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An analysis of the internal electrodes of various multilayer ceramic capacitors (MLCs) available today will reveal electrode com-positions as diverse as $1500 per pound palladium and $3.40 per pound nickel!

In this issue of Tech Topics, we attempt to place the diversity of MLC internal electrode compositions in perspective.

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Electrode Materials for Multilayer Ceramic Capacitors

Historical

The early development of barium titanate dielectrics is shown in Figure 1.[1] By the mid-1950's the technology had clearly formed two branches, which eventually led to the "low fire" silver-palladium electrode and "high fire" palladium electrode materials systems. Also in the 1950's, John M. Herbert,[2] in England, invented the nickel base-metal electrode (BME) MLC. The three technologies have evolved, but the important differences remain today.

High-fire Systems

These ceramic dielectrics are normally composed of relatively stable and refractory oxides, which sinter together to make dense bodies only at high temperatures (approximately 1300°C or greater). Because of the chemical stability of the oxides, the dielectric compositions are compatible with co-fired palladium electrodes. Silver may be added in small quantities (up to 30%), as long as the melting point of the alloy is well above the ceramic sintering temperature.

Silver-palladium alloys, however, exhibit a maximum in their electrical resistivity of about four times the pure palladium value in the vicinity of 30% Ag addition. So there is often a trade-off: capacitor effective series resistance, electrode thickness, and silver content.

"High-Fire" technology is commonly used by Japanese MLC manufacturers.

Co-fire (BME) Systems

BME systems are similar to high-fire systems in that they normally use only very stable oxides in the dielectric composition. The use of nickel (occasionally copper or cobalt) electrodes, however, requires that the firing process be carried out in an inert or reducing atmosphere to avoid oxidizing the base metal electrode. It is, however, relatively easy to partially reduce barium titanate, creating oxygen vacancies. These vacancies will migrate under electric fields, causing further degradation of the dielectric. The processing of BME capacitors amounts to a balancing act between reducing the dielectric and oxidizing the electrode. If the nickel becomes oxidized it will in turn react with and degrade adjacent dielectric material. Innovative dielectric chemistry has been applied to in efforts to mitigate this problem.[3]

BME capacitors have been in intermittent manufacture for over 20 years, primarily by manufacturers using high palladium-content electrodes.

Low-fire Systems

Early in the development of barium titanate dielectrics, it was recognized that several low-melting oxides could be added to barium titanate to jointly modify the temperature coefficient of the dielectric constant and lower the firing temperature of the dielectric (see Figure 1). Binary oxides containing bismuth became popular modifiers, but because bismuth reacts with palladium, only low palladium-content electrodes were tolerated by these dielectrics.

To avoid the reaction between bismuth and palladium, palladium-gold (sometimes with platinum added to raise the melting point of the alloy) was used. Further refinements of the technology led to the substitution of the gold with silver. In the last decade, silver alloys with 15 to 35% palladium have been in widespread use.

"Low-fire" technology is in common use by U.S. MLC manufacturers.

Comparison of Quality, Cost and Performance

Each of the three technologies described above has key advantages and disadvantages, as illustrated by the rankings in Figure 2. Each key factor is described in the discussion below.

Dielectric Constant

The sintering aid/modifier additives traditionally used in the low-fire dielectrics also depress the dielectric constant relative to a similar high-fire dielectric. The effect is partially offset by the usually superior voltage dependence of the dielectric constant. Typically, the capacitance decreases less with the application of voltage in capacitors made with the low-fire materials. At rated voltages, low-fire dielectrics often exhibit higher dielectric constants than equivalent high-fire bodies.

KEMET's dielectrics research has demonstrated that some non-traditional sintering aid/modifiers greatly reduce depressant effects. Dielectric constant differences between high- and low-fire systems will decrease significantly in the next few years.

The firing atmosphere required for BME capacitors limits the choice of dielectric constituents to very reduction-resistant oxides. These limited choices in turn constrain the dielectric engineer's ability to maximize the dielectric constant.

Dielectric Thickness/Reliability

The BME system is a clear third. The balancing act between oxidation of the electrode and reduction of the dielectric required by the process was discussed earlier. The rate of degradation of dielectrics containing oxygen vacancies is related to the applied

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electric field, hence dielectric thickness. With a constant thickness reaction zone, oxidized nickel will react with a greater percentage of a thin dielectric than a thick one.

The difference between the high and low-fire technologies is small. The lower voltage coefficients of capacitance typical of low-fire dielectrics gives the technology an edge.

Mechanical Robustness

One very attractive feature of low-fire dielectrics is their high mechanical strength compared to that of high-fire systems. As Figure 3 illustrates, the modulus of rupture* of various commercial MLCs is considerably greater for low-fire product. At KEMET, Koripella and Bergenthal[4] have demonstrated that this strength is related to sintering aid/modifier additives.

