PROPERTIES OF X7R MLC CAPACITORS CONTAINING 70AG/30PD OR 60AU/20PD/20PT INTERNAL ELECTRODE COMPOSITION.

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SUMMARY

The effects of internal electrode compositions 70Ag/30Pd and 60Au/20Pd/20Pt on the physical and electrical properties of low-fired X7R dielectric (K=3200) were examined in MLC capacitors with dielectric thickness in the range of 10 to 15 microns.

For MLC capacitors made with same powder and sintered simultaneously, physical and electrical properties of chips with Ag/Pd electrode are similar or superior to those with Au/Pd/Pt electrode system. The fired density, dielectric constant and high temperature high voltage insulation resistance are higher for MLC capacitors with 10 micron thick active dielectric layers. These properties are nearly the same when active dielectric thickness is 15 microns. Based on these preliminary results, it is believed that volatility of silver from electrode during sintering at 1110°C tends to enhance densification. Concentration of Ag may range between 0.01 to 0.2 wt% depending on sintering temperature, dielectric composition and grain size.

Although excellent physical and electrical properties have been reported[7] on MLC capacitors with 6 micron active dielectric layers, a comparison with ternary system is yet to be made. The results of this study will be reported at a future date.

INTRODUCTION

The growing demand for high volumetric efficiency MLC capacitors has accelerated research activities in raw materials, dielectric compositions and manufacturing technology during the past decade. At the same time, selling price of these capacitors has been continuously declining. A recent survey by Sakabe[1] describes past and future trends in MLC technology.

Relative materials cost of the internal electrode in MLC capacitors is quite significant. Therefore, efforts to reduce this cost have taken several routes. These include: high silver Ag/Pd systems[2], base metal electrodes[3,4], and Pb injected electrodes[5]. Efforts were also undertaken to increase the dielectric constant and to reduce active dielectric layer thickness. Properties of various classes of dielectrics[6], and MLC capacitors with 6 micron active dielectric layer thickness have been reported[7,8,9].

Although MLC capacitors with high silver containing electrodes have been commercially manufactured and marketed successfully, the potential effect of silver diffusion into the dielectric during sintering has not been thoroughly studied.

Accordingly, the objective of this paper is to report some preliminary results of a study comparing physical and electrical properties of MLC capacitors with Ag/Pd and Au/Pd/Pt internal electrodes.

SAMPLE PREPARATION

The dielectric composition used in this experiment is based on a flux-modified, high purity, fine-powder barium titanate. Physical and electrical properties of this formulation have been reported[10]. Multilayer ceramic capacitors in 1210 size chips (3.20mm x 2.50mm) with 10 active layers of 10 and 15 microns dielectric thickness were manufactured. The precious metal (Ag/Pd) and (Ag/Pd/Pt) powders for internal electrodes were purchased commercially, and separate-

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ly made into screenable paste using same solvent/dispersant/binder system. Ceramic pieces without electrode were made at the same time and used to determine fired density.

Green chips were heated slowly in air to 800°C on open slab to remove binder and then sintered in separate high purity alumina crucible with lapped covers. A sufficient quantity from each group was processed and measured for the following properties: fired density, capacitance, dissipation factor, insulation resistance, dielectric breakdown, temperature coefficient of capacitance, degradation under life test, and microstructure of polished and fractured surfaces.

RESULTS AND DISCUSSION

A summary of some of the physical and electrical properties of the two electrode systems for 10 and 15 micron thick layers and for two sintering temperatures is shown in tables 1 through 4. Changes in capacitance with temperature (TCC) for both groups sintered at 1110°C are described in figures 1 and 2 respectively. Microstructure of polished and fractured surfaces of both electrode systems are shown in figures 3 through 6.

Table I. Properties of 1210 size MLC Capacitors with 10μ Thick Active Dielectric Layers.

