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... THE LEADING EDGE

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A growing percentage of multilayer ceramic capacitors (MLCCs) worldwide are being manufactured with nickel (Ni) internal electrodes in place of more traditional palladium (Pd) or silver/palladium (Ag/Pd) alloy materials. These products are often referred to as "base metal electrode," or BME MLCC. Murata and TDK, which have utilized 100% Pd internal electrodes in the past, have been the first to convert some MLCC products to BME technology. KEMET is in the process of establishing the capability to produce MLCC using Ni electrodes, but its incentive to bring this capability on-line is somewhat diminished by KEMET's established technology for utilizing Ag/Pd alloy electrodes, which already offer substantial cost savings as compared to pure Pd electrodes.

The critical issues associated with the manufacture of BME MLCC and KEMET's development activities in this area are described in the following article written by Dr. Hyun Park, Senior Technical Associate, and Dr. Doug McBrayer, Manager Ceramic Technology, in KEMET's Ceramic Technology Development Group.

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Base Metal Electrode (BME) Multilayer Ceramic Capacitors (MLCCs)

by: Hyun Park and Doug McBrayer

Nickel internal electrode (BME) ceramic capacitors were first developed and introduced in the mid-1970s by a U.S. manufacturer (no longer in the ceramic capacitor business) in an attempt to avoid the cost associated with using precious metal internal electrodes (alloys of gold and platinum were commonly used at that time). These early Ni electrodes MLCCs were quickly withdrawn from the marketplace because of serious reliability problems. Other U.S. ceramic capacitor manufacturers chose alternative approaches to lower cost, with most, including KEMET, deciding to utilize low-fire dielectrics that were compatible with Ag/Pd alloys containing no more than 30% Pd. Meanwhile, most Japanese manufacturers developed high-fire dielectrics systems that required 100% Pd electrodes.

The need for improved volumetric efficiency has driven all MLCC manufacturers to utilize thinner dielectric layers and larger numbers of active layers. This trend has exposed serious problems with the use of Pd electrodes due to the stresses generated by the oxidation-related expansion during binder burnout and the subsequent reduction back to Pd during firing. To overcome these problems, special Pd powders must be used and extra precautions must be taken during bakeout and sintering processes.

These difficulties, combined with the rising price for Pd, have driven Japanese MLCC manufacturers back to the Ni base metal electrode alternative. A major drawback of BME systems is that MLCCs fabricated with inner nickel electrodes must be fired in a reducing atmosphere to protect the nickel electrodes from oxidation. Oxygen partial pressures in the range $10^{-6} \sim 10^{-10}$ MPa's are required at the peak firing temperatures of 1300-1350°C. This type of atmosphere can be maintained, for instance, by using wet nitrogen and hydrogen gas mixtures. The end termination of BME MLCC is also composed of a base metal, either copper or nickel, and should be fired in a protective nitrogen atmosphere as well.

The reducing atmosphere required to prevent oxidation of the Ni electrodes poses a problem in maintaining high quality dielectric properties in the ceramic. Dielectrics based on $BaTiO_3$, which are predominantly used in the manufacture of MLCC, are subject to reduction to semiconductivity when fired in a depleted oxygen atmosphere by free electrons released by either Ti^{+3} or oxygen vacancies in the ceramic. This results in low insulation resistance of the dielectric and poor reliability. To prevent degradation of the dielectric's insulation resistance and to improve reliability performance, dielectrics must be reduction resistant and the number of oxygen vacancies must be minimized. The resistance of dielectrics to reduction can be enhanced by acceptor doping and by using, nonstoichiometric Ba-site rich $BaTiO_3$ as a starting material. Oxygen vacancies can be decreased by incorporating a reoxidation process into the firing cycle. During the cooling process, after densification is completed at high temperature (>1300°C), a small amount of oxygen is introduced into the kiln atmosphere and the temperature is maintained for a period of time. The insulation resistance of the dielectrics can thus be improved while avoiding oxidation of the sintered nickel electrodes if the oxygen content of the atmosphere is kept below the equilibrium curve of Ni/NiO.

Millions of dollars have been spent in Japan developing materials and manufacturing processes based on these principles to manufacture MLCCs with Ni electrodes. A few manufacturers have been successful in using these techniques to produce MLCCs with Ni electrodes that have performance and reliability characteristics, which approach those for Ag/Pd electrode products. According to a recent survey in 1996 more than half the MLCCs manufactured in Japan were made with nickel electrodes. Some manufacturers have predicted that more than 90% of all MLCCs will be made with nickel electrodes by the year 2000 if the price of palladium continues to rise.

At present prices for Pd, KEMET is able to provide MLCC products with Ag/Pd alloy electrodes that are cost competitive with similar Ni electrode product. As shown in Table 1, the materials cost of palladium electrodes for high fire dielectric systems is 22 times higher than for nickel electrodes, while the cost of 70Ag/30Pd electrodes for low fire dielectric systems is only approximately 7 times that for BME systems.

