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Effect of Firing Atmosphere on Air-Fireable Glass-Free Electrically Conductive Thick Film

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The firing atmosphere (air, oxygen, and argon) was found to affect the electrical and mechanical properties of an air-fireable electrically conductive glass-free silver-based thick film. For the optimum firing temperature of 930°C, air results in the lowest resistivity, but a minor amount of pinholes; oxygen results in the largest thickness, the smoothest surface, and no pinhole; and argon results in the highest resistivity, large pinholes, the smallest thickness, vanishing of macroscopic parts of the film, and the poorest scratch resistance. Argon gives higher resistivity than air or oxygen at essentially all firing temperatures.

Key words: Thick film, silver, firing, electrical resistivity, mechanical property

INTRODUCTION

Electrically conductive thick film pastes are widely used as interconnections and terminations in electronic components such as resistors, capacitors, heaters, and sensors.[1–3] Pastes consisting of precious metals, such as gold, silver, platinum, and palladium,[4–6] are usually fired in air. However, pastes containing copper or other active metal components usually need to be fired in vacuum or in an inert or reducing atmosphere, in order to avoid oxidation. However, firing in vacuum or an inert or reducing atmosphere is expensive compared to firing in air.

Conventional conductive thick-film pastes use glass as the binder, in spite of the nonconductive nature of glass. During firing, the glass (frit) becomes viscous and flows, thereby resulting in binding within the thick film and adhesion between the film and the substrate. For the purpose of increasing the electrical conductivity, which is increasingly demanded by high power electronics, the substitution of the glass binder with other binding mechanisms is desired. Therefore, this paper addresses glass-free all-metal thick films.[7–11]

Active metal components, such as titanium, are often used as the binder in a glass-free conductive paste. The reaction between the active component and the ceramic substrate (e.g., alumina) enhances the bond between the film and the substrate. A paste containing an active metal component is usually fired in vacuum or an inert atmosphere. Otherwise, the active metal component is oxidized during firing, thus losing its activity and consequently becoming unable to function as the binder. Titanium is well known for this function, as it is used in active brazing alloys.[12] High adhesion strength can be attained by having a titanium-rich layer at the interface between thick film and an aluminum nitride substrate if firing is conducted in vacuum.[10,13,14] A thick film based on a copper-silver eutectic alloy and containing titanium attains good bonding with an aluminum nitride substrate after firing in argon.[10,13] Thick-film conductors with base metals such as Ni, Cr, Al, and Cu and fired in air suffer from inadequate bonding.[15]

Passivating components are usually used in developing air-fireable thick-film conductor inks with base metals such as Ni, Cr, Al, and Cu.[15–18] A boron compound, which tends to be reduced during the pyrolysis of the organic vehicle, is used in a nickel-based thick-film conductor in order to make the paste fireable in air.[17] In the case that the firing atmosphere is oxidizing, elemental boron is used in the paste, so that it is oxidized and serves as a glass that protects the nickel particle from oxidation after vehicle removal. Boron has a higher tendency to oxidize than nickel when the temperature is over 400°C.

Several air-fireable glass-free electrically conductive metal thick-film pastes have been developed.[7,19] However, in order to determine the optimum firing

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procedure, it is important to understand the effects of the firing atmosphere on the formation, microstructure, and properties of the thick film. In spite of the prior work,[7,10,13,14,19] no systematic study has been reported on the effect of the firing atmosphere. This paper is focused on such a systematic study. The firing atmospheres included in this study are air, oxygen, and argon. The comparative study involved electrical resistivity measurement, scratch testing, and microstructural examination.

EXPERIMENTAL METHODS

An air-fireable, glass-free, electrically conductive thick-film paste (96.6% Ag, 1.38% Cu, 0.28% Al, 0.35% Ti, and 1.39% Sn, by weight)[19] was used in this paper. The firing atmosphere included air, oxygen, and argon. The standard commercial alumina substrate (96% Al_2O_3, 50.8 × 50.8 × 0.6 mm) was used.