Sintering Temperature: 1110°C

	ELECTRODE SYSTEM	
	70Ag/30Pd	60Au/20Pd/20Pt
Capacitance nF (1KHz, 1Vrms, 25°C)	118	105
Dissipation Factor	2.7%	2.28%
Density (gm/cc)	5.86	5.75
Dielectric constant	3800	3650
IR (100V, 150°C ohms)	5 exp(11)	6 exp(10)

Examination of results clearly show that samples with Ag/Pd electrode give higher fired density than those with the ternary electrode system. The difference in measured density using Archimedes method is consistent with the observed closed porosity discernable from fracture surfaces for both electrodes as shown in figure 7.

Table II. Properties of 1210 size MLC Capacitors with 10μ Thick Active Dielectric Layers.

Sintering Temperature: 1080°C

	ELECTRODE SYSTEM	
	70Ag/30Pd	60Au/20Pd/20Pt
Capacitance nF (1KHz, 1Vrms, 25°C)	107	102
Dissipation Factor	2.15%	2.2%
Density (gm/cc)	5.83	5.70
Dielectric constant	3475	3325
IR (100V, 150°C ohms)	1 exp(11)	1 exp(10)

Table III. Properties of 1210 size MLC Capacitors with 15μ Thick Active Dielectric Layers.

Sintering Temperature: 1100°C

	ELECTRODE SYSTEM	
	70Ag/30Pd	60Au/20Pd/20Pt
Capacitance nF (1KHz, 1Vrms, 25°C)	65	63
Dissipation Factor	1.65%	1.66%
Density (gm/cc)	5.79	5.67
Dielectric constant	3500	3400
IR (100V, 150°C ohms)	1.7 exp(11)	4 exp(10)
Life Test (200V, 150°C, 48hrs)	No degradation	No degradation

Table IV. Properties of 1210 size MLC Capacitors with 15μ Thick Active Dielectric Layers.

Sintering Temperature: 1080°C

	ELECTRODE SYSTEM	
	70Ag/30Pd	60Au/20Pd/20Pt
Capacitance nF (1KHz, 1Vrms, 25°C)	57	57
Dissipation Factor	1.37%	1.5%
Density (gm/cc)	5.81	5.70
Dielectric constant	3200	3200
IR (100V, 150°C ohms)	1 exp(11)	1 exp(10)
Life Test (200V, 150°C, 48hrs)	No degradation	No degradation

Observed dielectric constant and dissipation factor at 1 KHz and 1 Vrms for samples with Ag/Pd electrodes are significantly higher for 10 micron layers at

1110°C than for samples with ternary system electrodes. However, these properties are nearly the same for 15 micron thick layers, and samples sintered at 1080°C.

The shape of the TCC curves with either electrode system or with either dielectric layer thickness are nearly the same. Temperature coefficient of capacitance is with in 10% deviation relative to 25°C over the X7R temperature range (figures 1 and 2). However, MLC capacitors with Ag/Pd electrode system showed a few percent larger deviation than with the ternary system. These results are consistent with observed dielectric constant for each group (3800 vs 3650).

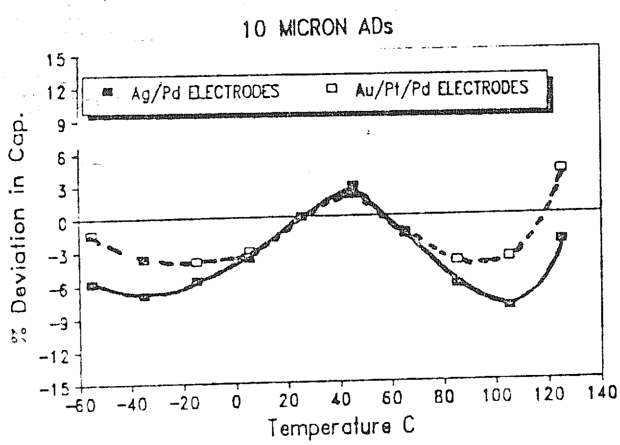


Figure 1.Change of capacitance with temperature for 1210 size MLC capacitors with 10μ layers.

