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Sintering and microstructure development of glass-bonded silver thick films

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The sintering of glass-bonded silver thick films has been studied by dilatometry and microscopic analysis. Effects of particulate characteristics of silver and glass frit powders, glass composition, silver/glass ratio, and substrate materials have been discussed. It is shown that the silver–glass interaction is one of the most important factors responsible for the microstructure. Most of all, glasses promoted the densification of the thick film. Microstructure development has been understood by the stage of sintering as determined by the combined effects of temperature and silver/glass ratio.

1. Introduction

Stable and good adhesion is one of the most important requirements imposed on the glass-bonded metal thick films for hybrid microelectronics [1–9]. However, it is felt that the nature of adhesion strength has not been fully understood because of many factors involved in the fabrication process. In addition, the degradation of adhesion on repeated heating encountered in practical application of thick films is another problem which makes the situation more complicated.

The present work was undertaken as a first part of the program to develop thick films having high and stable adhesion, and the microstructure development the glass-bonded silver thick films has been studied with special emphasis on the effects of material parameters. The effects of glass compositions and particulate properties of glass and silver powders on the sintering of glass-bonded silver thick films printed on the Al_2O_3 substrate were examined by dilatometry. Next, the microstructure development was studied by SEM using a resin impregnation technique.

It is shown that the structural change of thick films during heating depends principally on the sintering of silver powder as well as on the glass-bonded silver interaction, and that the substrate material has a slight influence on the sintering and microstructure. Based on the experimental findings a mechanism of microstructure development of glass-bonded silver thick films and criteria for evaluating glass and metal powders have been proposed.

2. Experimental details

2.1. Materials

The silver frit-bonded pastes were tailor-made by combining silver and glass frit powders available in the market. Fig. 1 shows SEMs of silver and glass frit powders. Spherical fine (SF) silver, and spherical coarse (SC) silver particles are almost spherical, while flaky (FL) silver particles and flaky and have a wide size distribution. All kinds of glass frit particles are irregularly shaped and their size distributions are rather wide ranging from 1 to 10 μm. The particulate characteristics of these powders are listed in Table I. The values of pore volume, determined by using butyl carbitol, indicate the sufficient amount of resin to make paste. These data show that FL silver powder requires less resin for making paste than others. Three kinds of glass frits were not quite different in powder characteristiics.

In Table II are listed properties of glass frits together with main compositions. Glasses I, II, and III are arranged in increasing order of glass transition temperature and working temperature.