Table 1. Electrode Comparison

Electrode Material	Cost per Troy oz.
100% Pd	$200
70% Ag / 30% Pd	$65
Ni	$9

The cost advantage of Ni electrodes is somewhat offset by the increased capital and operational costs of atmosphere control required for the associated bakeout, firing, and termination processes. As the number of active layers in an MLCC increases, Ni electrodes become an attractive alternative to Ag/Pd alloy electrodes from a cost standpoint, in spite of the increased capital and operational costs. Obviously, the break-even point between Ni and either Pd or Ag/Pd electrode systems is strongly dependent on the cost of Pd.

KEMET began the development of BME capacitors in 1995. Figure 1 illustrates BME capacitors fabricated in KEMET's Ceramic Capacitor Technology Development Center. Both X7R and Y5V BME MLCCs were fabricated with inner nickel electrodes, terminated with copper, and plated with nickel and tin. 1206 1uE X7R chips were fabricated with 90 layers of 9 micron thick dielectric, and 1206 3.3 micro-farad Y5V chips were built with 80 layers of 6 micron thick dielectric. Electrical properties of these BME MLCCs are listed in Table 2.

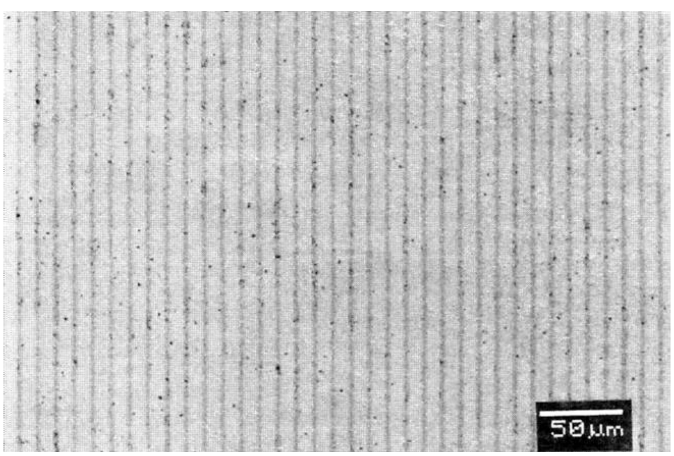

Figure 1a. SEM micrograph of polished surface of BME Y5V capacitor.

As contrasted with the largest Japanese manufacturers, who predominantly use solvent-based coating systems to make their dielectric sheets, KEMET has consistently used water based coating systems. KEMET elected to take advantage of its strong technical position in water-based coating systems and is developing an environmentally friendly water-based BME dielectric sheet coating process.

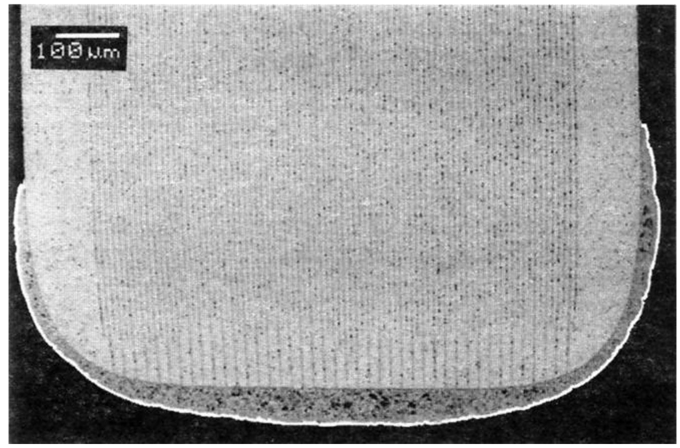

Figure 1b. Cross section of copper terminated and nickel plated BME X7R capacitor.

Table 2. Electrical Properties of KEMET BME MLCs.

Batch# Dielectric	Firing Temp	Cap nF	% DF	25°C IR ohms	Hot IR ohms	Low end TCC, %	High end TCC, %
TJN194QF X7R	1325°C	1073 ±27	3.3	1.8G	400M (125°C)	-12.12 (-55°C)	-3.17 (125°C)
TRV0403JN Y5V	1300°C	3229 ±169	5.8	10.6G	5.5G (85°C)	8.17 (-30°C)	-71.25 (85°C)

In late 1996, the decision was made to build a 24,000 square-foot addition to KEMET's Fountain Inn South Carolina plant for BME development and production. This manufacturing facility is allowing simultaneous development of the materials systems and manufacturing processes required to manufacture high layer count MLCC with Ni electrodes. Construction was begun in December, 1996, and manufacturing process development using production scale equipment was begun in August, 1997. The simultaneous development of the materials systems and manufacturing process will allow KEMET to offer BME product for sale in mid-1998.

At the same time, KEMET continues to develop new, advanced dielectrics that are compatible with Ag/Pd electrode systems, focusing on increasing dielectric constant and de-creasing dielectric thickness to address market needs for higher unit capacitance at lower cost. KEMET is also actively working with precious metal suppliers to develop Ag/Pd powders that can be deposited in very thin layers, thus extending the cost competitiveness of standard low-fire Ag/Pd technologies to higher capacitance value products. KEMET is committed to extending Ag/Pd technology as far as possible and has demonstrated thin dielectric (3 micron) capability with >500 layers in the laboratory.

The development and introduction of BME technology will complement KEMET's current Ag/Pd technology and ensure that KEMET maintains its position as one of the world's leading suppliers of high quality MLCCs.