The thick film paste consisted of three parts, which are referred to as part A, part B, and part C. Part A is the organic vehicle. Part B is a commercial paste, which includes active metal components such as titanium and aluminum. The silver particles (95Ag-5Cu) in part B have a particle size ranging from 15 to 30 μm and a spherical shape.[19] These particles are referred to as coarse silver particles. Part C is fine silver particulates, which are irregularly shaped, with size ranging from 1.5 to 2.5 μm.

The pastes were applied on alumina substrates manually. Firing was conducted at 400°C, 450°C, 600°C, 750°C, 850°C, 900°C, or 930°C for 60 min, all with a heating rate of 15°C/min and a cooling rate of 40°C/min. All the samples were fired after drying in air at room temperature for 2 days. The surface morphology of the thick films after firing was examined under a scanning electron microscope.

The direct-current volume electrical resistivity of the thick films after firing was measured using the four-probe method. This method involved the use of four electrical contacts. The outer two contacts (48.5 mm apart) were for passing current, while the inner two contacts (41.5 mm apart) were for voltage measurement. The volume resistivity was calculated from the measured resistance and thickness; both quantities were separately measured for each specimen. The four electrical contacts were made by soldering, using a tin-lead solder. The film thickness was measured using an optical microscope. Five specimens were tested for each combination of composition and firing temperature.

The sheet resistivity (a commonly used attribute for thick films) was obtained as R.W/L, where R is the resistance measured by using the four-probe method, as mentioned above; W is the width of the thick film; and L is the length in the direction of resistance measurement.

Scratch testing of the thick films was conducted using a 502 shear/scratch tester manufactured by Teledyne Taber (North Tonawanda, NY). The specimen was mounted on a horizontally rotatable plate. A diamond scratching tool in the shape of a cone was used. The scratching tool was attached to a finely balanced scale beam that had been calibrated in grams. The load was 500 g. The scratch width was measured by scanning electron microscopy (SEM). The scratch morphology was also observed by SEM. In this work, the scratch was not deep enough to cause substrate exposure for thick films fired at 930°C in different atmospheres. The scratch test is informative, because the smaller the scratch width, the higher is the shear strength, which relates to both the bond strength of the thick film to the substrate and the shear strength within the thick film. Three specimens with three scratches on each specimen were measured for each combination of composition and peak firing temperature.

RESULTS AND DISCUSSION

Electrical Resistivity

Table I shows the sheet resistivity. It decreases with increasing firing temperature, whether the firing atmosphere is air, oxygen, or argon (except for the case of argon at 930°C). Thus, the recommended firing temperature is 930°C for firing in air or oxygen. The sheet resistivity is higher for firing in argon than firing in air or oxygen for all firing temperatures except 900°C. For 900°C, the sheet resistivity is the same for all these firing atmospheres. Though the difference in sheet resistivity between air and oxygen is small, the sheet resistivity is higher for oxygen than air, except for 600°C, 750°C, 850°C, and 900°C. Hence, air gives the lowest sheet resistivity at 400°C, 450°C, and 930°C, whereas oxygen gives the lowest sheet resistivity at 600°C, 750°C, and 850°C. For a firing temperature of 930°C, air is the recommended atmosphere. However, for

Table I. Sheet Resistivity (mΩ/Square) of Thick Films after Firing Using Various Combinations of Firing Atmosphere and Firing Temperature

	Firing Temperature (°C)						
Firing Atmosphere	**400**	**450**	**600**	**750**	**850**	**900**	**930**
Air	8.4 ± 1.5	8.4 ± 1.6	7.3 ± 1.2	6.2 ± 1.1	3.4 ± 0.4	1.9 ± 0.2	0.8 ± 0.1
Oxygen	11.3 ± 1.4	9.6 ± 1.1	6.9 ± 0.9	3.8 ± 0.4	2.3 ± 0.2	1.8 ± 0.2	1.1 ± 0.1
Argon	18.1 ± 2.6	12.1 ± 1.9	8.9 ± 1.4	7.2 ± 0.8	4.1 ± 0.3	1.8 ± 0.2	2.5 ± 0.2

Table II. Thickness (μm) of Thick Films after Firing Using Various Combinations of Firing Atmosphere and Firing Temperature

Firing Atmosphere	Firing Temperature (°C) 400	450	600	750	850	900	930
Air	54 ± 8	52 ± 6	48 ± 7	31 ± 4	27 ± 3	29 ± 3	30 ± 2
Oxygen	57 ± 5	55 ± 4	51 ± 4	48 ± 2	47 ± 2	42 ± 3	33 ± 2
Argon	55 ± 7	51 ± 6	46 ± 4	35 ± 2	31 ± 2	34 ± 3	22 ± 2

firing temperatures of 600°C, 750°C, and 850°C, oxygen is the recommended atmosphere.