2.2. Paste and film preparation

Silver powder and glass frit were mixed with an

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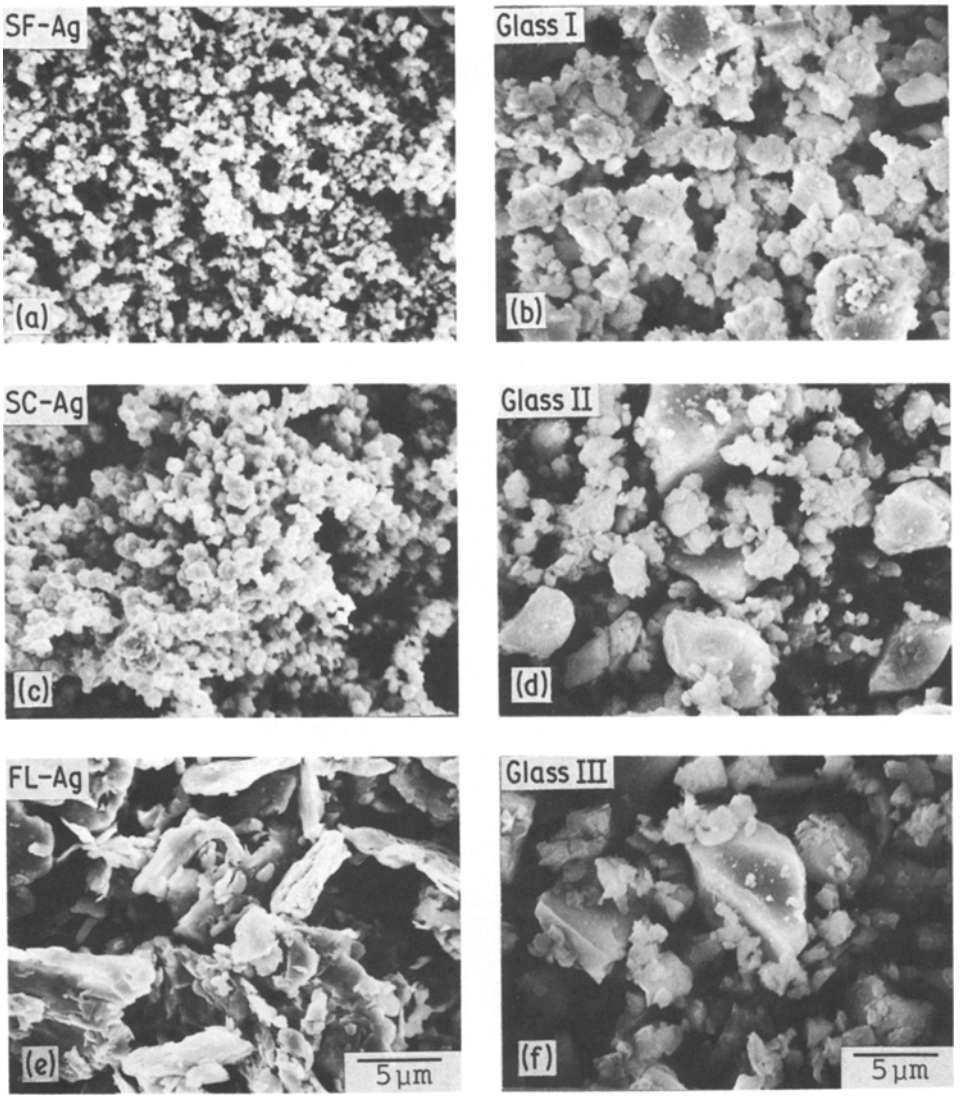

Figure 1 SEMs of silver and glass frit powders.

appropriate amount of ethyl cellulose butyl carbitol solution in a triple-roll mill. The silver/glass frit ratio was expressed in volume per cent of silver unless otherwise specified.

2.3. Printing and firing

The obtained silver–glass paste was printed manually on the 96% alumina substrate AE-96 by TDK Electronics using a palette knife. Films

TABLE I. The characteristics of silver and glass powders

Powder	Particle* size (μm)	BET ($g\,cm^{-3}$)	Pore volume ($ml\,g^{-1}$)	Shape
SF silver	0.1–0.5	3.13	0.43	spherical, fine
SC silver	0.5–1.0	0.73	0.52	spherical, coarse
FL silver	2.0–20	0.82	0.15	flaky
Glass I	1.0–10	2.11	0.24	angular
Glass II	1.0–10	2.86	0.40	angular
Glass III	1.0–10	1.70	0.34	angular

*Measured from SEM.

Ag powders and glass frits were made by Shoei Chemical Co. Ltd and Asahi Glass Co. Ltd, respectively.

TABLE II The properties of the glasses

Glass number	I	II	III
Main components	$PbO-B_2O_3-ZnO$	$PbO-SiO_2$	$SiO_2-Al_2O_3-CaO$*
Transformation point (° C)	400	560	700
Softening point (° C)	470	695	–
Sealing temperature (° C)	700	850	900
Thermal expansion coefficient (10^{-7} °C^{-1})	69	59	46

*Crystalline phase is contained.

printed on the alumina substrate were dried at 80° C for 1 h. Precautions were taken to keep the thickness of dried film between 50 and 100 μm. The dried films were fired at temperatures ranging from 400 to 950° C in an infrared image furnace in air. Times at peak temperatures were 10 min and the rate of temperature change was 20° C min^{-1} throughout the run.

2.4. Dilatometry

The denisification characteristics of the printed films were determined by dilatometry. Films were >100 μm thick printed manually on the alumina substrates using a palette knife and dried, and then heated at 20° C min^{-1} in a transducer-type dilatometer. A small alumina chip was inserted between the film and a SiO_2 push rod. The pressure applied to specimen was kept <0.5 g cm^{-2}.

2.5. Microscopy

After firing, the films were reinforced by a resin impregnation technique. The fired films were impregnated with polyester resin containing initiating agent under the pressure of 500 kg cm^{-2}. After the complete polymerization, the pressure was released. The obtained specimens were strong enough to be polished. The finished cross-sections were subjected to scanning electron microscopy (SEM) and EMX.