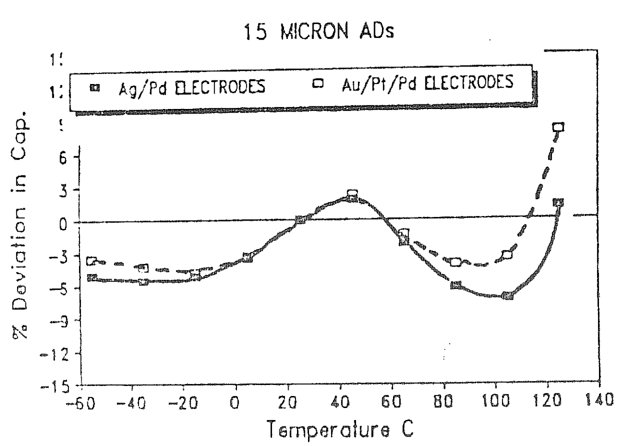
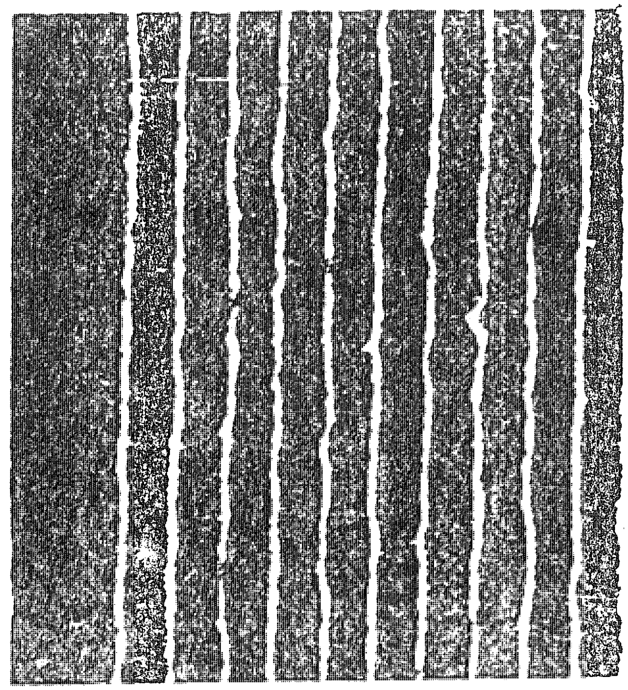
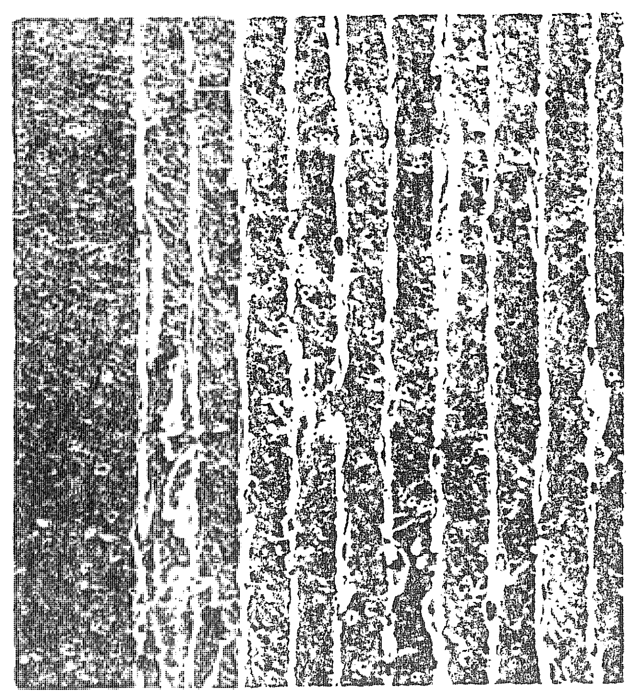


Figure 2. Change of capacitance with temperature for 1210 size MLC capacitors with 15μ layers.

