Effect of the Oxide Glass on the Metal Sintering Behavior in Silver Thick-Film System

Young Sir Chung and Ho-Gi Kim

Dept. of Materials Science and Engineering
Korea Advanced Institute of Science and Technology

ABSTRACT

The sintering behavior of silver-oxide glass composite thick-film has been studied with varing glass content. It is shown that during heat treatment glass became liquid phase to deeply affect the microstructure development of the silver particles and to control the physical properties of the thick-films. As glass content increased, the initial repacking of silver particles took place rapidly but the homogeneities of the microstructure showed different features.

When the glass content was over some range, the silver particles exuded glass to decrease net energy and glass formed liquid pools separated from the solid skeletons. Finally the relations between the microstructures and electrical properties of the thick-film were discussed.

I. INTRODUCTION

Thick-film technology of metal-oxide glass composite system have been used over thirty years in electronic industry. It is, however, surprising that no detailed study of microstructure development during heat treatment have been made. Recently, Yajima and Yamaguchi (1) reported that the densification of Ag-glass thick-films take place at lower temperatures with increasing Ag content and the temperature at which the uniform Ag-glass composite structure developed decreased with increasing glass content. But our results are quite different from their results. In the present study we shall systematically elucidate the effect of oxide glass on sintering behavior and microstructure development of metal (Ag) particles with varing glass content and thn correlate with electrical properties of the thick-film.

Sintering of pure silver powders has been investigated extensively (2-4). But papers on sintering of silver-glass composite are rarely found. Cole (5) investigated solution-reprecipitation sintering in the presence of a reactive liquid by comparing sintering rates. One objective of this study is to establish sintering mechanism of Ag particles in the liquid matrix of the oxide glass and to understand the effect of microstructures on electrical properties of Ag thick-film conductors.

II. EXPERIMENTAL

Glass melt of lead bismuch borosilicate was prepared by mixing appropriate quantities of reagent grade PbO, Bi_2O_3, B_2O_3, and SiO_2 in a rolling jar. Mixed powders were heated to 1000°C for 20 min. and melt was poured into distilled water. After this glass was powdered using alumina mortar, it was size separated, and a particle size under 325 mesh was used.

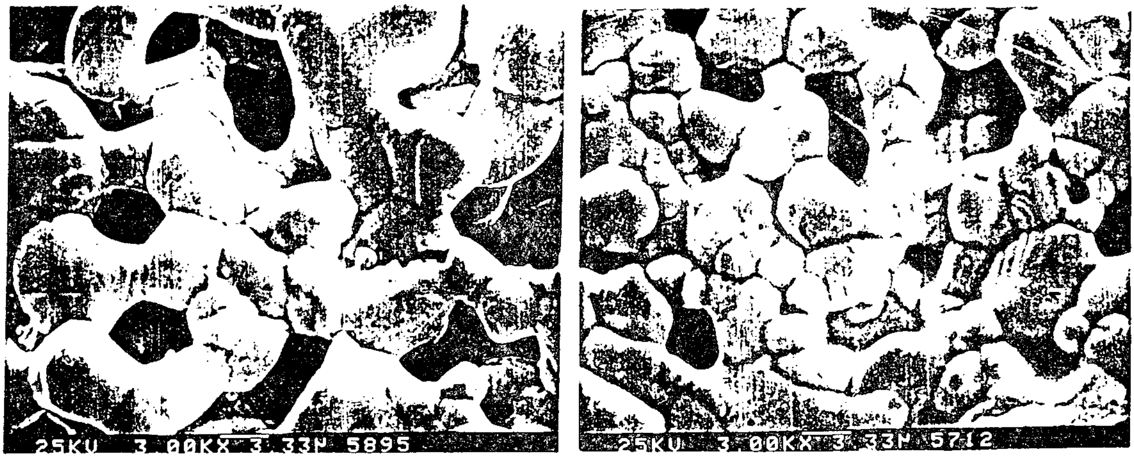
Silver powder (No. 63208000 by Demetron Co.) and glass frit were mixed with appropriate amount of ethylcellulose-butyl carbitol acetate solution in a three roll mill. The glass/silver ratio was expressed in volume per cent of glass. The obtained silver thick-film paste was printed on the 96% alumina substrate (Rubalit 708 by Hoechst CeramTec) using screen printer (DEK 65). Films printed dried at 100°C for 10 min and fired at temperature ranging from 600°C to 800°C in air. The rate of temperature change was 13°C min^{-1} and soaking time at peak temperatures was 10 min. After firing, electrical resistivity was measured using electrometer and optical microscopy and SEM were used for microstructural analysis.