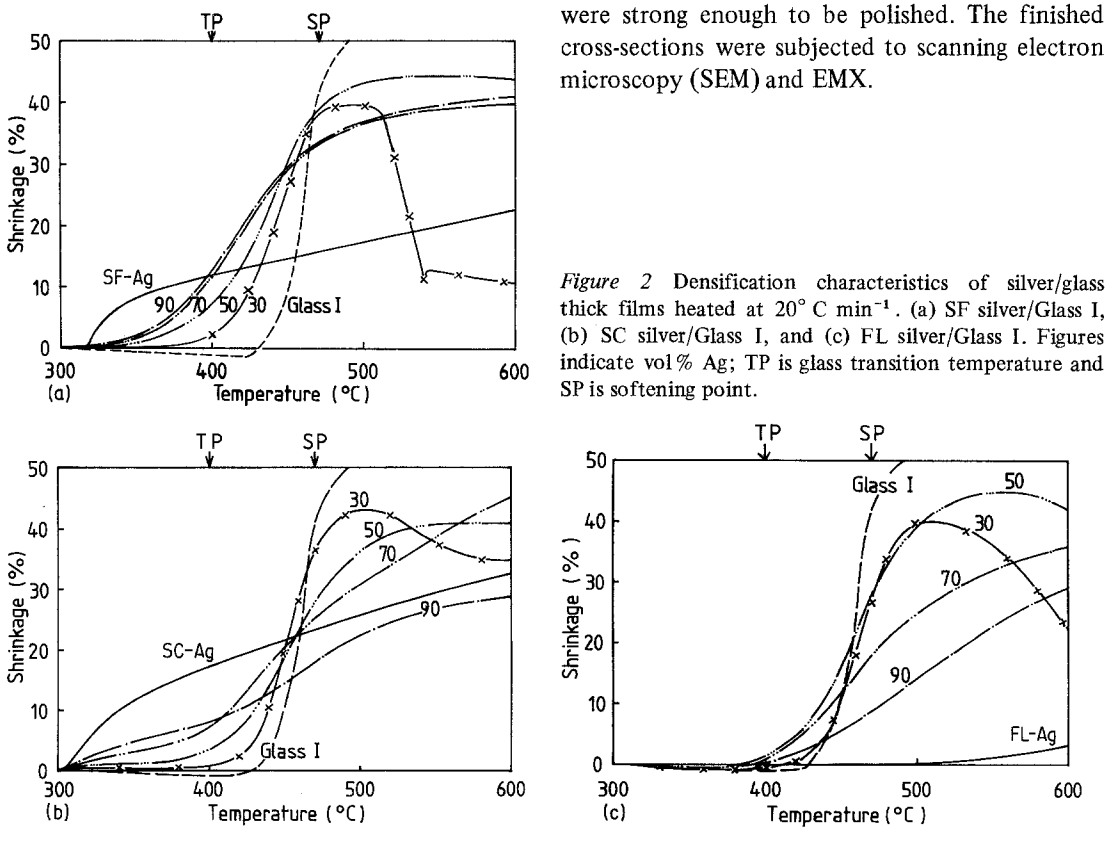

Figure 2 Densification characteristics of silver/glass thick films heated at 20° C min^{-1}. (a) SF silver/Glass I, (b) SC silver/Glass I, and (c) FL silver/Glass I. Figures indicate vol% Ag; TP is glass transition temperature and SP is softening point.

3. Results and discussion

3.1. Densification behaviour of silver–glass films

3.1.1. Effect of silver powders

Fig. 2 illustrates the densification characteristics of glass-bonded thick films containing various concentrations of glass frit (Glass I) as a function of temperature. The dimensional change below 300° C, which is solely due to that of binder, has been subtracted from the curves for the sake of clarity. Fig. 2a shows the densification behaviour SF of silver/Glass I films. The densification of pure silver film starts just above 300° C and levels off at about 400° C. Obviously, incorporation of glass frit retards the onset of densification. Thus, the addition of 10 vol% of glass frit raised the densification temperature by 70 to 80 degrees and gave a densification curve similar to that of the glass film. Further addition of glass frit does not increase the densification temperature significantly, but the densification curve becomes steeper. Apparently, the marked densification near 400° C (T.P.) is a consequence of silver–glass frit interaction.