Table II shows the film thickness after firing in air, oxygen, or argon at various temperatures. With the same firing atmosphere, the thickness tends to decrease with increasing firing temperature, as expected. Firing in air or oxygen results in less decrease in thickness than firing in argon. This is probably caused by the oxidation of the active metal components in the case of firing in air or oxygen. Firing in argon at 930°C results in the smallest thickness (i.e., 22 μm), probably because of the partial evaporation of the thick film. In fact, some parts of the thick film disappeared after firing in argon at 930°C (SEM image not shown).

Table III shows the volume electrical resistivity. Due to the error in thickness measurement (Table II), the error is larger for the volume resistivity than the sheet resistivity. Nevertheless, Table III is consistent with Table I in showing that argon gives the highest resistivity and that air is preferred to oxygen for high and low firing temperatures (but not intermediate firing temperatures). Although the sheet resistivity (Table I) is essentially the same for air, oxygen, and argon at 900°C, the volume resistivity is lower for air than oxygen at 900°C (Table III).

Scratch Resistance

For a firing temperature of 930°C, the film fired in argon has a larger scratch width (i.e., poorer scratch resistance) than that fired in air or oxygen (Table IV). A possible reason for this difference is that, in the presence of air or oxygen, the oxidation of the metal components results in an oxide, which promotes the bonding between the thick film and the substrate, in addition to promoting the bonding among the metal particles in the thick film. For firing in air or oxygen, a smaller scratch width is obtained for a firing temperature of 930°C than 900°C. This is consistent with the lower sheet or volume resistivity for 930°C than 900°C (Tables I and III).

Figure 1a and b show typical SEM images of the scratched films after firing in air at 900°C and 930°C, respectively. Cracks were observed in the scratch of the film fired in air at 900°C. In contrast, the scratch of the film fired in air at 930°C is smooth, without cracks.

Figure 1c and d show images of the scratched films fired in oxygen at 900°C and 930°C, respectively. Both scratches are smooth, without cracks.

Figure 1e and f show the images of the scratched films fired in argon at 900°C and 930°C, respectively. Ledges (indicated by arrows) were observed in the scratch of the film fired in argon at 900°C (Fig. 1e). They result from the ploughing of the scratch tip into the surface of the scratch and reflect that the scratching direction is from right to left along the length of the scratch. The ledges suggest low strength in the thick film. In contrast, the scratch of the film fired in argon at 930°C is smooth, with no ledge (Fig. 1f).

For firing in air or argon, a firing temperature of 930°C gives smoother cracks than a firing temperature of 900°C. This is consistent with the smaller scratch width for 930°C than 900°C (Table IV).

For firing at 900°C, the scratches of the films fired in air or argon are rougher than those fired in oxygen. This is consistent with the slightly lower scratch width for oxygen than air or argon (Table IV).

For firing at 930°C, no debonding or chipping was observed in the scratched films, whether the firing atmosphere was air, oxygen, or argon. However, the edges of the scratches of the thick films fired in argon at 930°C (Fig. 1f) are more irregular than

Table III. Volume Resistivity (10^{-6} Ω.cm) of Thick Films after Firing Using Various Combinations of Firing Atmosphere and Firing Temperature