III. RESULTS AND DISCUSSION

A. The Comparison of Representative Microstructures and Electrical Properties between Pure Silver and Silver-Glass Composite Thick-Films

Fig. 1 (a) shows the surface microstructure of pure Ag thick-film sintered at 800°C for 10 min. According to Johnson and Clarke (4), sintering of silver is controlled by grain-boundary diffusion rate. Packing state and homogeneity of metal phase are very coarse. The resultant overall structure of the film is made up of porous network of large silver grains. But when Ag thick-film contains 10 vol. % glass, densification and homogenization of silver particles are fairly improved, shown in Fig. 1 (b). Even restraining grain growth by retarding grain-boundary diffusion, glass phase leads to higher densification of silver particles. This consequent microstructures heavily influence upon the physical properties of thick-film conductors.

The change of electrical resistivities with firing temperature is illustrated by Fig. 2. Increasing sintering temperature, resistance value of 10 vol. % glass-bearing thick-film drops more rapidly than that of glass-free film. For sintered at 800°C, the sheet resistivities of pure silver film and silver-glass composite film (Fig. 1) measure 3.8mΩ/□ and 2.2mΩ/□, respectively. It is suprising result because electrical conductivity of the thick-film involving considerable amount of insulator glass is superior to that of pure silver film.



(a) glass-free (b) glass-bearing (10%)

Fig. 1. **SEM micrographs of glass-free and glass-bearing Ag thick-film fired at 800°C for 10 min.**

Originally, the primary role of oxide glass used in conductive thick-film systems is to improve adhesion strength between metal layer and ceramic substrate. Therefore, most of papers for thick-film have concentrated on the adhesion relations. From above results, however, it is clear that during heat treatment glass becomes liquid phase to deeply affect the sintering behavior of metal particles and to control the final properties of thick-films.

B. Effect of Glass Content on the Sintering Behavior of Metal (Ag) Particles.

In multiple phase materials, microstructure is characterized by grain size and shape, porosity, solid-solid contact, relative amount of each phase, and interactions between phases. In the case of conductive thick-film, it is most required to examine solid-solid contact, continuity, and homogeneity of metal phase from microstructure analysis in order to obtain better conductivity and solderability.

Fig. 3 shown the microstructures developed after sintered at 700°C for 10 minute with varing glass content ranging 5 vol. % to 30 vol. %. At this temperature range, during the liquid forms and spreads, metal particles are repacked by active rearrangement process under capillary force from a wetting glass liquid. Although solution and reprecipitation occurs concurrently, the rearrangement events dominate the early response.

A wetting glass liquid createsan attractive force between particles. As a consequence, in a three dimensional network of solid, liquid, and vapor, a hydrodynamic pressure exists on the pores. Therefore, silver particles will repack to a higher coordination. Rearrangement

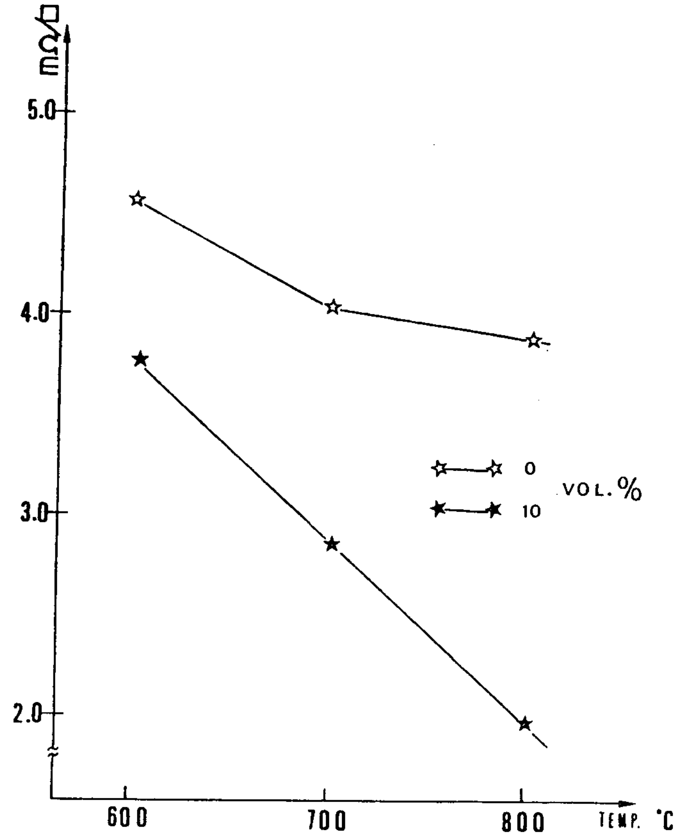


Fig. 2. Comparison of electrical resistivities of glass-free and glass-bearing Ag thick-films.