Similar densification characteristics were observed for SC silver with larger particle size (Fig. 2b). In Fig. 2b, the densification of pure silver film (solid line) starts just above 300° C, similarly to that of the SF silver film shown in Fig. 2a, but the curve is less steep than for SF silver. Therefore, the densification characteristics of SC silver/glass films are similar to those of SF silver/glass films in Fig. 2a. However, the effects of glass addition on the densification were not significant as compared to SF silver/glass films.

The densification characteristics of FL silver/Glass I films were quite different from these above two series of films. In Fig. 2c, the pure FL silver film does not shrink until 500° C is reached, which is higher than the softening temperature of the glass frit. Because of this, the densification of silver/glass films starts at the softening temperature of glass irrespective of the silver/glass ratios. However, the curve becomes steeper with increasing glass content in the films. Especially, the addition of 10 vol% glass improved significantly the densification of pure silver film. Thus, in the case of FL silver powder, the silver–glass interaction was not observed below the glass softening temperature.

The effect of glass addition on the densification is more pronounced with small silver powders. This could be interpreted in terms of silver–glass interaction; good sinterability of silver and a large silver/glass interfacial area are obtainable with fine silver powder.

3.1.2. Effect of glass frits

Since SF silver powder is considered to be a typical one, it was combined with various glass frits to make films and the densification characteristics were studied. Fig. 3a illustrates the densification characteristics of SF silver/Glass II films, of which glass transition temperature and softening point are higher than those of Glass I. The effect of glass/silver composition on the densification characteristics is similar to the SF silver/Glass I combination (Fig. 2a), but the densification curves are rather steeper. In addition, the densification takes place at temperatures much lower than the softening temperature as compared with Glass I (Fig. 3a). These results

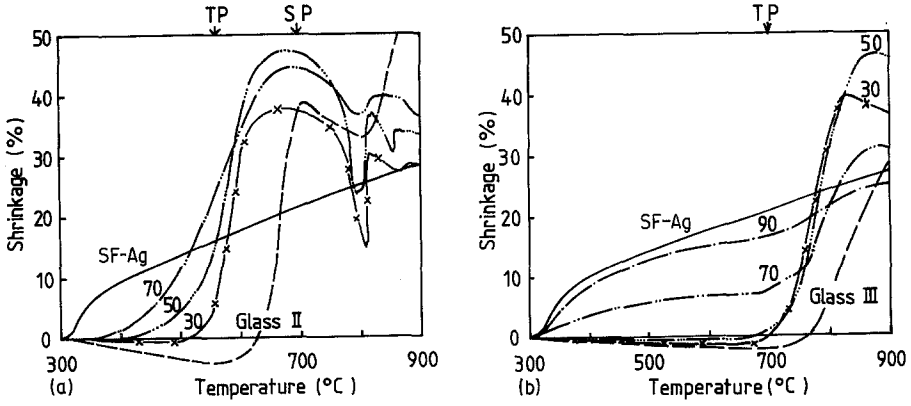

Figure 3 Densification characteristics os silver/glass thick films heated at 20° C min^{-1}. (a) SF silver/Glass II, and (b) SF silver/Glass III.

indicate not only that the glass phase promotes the sintering of silver powders, but also that the sintering of silver powders effects the softening of glass apparently.

Similar densification behaviour was observed when Glass III was used expecting for the films containing more than 70 vol % silver, for which the silver–glass interaction is not marked. Addition of small amounts of glass to silver powder does not influence the sintering behaviour of films significantly. However, for higher contents of glass the silver–glass interaction does still exist.

For the same content of glass in thick film, marked densification of the film occurs at lower temperature with having a lower softening temperature. Summarizing for the same glass–silver compositions the densification of films is more favourable with glass.

3.1.3. Effect of classified glass frits

The effect of particle size of glass frit on the densification characteristics was studied using the glass frits classified into four fractions (−3, 3–8, 8–15, +15 μm) and the results are shown in Fig. 4. The silver content of the films was fixed at 70 vol %. In Fig. 4a, with increasing particle size of glass frit, the densification takes place at lower temperatures and the slope of the curve becomes less steep. Above 560° C on the other hand, smaller particles favour the densification. The similar densification characteristics obtained above 560° C in Fig. 4a was observed when FL silver was used with classified Glass II (see Fig. 4b). For FL silver powder, the densification of pure silver film starts at a temperature much higher than the softening temperature of Glass II, so that the densification curve is determined by the particle size of glass frit.