Firing Atmosphere	Firing Temperature (°C) 400	450	600	750	850	900	930
Air	45.2 ± 8.2	43.9 ± 8.5	35.4 ± 5.9	19.2 ± 3.3	9.2 ± 1.1	5.3 ± 0.6	2.5 ± 0.2
Oxygen	64.4 ± 7.8	52.8 ± 6.3	35.1 ± 4.4	18.2 ± 1.8	10.8 ± 0.9	7.7 ± 0.7	3.8 ± 0.3
Argon	99.6 ± 14.5	61.6 ± 9.7	41.0 ± 6.6	25.4 ± 2.3	12.4 ± 0.8	6.2 ± 0.5	5.5 ± 0.4

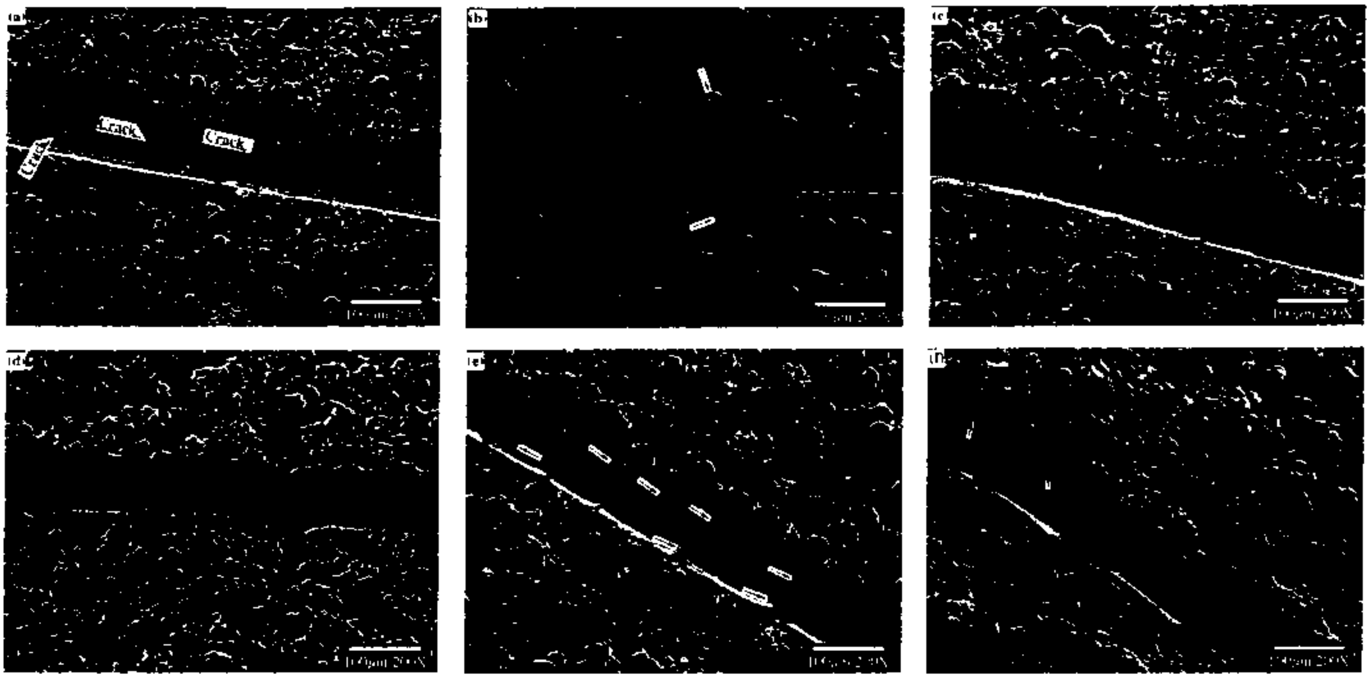

Fig. 1. Low-magnification SEM images of the scratched films fired in air at (a) 900°C and (b) 930°C, in oxygen at (c) 900°C and (d) 930°C, and in argon at (e) 900°C and (f) 930°C. The scratching direction is from right to left in every image.

those fired in air (Fig. 1b) or oxygen (Fig. 1d). The irregular edges in Fig. 1f are due to extensive plastic deformation of the film next to the scratch. They are indicated by the arrows (Fig. 1f) and suggest that the cohesion of the film fired in argon is poorer than that of the film fired in air or oxygen. This is consistent with the larger scratch width for argon than air or oxygen at 930°C (Table IV).

