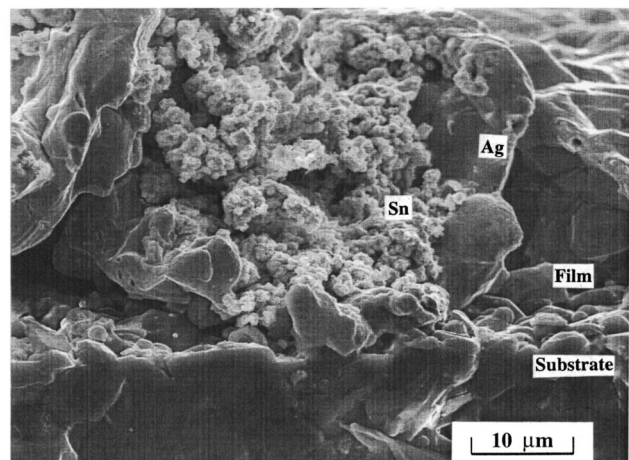
(b)

Fig. 3 The morphology and distribution of Sn on the surface (a) and in the cross section (b) of the thick film (corresponding to composition C)
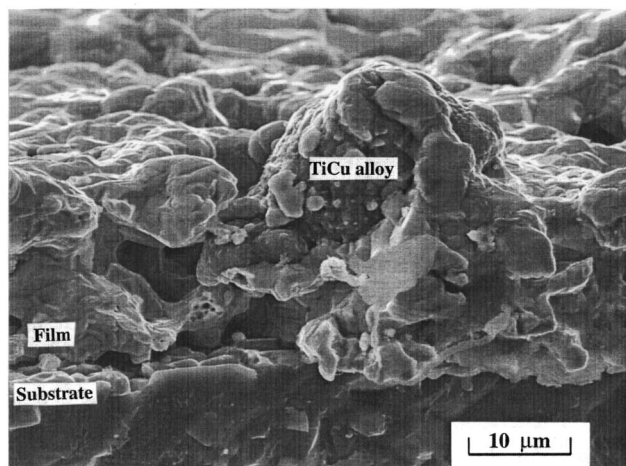
Fig. 4 The morphology and distribution of Zn on the surface of the thick film (corresponding to composition E)
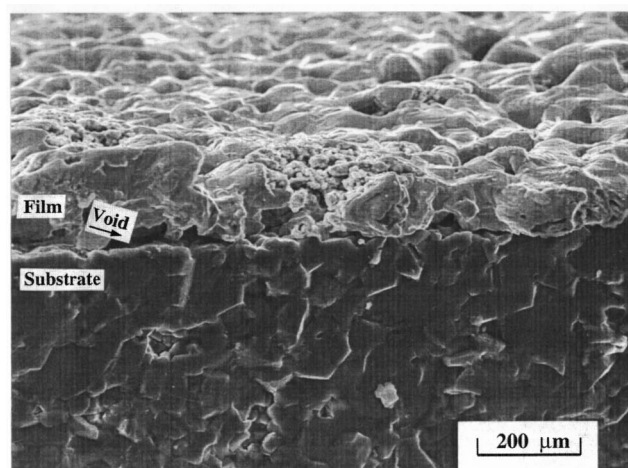

(a)

(b)

Fig. 5 The morphology and distribution of TiCu alloy component on the surface (a) and in the cross section (b) of the thick film (corresponding to composition C)

5 To attain good wetting and bonding, active metal alloy particles with a small size should be used. The paste containing Ti 14Al 21Nb particles (composition H) did not result in wetting and bonding to the substrate as the pastes containing Ti 25Cu particles (compositions A-E and J) did, although Ti 14Al 21Nb alloy has

limited oxidation at high temperature. The reason was inaccurate in two aspects. First, the large size (up to 177 μm) of the Ti 14Al 21Nb alloy particles resulted in poor distribution in the thick film. The activity was absent in some parts of the thick film due to the absence of the Ti 14Al 21Nb alloy particles in these parts. Second, by using metal substitutes (Sn and Zn here) for glass frit, it was more difficult to cover large size active metal particles and limit their oxidation in the thick film during air firing.

6 Thick films with low electrical resistivity and good bonding were obtained by using TiCu alloy, zinc and tin powders in the pastes, as shown by compositions B, C, and E.