From these results, densification depends on the contact area and the glass particle size distribution before and after the softening of glass, respectively. Thus, the densification behaviour is characterized by the dispersion of silver and glass frit particles and the silver–glass interaction. The former is determined by the powder characteristics and the latter, by the relation between sintering of silver and softening of glass.

3.2. Microstructure development

The microstructures of fired thick films obtained with different silver–glass combinations under the different heating conditions have been grouped into four according to the sintering stages. Fig. 5 shows the SEMs of four typical microstructures obtained in SF silver/Glass I thick films. The gray area at the bottom is the alumina substrate. The thick film consists of silver phase, gray glass phase and pore. Microstructure A, which is obtained before softening of glass, is characterized by the incomplete sintering, and glass frits are dispersed in silver powders. In this stage, slight growth of silver particles is the only process taking place. Microstructures B, C, and D were observed after softening of glass. In microstructure B, the sintering of silver was promoted by the glass phase, but the marked densification was not observed, so that many pores were included in the structure. For pure silver films, the grain growth in silver was observed with increasing heating temperature, but the densification was

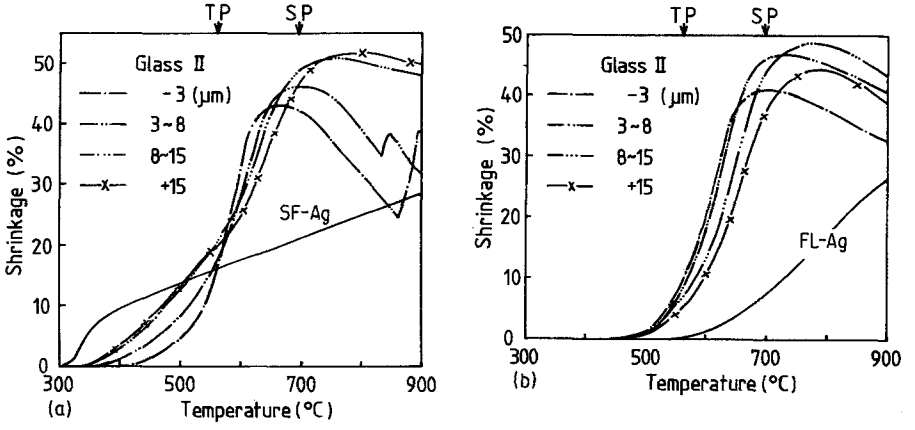

Figure 4 Effect of glass frit particle size on the densification characteristics of films heated at 20° C min^{-1}. Silver content of the films is 70 vol %.

TABLE IIIA Classification of silver/glass thick film microstructures in silver content and temperature axes: SF silver/Glass I.

Silver content (vol %)	Temperature (° C)				
	400	500	600	700	800
90	A	B	B	B(C)	B(C)
70	A	B(C)	C	C(D)	D(C)
50	A	C	D(C)	D	D
30	A	C	D	D	D

TABLE IIIB Classification of silver/glass thick film microstructures in silver content and temperature axes: FL silver/Glass I

Silver content (vol %)	Temperature (° C)				
	400	500	600	700	800
90	A	B	B	B	C
70	A	B	C	C	C
50	A	C	C	C	D
30	A	C	D	D	D

not. Therefore, the pure silver films are characterized by a porous matrix similar to structure B. Microstructure C forms a silver–glass composite structure, in which silver grains are bonded and the glass phase, well dispersed across the films, fills up pores. This structure seems to meet the requirements in the practical application. Microstructure D, generally observed in high glass contents in the film and at high temperatures, shows the glass layer on the alumina substrate. Probably, grain growth in silver squeezed the glass phase downwards.