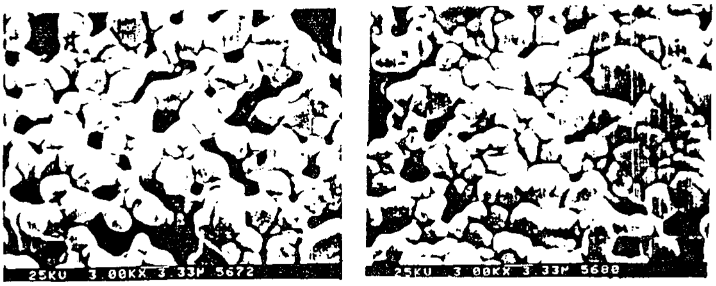
involves clusters of primary particles. The random packing of mixed powders and the uneven distribution of glass liquid will produce a process of successive clustering (6) shown in Fig. 3. (b). As glass content increases, the densification by arrangement take place actively. But when glass content exceeds some range (over 20 vol. %), the particle disintegration from solid contact occurs by liquid attack of the grain-boundaries.

After rearrangement process ends, microstructure development is associated with intermediate and final stages of liquid phase sintering, which is characterized by densification, grain growth, shape accommodation, contact flattening, pore elimination, coalescence and neck growth. In the system of low volume fraction of liquid, densification is mainly caused by grain shape accomodation, which takes place by contact flattening at grain contacts, dissolution of small grains with reprecipitation on large grains and coalescence. Capillary forces from glass liquid distributed along capillaries between particles act as the driving force of shape accommodation. Park and Yoon (7) reported on the minimum interface energy configurations of a uniformly intermixed grain-matrix system with varing dihedral angles and matrix contents. When dihedral angle, $\phi \gg 0$, grains from grain boundaries to stabilize shapes. As ϕ increases, stable grain shape is changed to a polygon.

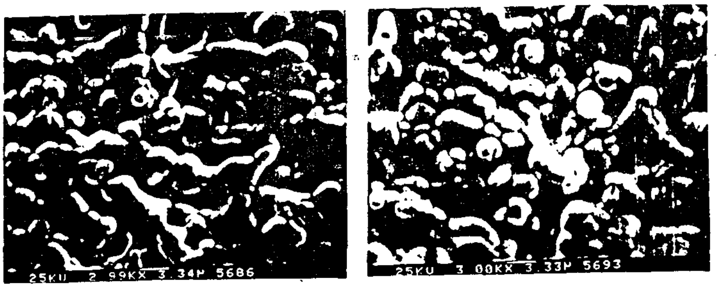
For a fixed dihedral angle, the system has optimum liquid content in which total interface energy is minimum and the most stable grain shape is determined. If liquid content is less than optimum, total interface energy increases. In this case shape-changed grains absorb liquid to tend to recover most stabe shape (Fig. 4 (a) and (b)). On the other hand, if liquid content is over optimum, solid skeletons exude liquid to form most stable grain shapes. As a result, the particles push up liquid to decrease net energy and glass liquid is separated from the solid skeleton to form liquid pool, which is shown in Fig. 4 (c). For 30 volume % glass, developed microstructure (Fig. 4 (d)) shows different result from the others of Fig. 4. When the particle arrangement occured, most of each particle was immersed in liquid matrix, so that too much glass liquid disturbed forming compact of metal particles.

C. Effect of the Microstructure Development on the Electrical Properties of Ag Thick-Film.

Fig. 5 illustrates the variation of sheet resistivities of glass with firing temperatures. Electrical resistance depends on the microstructure development of the thick-film, that is, it is essential for metal particles to enlarge their contact area and to decrease current path in order to obtain low value of resistance (8).

