70%Ag30%Pd COATED BaTiO₃ POWDER FOR INTERNAL ELECTRODE APPLICATIONS*

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Recent trends in the electronic passive component manufacturing industry have been to eliminate or reduce reliance of pure Pd and high palladium contained Ag/Pd electrodes by substituting nickel or significantly lowers palladium content in Ag/Pd alloys. The conversion to base metal technology represents a substantial capital expense; the resistance to replace traditional air-fired kilns to nitrogen or reducing atmosphere kilns has created the need for new low cost air fired electrode technology. This paper presents a new electrode technology incorporating a uniform, continually coated AgPd over engineered dielectric particles. The resulting powder greatly reduces the consumption of precious metal, and provides superior thermal mechanical properties. This is achieved by matching the core ceramic structure of the powder to the manufacturer's dielectric, thereby controlling shrinkage while maintaining desired electrical properties.

Keywords: MLCC manufacturing, Internal electrodes of MLCC capacitors, BaTiO₃ powder, capacitor electrode powder technology.

INTRODUCTION

Developments in composite powder technology have enabled MLCC manufacturers to utilize AgPd coated dielectric particles, such as BaTiO₃, in direct substitution for AgPd. These composite powders can be made for any AgPd ratio, and contain as much as 40 wt.% dielectric while providing excellent electrical characteristics in the finished MLCC component.

The development of the AgPd coated BaTiO₃ powder was in response to MLCC manufacturers wanting to reduce the amount of Pd used in the internal electrode application. To meet the need, it was critical that the composite powder have (1) a uniform, continually coated AgPd surface, (2) precise AgPd ratio, and (3) assured good electrical properties.

Other advantages arise from this powder structure in the form of superior thermal characteristics, such as reduced oxidation behavior and minimized thermal shrinkage/expansion mismatch with the dielectric body of the MLCC. This allows the construction of high layer count parts with significantly less internal stress.

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FIGURE 1 SEM of 70%Ag30%Pd at 60 wt.% on 40 wt.% BaTiO₃.

POWDER SYNTHESIS AND PROPERTIES

Many different processes exist for making powders. These include, but are not limited to, spray pyrolysis, solid-state reactions, atomization, and precipitation. Composite powders can also be made in a variety of ways; however, the success of the method of synthesis depends on the properties of the materials involved and the desired physical and chemical characteristics of the final powder. In this work, the AgPd coated BaTiO₃ was made by a precipitation technique.

Internal electrode powders for MLCC's are generally spherical and nearly monodisperse. To achieve the desired qualities in the composite powder, careful design and selection of feed materials and reaction conditions are necessary. Such factors as metal ion source, reaction temperature, pH conditions, reagent concentrations, and dispersing agents are critical to successfully controlling the AgPd coating on a BaTiO₃ particle. In addition, intimate understanding of the surface chemistry of BaTiO₃ is crucial.

Figure 1 shows a typical scanning electron microscope (SEM) image of a 70%Ag30%Pd at 60 wt.% on 40 wt.% BaTiO₃. Table I lists the corresponding physical properties of the powder shown in Figure 1. Figure 2 shows the particle size distribution (PSD) curve for the powder shown in Figure 1.

Extensive testing was performed on the thermal properties of the AgPd–BaTiO₃ powder. Figures 3 and 4 show the thermal behavior of four powders (thermal profile: 30 °C to 1000 °C at 10 °C min⁻¹ in air). The solid line shows the mass change and expansion/shrinkage behavior (Figs. 3 and 4, respectively) of 70%Ag30%Pd. This is typical of AgPd at this composition. The dash-line represents the thermal trace of a mixture of 70%Ag30%Pd and BaTiO₃ at 60 wt.% metal and 40 wt.% dielectric. These traces are also typical of an admixture of metal and dielectric powder. The dot-line shows the thermal

TABLE I Composite Powder Properties.

Surface area	4.23 m ² /g
Tap density	1.5 g/cm ³
Moisture content	0.07%

FIGURE 2 Particle size distribution curve for 70%Ag30%Pd on 40 wt.% BaTiO₃.

FIGURE 3 Thermal-gravimetric curves of 70%Ag30%Pd, 70%Ag30%Pd + BaTiO₃, 70%Ag30%Pd coated onto BaTiO₃, and BaTiO₃.