** The modulus of rupture test and calculation correct for any thickness differences among samples.*

Materials Cost

Figure 4 shows the relative values of the internal electrode metal of the three technologies, calculated using typical industry dielectric constants and thickness. The three columns for each capacitor model correspond to high-fire (palladium), low-fire (silver-palladium), and co-fire (nickel) systems, respectively. As the chart illustrates, low-fire capacitors with 70-30 or 75-25% silver-palladium electrodes achieve about 3/4 of the savings available by replacing palladium with a low-cost metal. Further advances in low-fire materials technology now permit the manufacture of MLCs with little or no palladium in the electrodes.[5] However, the cost saved by this technology is small, and other factors must be considered in their commercialization.

Process Costs

The palladium scrap and inventories necessary for the high-fire system and the additional costs of controlled-atmosphere firing required for BME capacitors, make these processes more expensive than that of the low fire.

Process Control Cost

Again, BME capacitors are at a disadvantage: the difficulty of precisely controlling the atmosphere during the firing of each capacitor is a very significant process control cost, overshadowing other considerations in this category.

Conclusion

None of the three technologies described in this paper is new, and each has been refined and improved through years of research. Although each technology has clear advantages, the low-fire materials system KEMET uses remains an overall very good choice.

References

1. John Piper, Joint Japan-U.S. Study Seminar on Dielectric and Piezoelectric Ceramics, Tokyo, May 24-26, 1982.
2. U.S. Patent 2,750,657
3. For example, U.S. Patents 3,041,189 and 4,115,493.
4. Some early results were presented by Jim Begenthal in the Proceedings of the 11th Capacitor and Resistor Technology Symposium (CARTS) March 4- 7, 1991.
5. KEMET's U.S. Patent 5,011,803, describes materials and process for making reliable pure silver electrode MLCs, for example.

Early Development of Barium Titanate Dielectrics

1930's
TiO_2 Dielectrics
1940's
$BaTiO_3$ Dielectrics
TCC Modifier Additions (1315- 1400°C Firing Temperature)

Further Development of Modifiers for High Firing Bodies

Modifiers Which Reduce Firing Temperatures:
$PbTiO_3$ (1288°C)
CoO (1200°C)
1950's $PbSnO_3$ (1204°C)
$Bi_2(SnO_3)_3$(1260°C)
Bi_2O_3 Additions

Chart based in part on the following U. S. Patents:

925,257	2,525627	2,582,953	2,558,575
2,452,532	2,563,357	2,624,709	
2,469,584	2,576,375	2,658,832	

Figure 1

MLC Materials Technology - Ranking of Differences

Parameter	Ranking		
	Base Metal Electrode	Pd Electrode High-Fire	AgPd Electrode Low-Fire
Dielectric Constant	2	1	2
Dielectric Thickness/ Reliability	3	2	1
Mechanical Robustness	2	2	1
Material Costs	1	3	3
Process Costs	3	2	1
Process Control Costs	3	1	1
1=Best 3=Poorest			

Figure 2

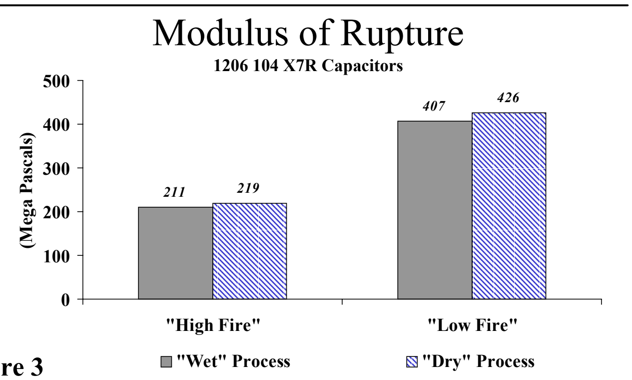

Figure 3

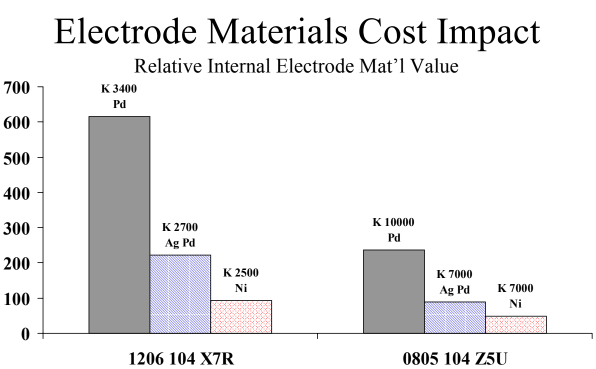

Figure 4

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