Table IIIA lists the structural types obtained with Ag-Sf/Glass I thick films as functions of silver content and heating temperature. The grain growth in 90 vol % silver film is pronounced above 500° C, bur fairly dense structures are developed above 700° C. In 70 vol % silver film, the structure C favourable for practical application is obtainable between 600 and 800° C. An increase in glass content seems to destroy the structure especially at high temperatures. In 50 and 30 vol % silver films, the structure C in which only the glass phase fills pores is observed at 500° C. But an

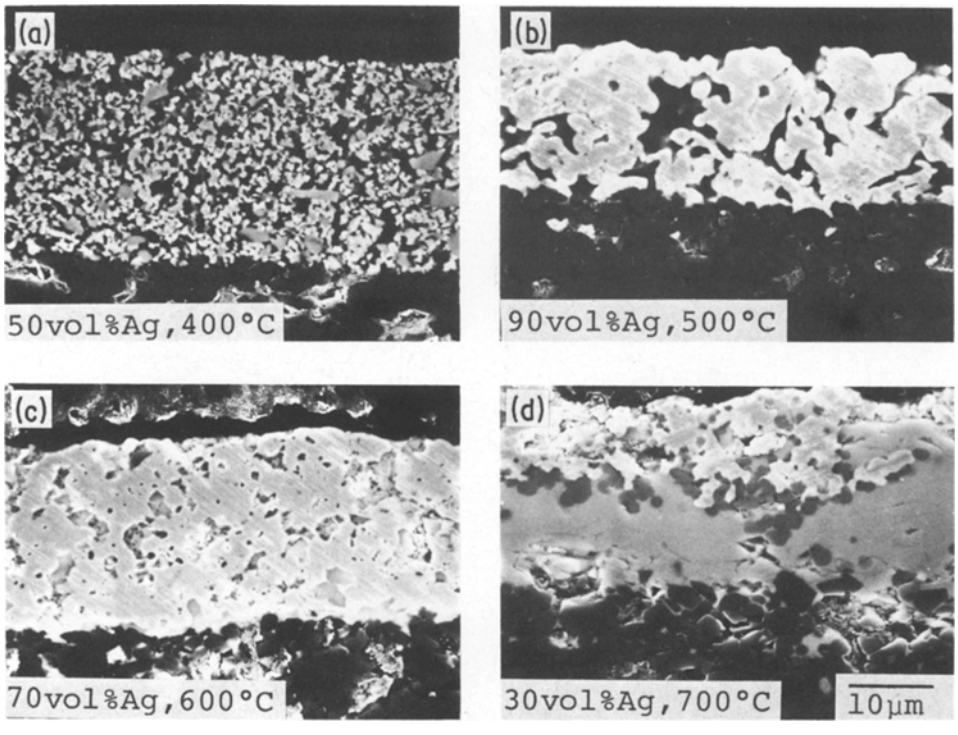

Figure 5 SEMs of four typical microstructures obtained in SF silver/Glass I thick films.