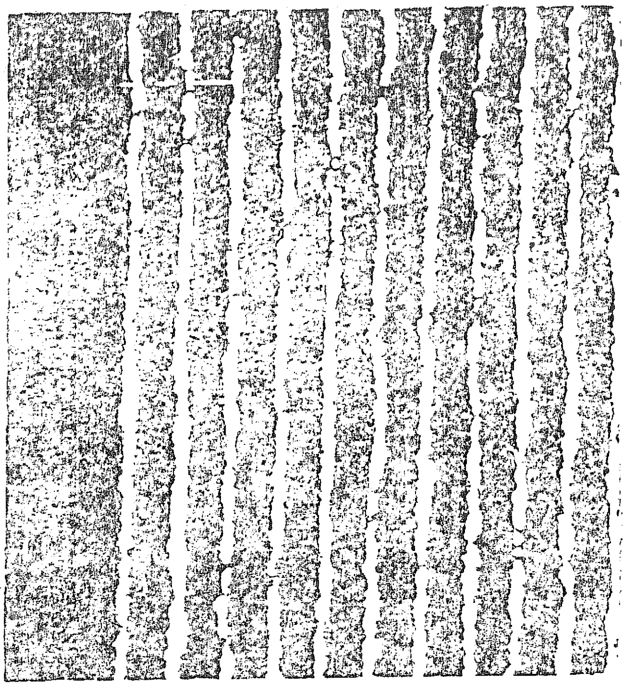


(a) Polished surface

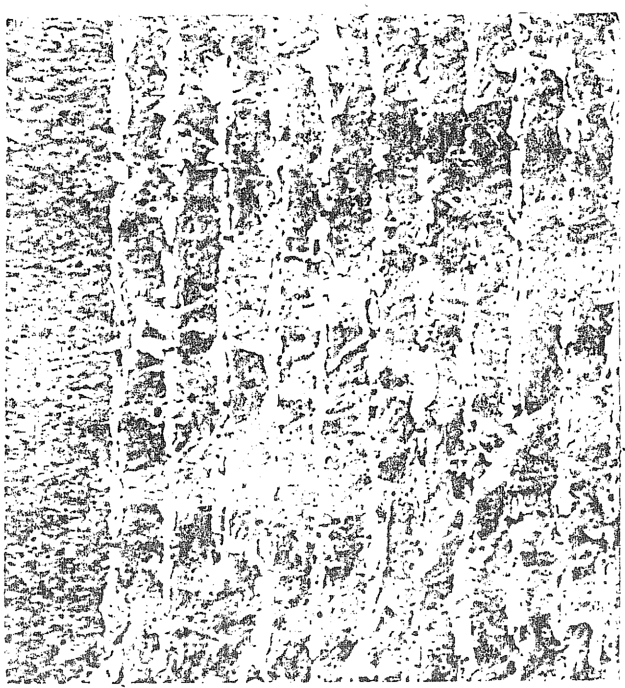


(b) Fracture surface

Figure 3. Microstructure of MLC capacitors with 10μ layers and 70Ag/30Pd electrodes.
500x Bar=10μ