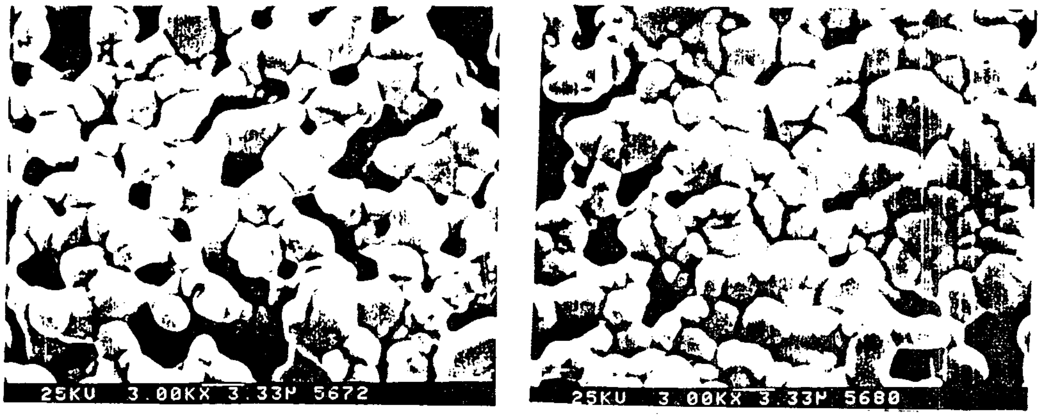


(a) 5 vol. %   (b) 10 vol. %



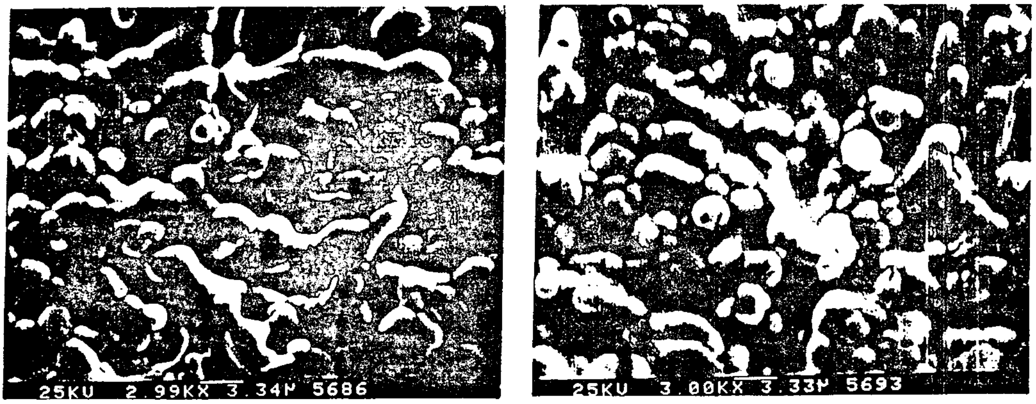
(c) 20 vol. %   (d) 30 vol. %

Fig. 3. SEM micrographs of thick-films fired at 700°C for 10 min. with variation of glass volume fraction ---------- after rearrangement. volume



(a) 5 vol. %

(b) 10 vol. %



(c) 20 vol. %

(d) 30 vol. %

Fig. 4. SEM micrographs of thick-films fired at 800°C for 10 min. with variation of glass volume fraction.

Relations between microstructures and electrical properties can be schematically expressed by Fig. 6. For low volume fraction of glass (5 vol. %), the developed microstructure, in which sintering is controlled by grain-boundary diffusion and shape accommodation, contains many voids in a compact (Fig. 6 (a)). The variation of resistance values corresponding to the degree of densification results in the plot of Fig. 5 (5 vol. % line). For 10 vol. fraction of glass, the decreasing rate of resistivity with sintering temperature is steep, shown in Fig. 6. At this range of glass content, glass liquid phase accelerates the repacking of metal particles by active rearrangement and coarsening process to lead to the fast densification and high homogeniety of metal phase (Fig. 6 (b)). As a result, increasing contact area between the metal grains, current path is shorten and relative cross section is most effectively enlarged. Finally, the