Surface Microstructure

The SEM images in Fig. 1 are at low magnification. For studying the surface microstructure, this section provides SEM images of the unscratched region at a high magnification.

Figure 2a and b show the images of the films after firing in air at 900°C and 930°C, respectively. Holes (labeled H) were observed in the film fired at 900°C (Fig. 2a). In contrast, holes were not observed in the film fired at 930°C (Fig. 2b). The bright regions in Fig. 2b are rich in Cu, Al, Ti, and Sn, as shown by x-ray spectroscopy in conjunction with SEM. In contrast, the bright regions in Fig. 2a are rich in Sn only. This suggests that alloying among the metal components occurs more readily at 930°C than 900°C. In addition, silver particles were observed in the film fired at 900°C, but not in that fired at 930°C. This means that flow of both fine silver particulates and coarse silver particles occurs more extensively at 930°C than 900°C. At 930°C, the flow is so extensive that silver spreads out to form a uniform dense film with only a minor number of pinholes (indicated by arrows in Fig. 1b).

Table IV. The Scratch Width (μm) of Thick Films after Firing Using Various Combinations of Firing Atmosphere and Firing Temperature; Scratch Testing was Performed at a Load of 500 g

	Firing Temperature		
Firing Temperature (°C)	Air	Oxygen	Argon
900	110 ± 13	105 ± 6	115 ± 12
930	75 ± 8	72 ± 6	105 ± 10

Figure 2c and d show the images of the films fired in oxygen at 900°C and 930°C, respectively. Both silver particles (labeled Ag) and pinholes (labeled H) were observed in the film fired at 900°C (Fig. 2c). Both features are absent in the case of firing at 930°C (Fig. 2d). The dark regions (labeled Al) in Fig. 2d are aluminum-rich areas (as identified by x-ray spectroscopy), which may be alumina caused by the oxidation of aluminum in the thick film. The regions protruding from the surface are rich in Cu, Al, Ti, and Sn (indicated by arrows in Fig. 2d). As in Fig. 2a, Sn-rich regions were observed in the film fired in oxygen at 900°C (Fig. 2c).

Figure 2e and f show images of the films fired in argon at 900°C and 930°C respectively. The Sn-rich regions are present in Fig. 2f. Holes (labeled H) are present in both Fig. 2e and f. Silver particles (labeled Ag) with a size as large as 37 μm are present in Fig. 2e. The large size compared with the initial size of 15–30 μm suggests that diffusion of silver from some coarse silver particles to their surrounding areas has occurred negligibly, if at all. In contrast, in Fig. 2c, the size of the remaining coarse silver particles in the film fired in oxygen at 900°C is less than 22 μm, suggesting that more diffusion has occurred after firing in oxygen than in argon.