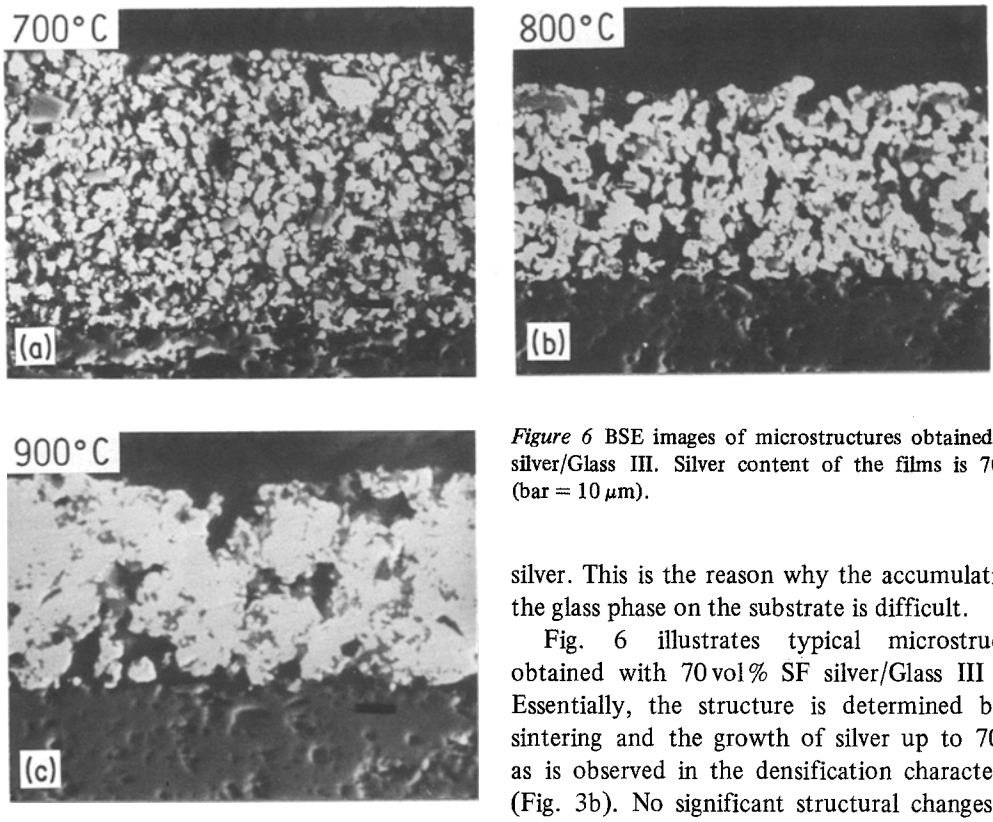

Figure 6 BSE images of microstructures obtained in SF silver/Glass III. Silver content of the films is 70 vol% (bar = 10 μm).

excessive amount of glass phase is accumulated on the alumina substrate caused by the grain growth of silver above 600° C in 30 and 50 vol% silver films indicated D. From Table IIIA the silver–glass composite structure C is formed for lower contents of glass in the films at higher heating temperatures.

Above 700° C, the film/substrate boundaries become ragged by the interaction between glass and alumina. This was readily understood by rounding off and growth of Al_2O_3 grains near the film/substrate boundary (Fig. 5d). Furthermore, the precipitates seen as grey dots in the upper side of accumulated glass phase were identified PbO–Al_2O_3 compound by EMX.

Similar features in Table IIIA were observed for SC silver, and/or Glass II. Table IIIB indicates the structural types for FL silver/Glass I instead of SF silver. The structure C remains over the fairly wide temperature ranged compared with Table IIIA. Although the pore volume of FL silver is smaller than that of SF silver, the sintering of FL silver is poor. Therefore, the capacity to incorporate the glass phase in silver skeleton is large with increasing heating temperature for FL silver. This is the reason why the accumulation of the glass phase on the substrate is difficult.

Fig. 6 illustrates typical microstructures obtained with 70 vol% SF silver/Glass III films. Essentially, the structure is determined by the sintering and the growth of silver up to 700° C, as is observed in the densification characteristics (Fig. 3b). No significant structural changes were observed until the extensive densification takes place at about 900° C (Fig. 6). Even for 50 and 30 vol% silver films heated at 900° C, the microstructure of the films containing Glass III was of the type B, in which the sintering of silver and glass proceeds independently. The microstructures of the films containing Glass III are interpreted in term of high densification temperature and its poor spreading on silver and the alumina substrate. The interaction between the glass phase and Al_2O_3 was not detected.

Although the structure type was not influenced by the particle size of glass, the dispersion of glass phase in the films was better for finer glass frits. The same experiments were conducted using 99% Al_2O_3 and silver plate as a substrate material. In spite of the possible interaction with Al_2O_3 substrate, no appreciable differences have been detected in dilatometry and microstructure. Probably other tests such as ageing or adhesion might be better correlated.

4. Summary

The firing process of glass-bonded thick films has been studied by dilatometry and microscopic analysis. Densification behaviour and microstructures are interpreted in terms of the silver–

glass interaction; the glass content, the powder characteristics of silver and glass, and glass properties are highly responsible. Features in microstructure development are summarized below.

1. The microstructures of glass-bonded thick films are classified into four types, which are generally determined by the glass content of the films and heating temperatures.

2. A silver–glass composite structure desirable for the structure type C is formed with low glass contents at high temperatures. This type of structure is obtained with 70 vol% silver films over the wide temperature range in any silver/glass combinations excepting Glass III.

3. Characteristics of silver powders have not substantial effect of the microstructures, but FL silver extended the temperature range for obtaining a desirable structure C.

4. Glass III containing a crystalline phase does not promote the densification of the film, and the microstructures containing Glass III are only of the type A or B even in 30 vol% silver films.

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