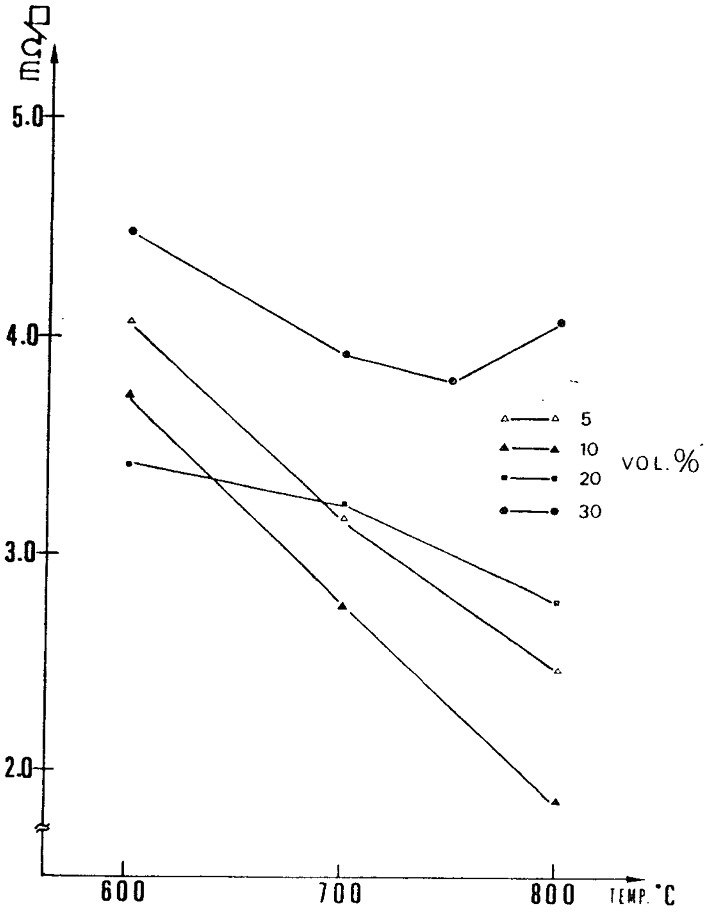
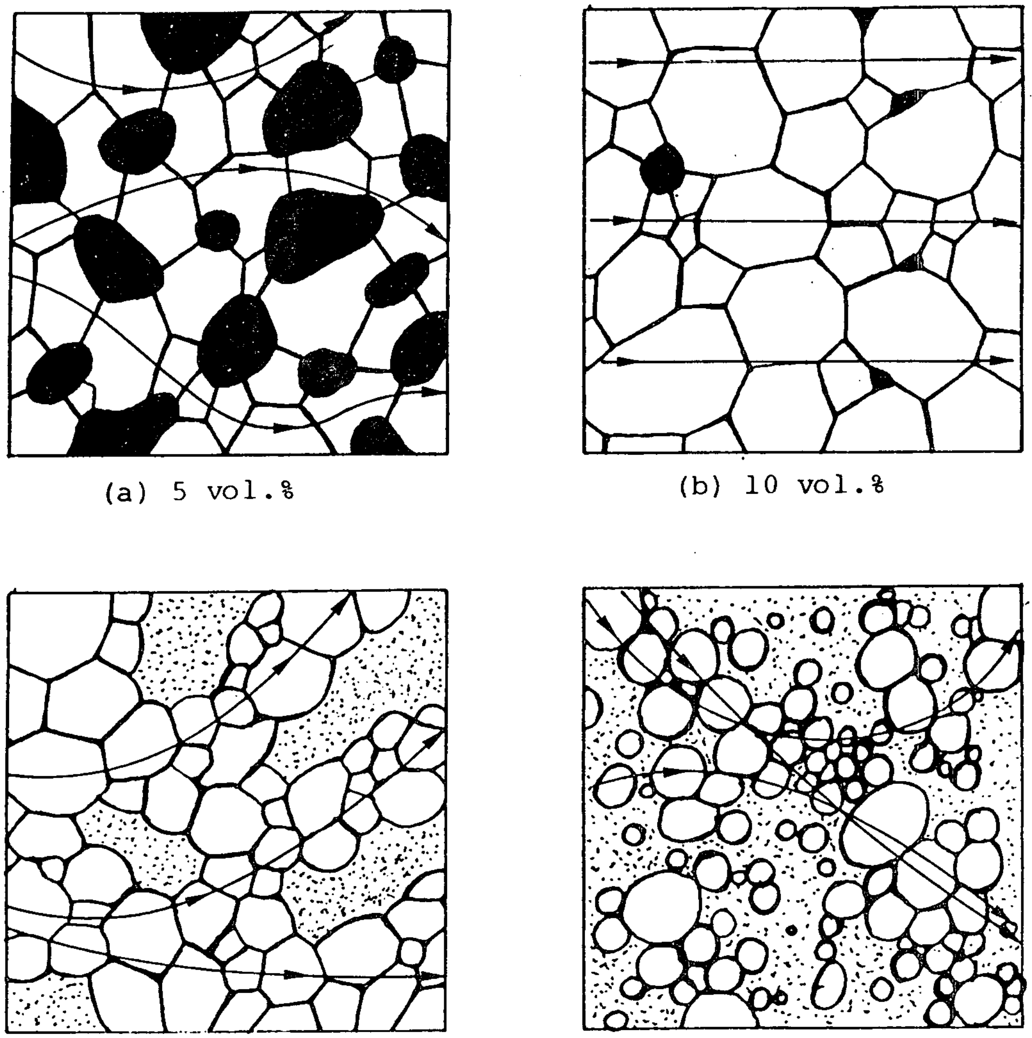