FIGURE 4 Thermal-mechanical traces of 70%Ag30%Pd, 70%Ag30%Pd + BaTiO₃, 70%Ag30%Pd coated onto BaTiO₃, and BaTiO₃.

FIGURE 5 TEM image a cross-sectioned metal (darker material) coated barium titanate (lighter material) and corresponding ED patterns.

trace for the 70%Ag30%Pd coated onto 40 wt.% BaTiO₃. The dash-dot-line shows the thermal trace of BaTiO₃. Clearly seen in the comparison of the thermal traces of Figures 3 and 4 are the reduced oxidation peak of Pd (in Fig. 3) and the significant displacement reduction (in Fig. 4) of the metal coated BaTiO₃.

Figure 5 shows the Transmission Electron Microscope (TEM) image of a cross-sectioned powder sample of metal coated barium titanate. Clearly seen here is the metal deposited onto the barium titanate core. Electron diffraction was also done to show composition of each component.

PASTE AND COMPONENTS

Making electrode paste from the AgPd coated BaTiO₃ is no different than for traditional AgPd powders. This feature provides the paste maker a “drop-in” replacement, while

FIGURE 6 Image of final part made with 70%Ag30%Pd at 60 wt.% on 40 wt.% BaTiO₃. Dielectric layers are X7R.

TABLE II MLCC Electrical Properties.

<i>Paste composition</i>	<i>Paste A</i>	<i>Paste B</i>
Metal	45% AgPd 7001	47% 7001BT-60
Ceramic	7.50%	0.00%
Organics	47.50%	53.00%
Total	100.00%	100.00%
<i>Paste Performance</i>	<i>Paste A</i>	<i>Paste B</i>
Delaminations	2/1000	0/1000
C _{PAVE} (nF)	123.654	115.817
C _{PSTD} (nF)	3.13	2.21
DF _{AVE} (%)	1.76	1.84
DF _{STD} (%)	0.06	0.05

reducing the metal quantity, improving the performance of the paste, and providing superior thermal properties.

Figure 6 shows the cross-sectioned part made with the AgPd coated BaTiO₃ powder and X7R dielectric.

Table II compares the paste composition of a standard AgPd70%Ag30%Pd paste and electrical test properties for an X7R body with >50 active layers and a paste composition with corresponding electrical properties made with 60% 70Ag30Pd on 40% BaTiO₃ with the same number of active layers.

Paste A was made by adding 7.5 wt.% ceramic to the paste composition. The resulting delaminations were less than 0.2%. The corresponding electrical properties were good, with an average capacitance of 123.7 nF and an average dissipation factor of 1.76%. Paste B was made with the metal coated barium titanate powder and no added ceramic. However, the ceramic component of the metal coated powder comprises 18.8 wt.% of the paste, which is 2.5 times more ceramic than the “pure” metal paste composition with added ceramic. The parts made with the metal coated barium titanate did not show any delaminations, and also had very comparable electrical properties; average capacitance was 115.8 nF and the average dissipation factor was 1.84%.

In addition to the composition presented thus far in this paper, additional metal compositions have been made and are being tested. These include typical compositions of mid-fire and low-fire AgPd, such as 80%Ag20%Pd at 60 wt.% on BaTiO₃, as well as 85%Ag15%Pd at 60 wt.% on BaTiO₃, 90%Ag10%Pd at 60 wt.% on BaTiO₃, and also pure Pd versions; such as 100%Pd at 60 wt.%, 80 wt.%, and 90 wt.% on BaTiO₃. This composite powder technology has also been applied to a wide variety of dielectric materials in addition to BaTiO₃, such as alumina and zirconia, and can also be applied to “custom” dielectric compositions.

CONCLUSION

A new electrode powder technology was presented, which provides a uniform, continually coated AgPd exterior on BaTiO₃ particles. The new powder greatly reduces the precious metal content and provides superior thermal characteristics to standard AgPd powders while assuring good electrical properties. The AgPd coated BaTiO₃ powder enables a manufacturer to construct high layer count parts due to significantly reduced internal stress in the MLCC body. Paste fabrication and part construction with AgPd coated BaTiO₃ are accomplished in the traditional way, but allow manufacturers to produce superior components while reducing the metal quantity.