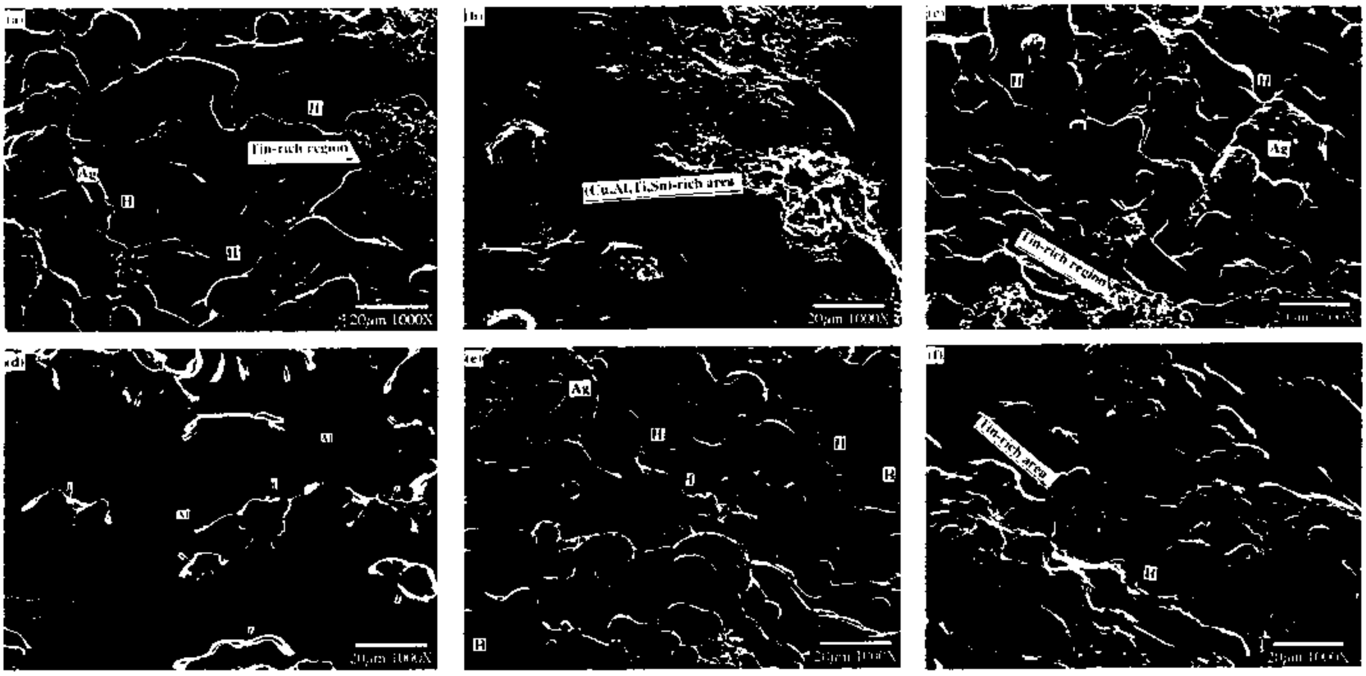

Fig. 2. High-magnification SEM images of the films fired in air at (a) 900°C and (b) 930°C, in oxygen at (c) 900°C and (d) 930°C, and in argon at (e) 900°C and (f) 930°C. Holes are labeled H. Aluminum-rich regions are labeled Al.

Figure 3a and b show low-magnification images of the films fired at 930°C in air and oxygen, respectively. The surface of the film fired in oxygen (Fig. 3b) is smoother (with a finer microstructure) than that fired in air (Fig. 3a). No pinhole was observed for the film fired in oxygen (Fig. 3b). A minor amount of pinholes was occasionally observed in the film fired in air. The pinholes are not shown in Fig. 3a, but are indicated by arrows in Fig. 1b.

For the film fired in argon at 930°C, macroscopic parts of the thick film disappeared (image not shown) and large pinholes were observed (labeled H in Fig. 4). A high-magnification image of the small bright spots on the silver surface in Fig. 4 is shown in Fig. 5. These spots were identified by x-ray spectroscopy to be rich in copper. This suggests that segregation of copper occurred when the thick film was fired in argon at 930°C. The small bright spots were not observed in the regions without pinholes in the same thick film that had been fired in argon at 930°C also (Fig. 2f), suggesting that segregation of copper is associated with pinhole formation.

Further Discussion

The coverage of the substrate by the thick film is enhanced by (1) the possible reaction of the active metals (Ti and Cu) with the substrate (Al_2O_3),[10,18] (2) the oxidation of metals (such as Cu) to form an oxide binder (such as copper oxide),[18,20,21] and (3) metal (silver) flow during heating. Extensive flow of the fine silver particulates occurs at 850°C and