Microstructure. Figure 1 shows a typical surface micrograph of the air-fired thick films. Silver (this and other elements confirmed by X-ray spectroscopy) exhibited a network structure in the thick film, as shown in Fig. 2 (corresponding to composition C). No single silver particle was found. Holes could be found in the silver matrix. This indicated that silver particles melted during air firing and resolidified together afterward. The distribution of Sn, Zn, and Ti was heterogeneous. Figures 3(a) and 3(b) (corresponding to composition C) show the morphology and distribution of Sn on the surface and in the cross-section of the thick film, respectively. Figure 4 shows the morphology and distribution of Zn on the thick film surface (corresponding to composition E); Zn was in a ~10 μm wide region near the center of Fig. 4. The
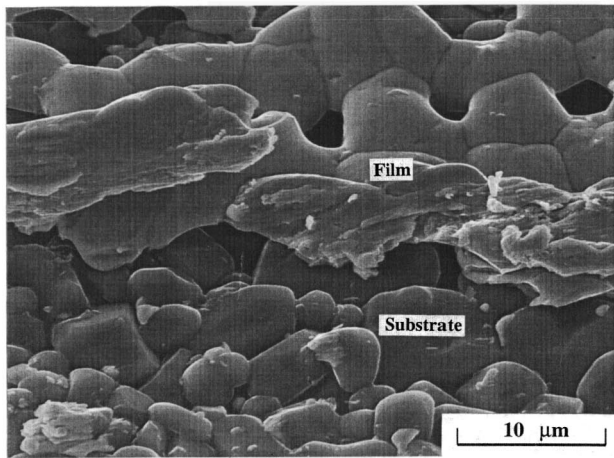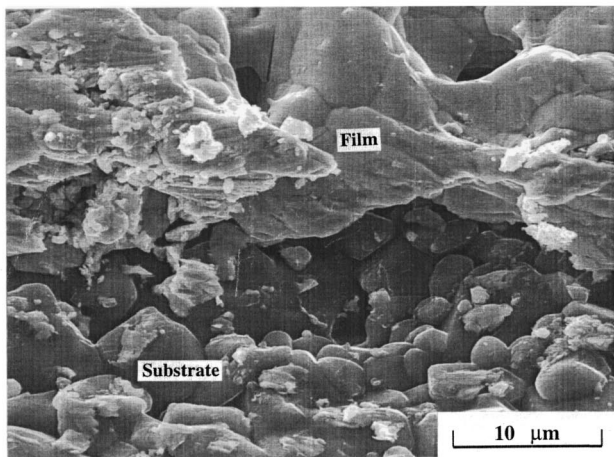

(a)
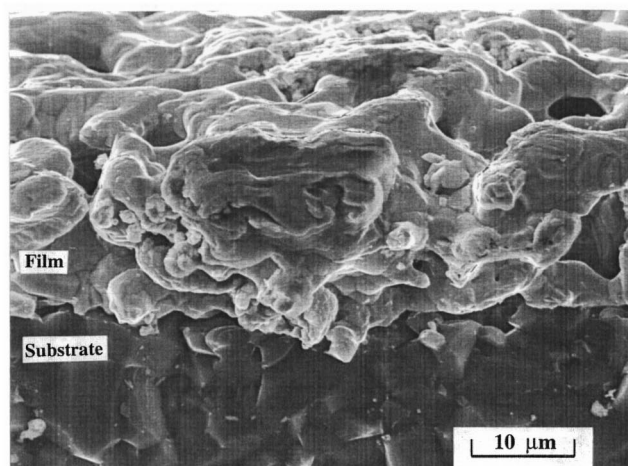
(b)

Fig. 6 The cross-section micrograph of the thick film. (a): corresponding to composition C; (b): corresponding to composition E

(a)

(b)

Fig. 7 SEM micrographs of the scratch path of thick films of (a) composition C, and (b) composition E

morphology of Sn and Zn suggested that Sn and Zn particles melted during air firing. Figures 5(*a*) and 5(*b*) are the morphology and distribution of the Ti 25Cu alloy component on the surface and in the cross-section of a thick film (composition C), respectively. The alloy component still existed in the form of particles. At least part of the Ti 25Cu alloy powder did not melt during air firing. The possibility of a reaction occurring between the Ti 25Cu alloy powder and the Al_2O_3 substrate or other metal particles in the thick film needs further investigation by TEM and XPS analysis. The attribution of the Ti 25Cu component to the adhesion between the thick film and the substrate may be supported by the diffusion of some Ti atoms to the interface between the thick film and the substrate, although this needs further investigation by X-ray spectroscopy. The smaller the size of the Ti 25Cu alloy particles, the better was its distribution in the silver matrix. The activity of the Ti alloy powder could be enhanced if a smaller size of Ti alloy powder was used, because the powder served as a glue, as in the case of glass frit in a traditional thick film. A homogeneous distribution of Ti alloy powder in the surface layer of the thick film is preferred. For this purpose, it is better to use AgTiM (M meaning other metal elements) alloy powder instead of the mixture of silver powder and Ti alloy powder. Figure 6(*a*) shows the cross-section of the thick film of composition C. Voids which were subsurface defects in the silver matrix and could be observed only in the cross-section direction (different from the holes in the thick films) were observed along the interface between the substrate and the thick film. Similar voids that were less clear could

be found in composition E, as shown in Fig. 6(*b*). Better adhesion between the thick film and the substrate could be obtained by the addition of the Zn component. Figures 7(*a*) and 7(*b*) are the SEM micrographs of the scratch path of compositions C and E, respectively. Much more thick film was attached to the Al_2O_3 substrate after scratch testing for composition E than composition C. This further indicates that better adhesion between the thick film and the substrate can be achieved by the addition of Zn.

Conclusions

1 Air-firable glass-free metal conductive thick films with low electrical resistivity and good bonding to alumina were obtained by using silver, zinc, tin, and TiCu alloy powders in the pastes.

2 The addition of zinc at a small proportion (<0.5 wt.%) to thick film pastes enhanced the adhesion between the thick films and the alumina substrate with negligible increase in the electrical resistivity.

3 Titanium component in the amount of 0.3–0.4 wt.% in the pastes resulted in both low electrical resistivity and good bonding.

4 It is preferred to use titanium alloy powder instead of pure titanium powder in the development of thick film paste compositions. In addition, better composition distribution and consequently better wetting and bonding are expected by using active metal particles of a smaller size.

5 The addition of a small amount of copper resulted in a decrease of the electrical resistivity. Further increase of the proportion of copper increased the electrical resistivity due to the oxidation of copper.

6 The addition of a flux to the pastes enhanced the adhesion between the thick film and the alumina substrate, but increased the electrical resistivity.

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