Fig. 5. **Electrical sheet resistivities with glass volume fractions fired at 600°C to 800°C for 10 min.**

best electrical properties are obtained.

Thick-film containing 20 vol. % glass have very low resistance value even fired at 600°C, but with increasing firing temperatures reducing rates of resistivity is slow (Fig. 5). The resultant plot indicates that during initial sintering stage active packing of metal particles due to the fast rearrangement process takes place. Continuing further densification, however, glass phase is pushed out from the metal skeletons to form separated glass pools. In this case, even though contact area of each grain increases by grain coarsening, the total homogeneity of the conductive metal phase get worse (Fig. 6 (c)). These results are unfavorable to improving electrical conductivity.



(a) 5 vol.%

(b) 10 vol.%

(c) 20 vol.%

(d) 30 vol.%

Fig. 6. **Relations between microstructure development and current path with glass vol. fraction.**

When glass content is extremely high (over 30 vol. %), the change of resistance value with firing temperature has different plot from others (Fig. 5). The more liquid glass speeds up densification, but over some range liquid can interupt the effective contact formation of metal grains. As seen in Fig. 4 (d), many silver particles are immersed in the separated glass pool not to be connected with the metal skeleton (Fig. 6 (d)). This sintering progress works against the electrical conduction, which results in increasing of the resistance value as further sinterings are continued.

IV. CONCLUSION

In the conductive Ag thick-film, glass phase affects the sintering behaviors and microstructure development of the metal particles to control electrical properties. As glass content in the thick-film increases, the rate of densification of metal particles becomes faster, but when glass content exceeds a some range, metal phase takes up glass liquid to decrease total interface energy, then glass is separated from the solid skeletons to form glass pools. For extremely high glass content (over 30 vol. %), contact formation of solid particles becomes unstable and metal particles are dispersed in the glass matrix during further sintering. As a result, the densification of metal phase is inhibited.

The electrical properties of thick films are associated with microstructure development. When glass content is optimum, compact and homogeneous microstructure can be obtained, then resistivity of the thick-film has minimum value.

REFERENCES

(1) Koh-Ichi Yajima and Takashi Yamaguchi, "A further study on the microstructure of glass bonded Ag thick-film conductor" IEEE Trans. on CHMT-7 No. 3, pp281-5 (1984).

(2) G.C. Kuczynski, "Measurement of self-diffusion of silver without radioactive tracers" J. Appl. Phys. 2(7), pp632-35 (1950).

(3) R.E. Hoffman and D.J. Turnbull, "Lattice and grain-boundary self-diffusion in silver", 'ibid', 22 (5) pp634-39 (1951).

(4) D.L. Johnson and T.L. Clarke, "Grain-boundary and volume diffusion in the sintering of silver" Acta Met., 12 (10) pp1173-79 (1964).

(5) S.S. Cole, Jr., "Sintering of Ag-Pd in the presence of a reactive glass" J. Am. Ceram. Soc., 55 (6) pp296-99 (1972).

(6) B. Meredith and D.R. Milner, "Densification mechanism in the Tungsten Carbide-Cobalt System" Powder Met., 19 pp38-45 (1976).

(7) H.H. Park and Duk N. Yoon, "Effect of dihedral angle on the morphology of grains in a matrix phase" Met. Trans. A, 16A pp923-28 (1985).

(8) Ho-Gi Kim and Young Sir Chung, "Development of thick-film conductor pastes" Final Tech. Rep. on Contract No. BST 1095-2582-1 September, (1986).