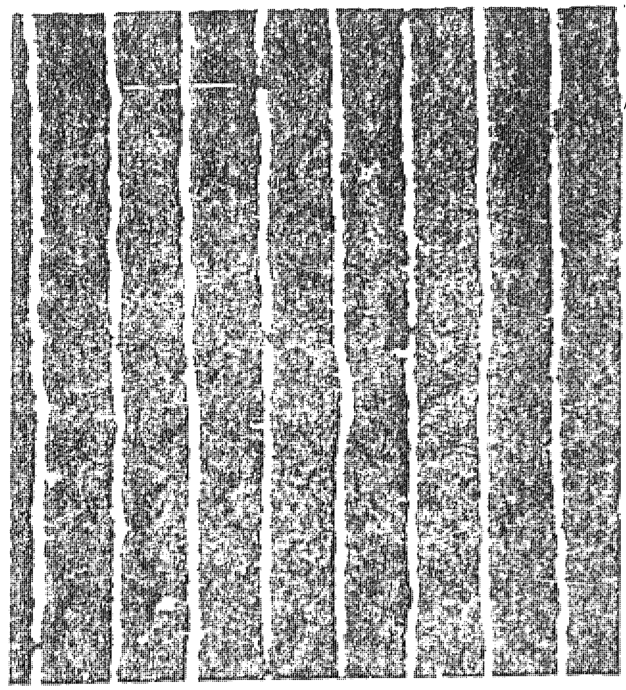


(a) Polished surface

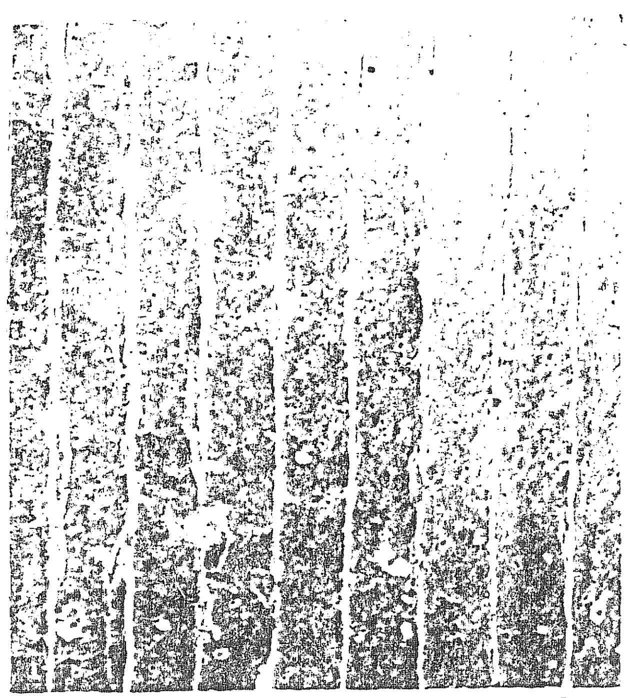


(b) Fracture surface

Figure 4. Microstructure of MLC capacitors with 10μ layers and 60/Au/20Pd/20Pt electrodes.
500x Bar=10μ

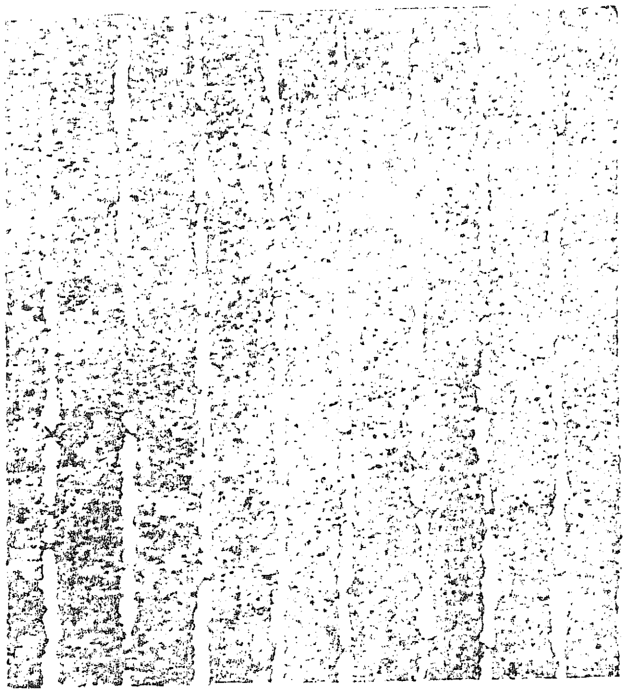


(a) Polished surface

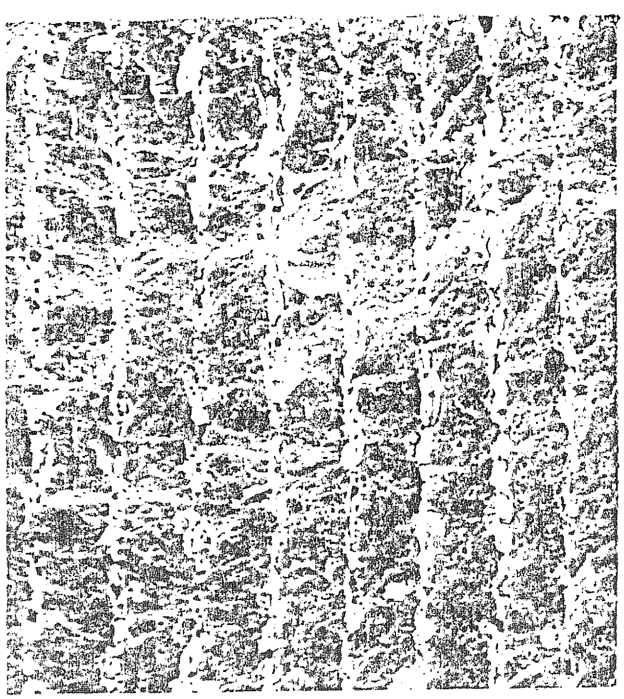


(b) Fracture surface

Figure 5. Microstructure of MLC capacitors with 15μ layers and 70Ag/30Pd electrodes.
500x Bar=10μ