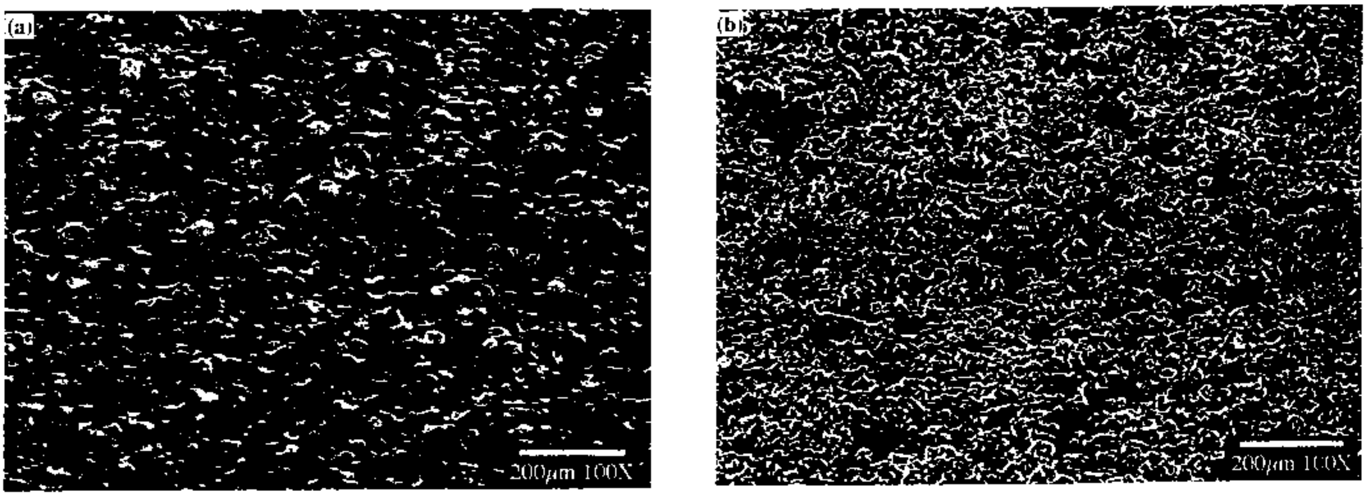

Fig. 3. Low-magnification SEM images of the films fired at 930°C in (a) air and (b) oxygen.

Fig. 4. High-magnification SEM image of the film fired in argon at 930°C. Holes are labeled H.

Fig. 5. A magnified image of the small bright spots on the silver surface in Fig. 4. These spots are rich in copper, as shown by x-ray spectroscopy.

extensive flow of the coarse silver particles occurs at 930°C, both for the case of firing in air, as shown in prior work of these authors.[22]

Good coverage of the substrate by the film means less pinholes in the film, i.e., a denser film. Firing in oxygen instead of air causes more metal oxide and consequently better bonding. This may be the reason for a denser film (Fig. 1b and d) with a smoother surface (Fig. 3) to be attained at 930°C in the case that the firing atmosphere is oxygen instead of air. In the case of firing in argon, due to the absence of oxygen, copper may not be sufficiently oxidized, as suggested by the copper-rich regions in Fig. 5. This results in poor bonding between the film and the substrate and consequently large pinholes (Fig. 4), poor scratch resistance, and high sheet or volume resistivity in the film fired in argon. In addition, this results in poor cohesion within the film, thereby decreasing the scratch resistance. The poor bonding of the film to the substrate also contributes to causing vanishing of macroscopic parts of the film fired in argon.

On the other hand, extensive oxidation of the metal components increases the content of metal oxides in the film. This probably results in the sheet or volume resistivity of the film fired at 930°C to be slightly higher for oxygen than air (Tables I and III).

Good bonding of the film with the substrate due to the formation of a metal oxide helps result in a dense film. This may be the main reason why the film fired in oxygen has a lower sheet resistivity than that fired in argon or air at corresponding firing temperatures (750°C and 850°C).

CONCLUSIONS

Firing atmospheres of air, oxygen, and argon result in air-fireable glass-free thick films, which differ in resistivity, thickness, scratch resistance, and surface microstructure. For any of these firing atmospheres, a firing temperature of 930°C gives lower sheet or volume resistivity and smaller thickness than lower firing temperatures. For a firing temperature of 930°C, air results in the lowest sheet or volume resistivity, but a minor amount of pinholes; oxygen results in the largest thickness, the smoothest surface, and no pinhole; and argon results in the highest sheet or volume resistivity, large pinholes, the smallest thickness, vanishing of macroscopic parts of the thick film, and the poorest scratch resistance. Argon gives higher sheet or volume resistivity than air or oxygen at all firing temperatures except 900°C. Oxygen gives lower sheet resistivity than air at 750°C or 850°C.

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