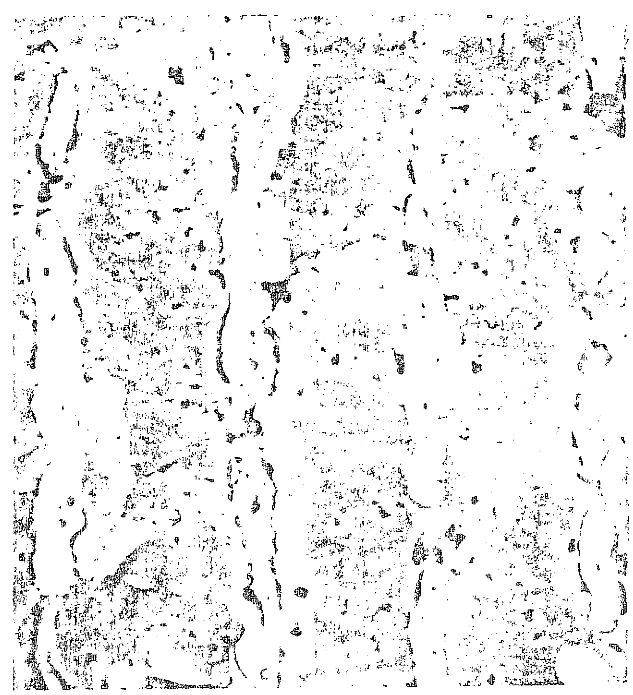
(a) Polished surface



(b) Fracture surface

Figure 6. Microstructure of MLC capacitors with 15μ layers and 60Au/20Pd/20Pt electrodes.
500x Bar=10μ

(a) 70Ag/30Pd electrodes



(b) 60Au/20Pd/20Pt electrodes

Figure 7. Microstructure of MLC capacitors with 15μ layers.
2000x Bar=1μ

Insulation resistance at 100V and 150°C is slightly lower for MLC capacitors with ternary system. It is not clear from this limited data whether the lower fired density could be responsible for the observed difference. Life test capability at 200V, 150°C for 15 microns appeared stable with time. Breakdown voltage for MLC capacitors with 15 microns is greater than 700V.

The uniformity of Ag/Pd electrodes is significantly better than the ternary system electrodes (figures 3 and 4). This difference is related to the particle size and size distribution of the starting metal powder. With Ag/Pd system thickness of electrode is about 1 micron (figure 3) while that for Ag/Pd/Pt is about 1.5 microns (figure 4). Polished cross sections of both groups show slightly thicker electrodes because of smearing caused by polishing.

The solidus line for 70Ag/30Pd solid solution is about 1165°C[11]. Therefore, sintering of MLC capacitors near this temperature may lead to some volatility of Ag from the alloy. This has been confirmed by detection of silver in edge ceramic pieces that do not contain any electrode but were sintered along with MLC capacitors in the same crucible. Concentration of silver within active dielectric layers has ranged between 0.01 and 0.2 weight%.

CONCLUSION

The physical and electrical properties of low-fired barium titanate based X7R dielectric were studied with MLC capacitors containing 70Ag/30Pd and 60Au/20Pd/20Pt internal electrodes with 10 and 15 micron thick active dielectric layers. The chips with Ag/Pd system, when sintered at 1110°C, show higher density, dielectric constant, dissipation factor and insulation resistance than chips with ternary system. However, properties at 1080°C for 15 micron layer chips are nearly equal.

This work will be continued to compare MLC capacitors with 6 micron active layers when a fine powder ternary system becomes available.

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