TECHNICAL PAPER

Multilayer Ceramic Capacitors Materials and Manufacture

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Abstract

The economical mass production of highquality, reliable and low-cost multilayer ceramic (MLC) capacitors requires a thorough understanding of the characteristics of the materials used, a knowledge of chemistry and electronics, as well as a high level of expertise in mechanical-equipment design and in-process technology.

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A multilayer ceramic (MLC) capacitor is a monolithic block of ceramic containing two sets of offset, interleaved planar electrodes that extend to two opposite surfaces of the ceramic dielectric (Figure 1). This deceivingly simple structure requires a considerable amount of sophistication, both in material and in manufacture, to produce it in the quantities used in today's electronic equipment.
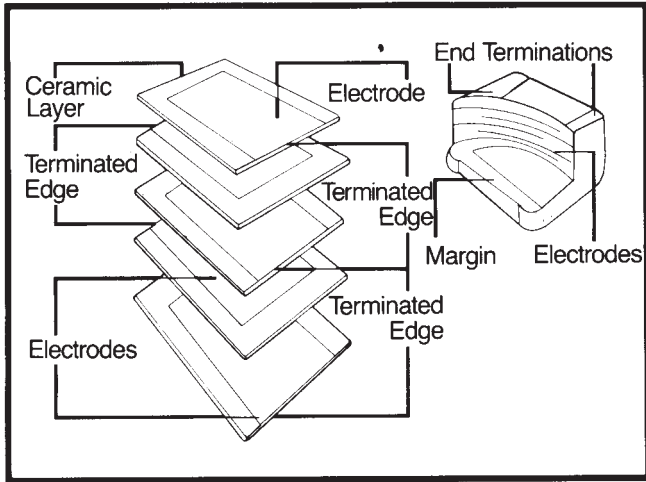

Figure 1. Construction of multilayer ceramic capacitor

The use of MLCs follows closely that of integrated circuits (Figure 2); approximately three billion multilayer ceramic capacitors are used in the United States annually. Their advantages stem from their small size, frequency performance and cost advantages that result from the utilization of barium titanate. This ceramic material has a significantly higher intrinsic dielectric constant than most other types of materials. It also displays a relatively high resistance to humidity and temperature, and is amenable to economical volume production.
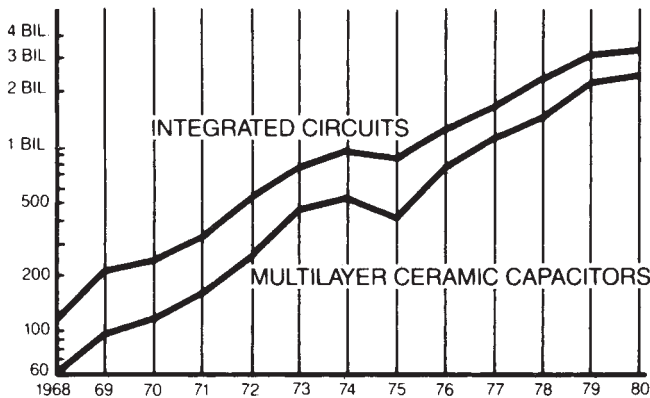

Figure 2. MLC capacitor sales parallel the increased sales of ICs

The Dielectric Material

Barium titanate exhibits a spontaneous and reversible polarization in a relatively narrow temperature range that coincides with the ambient temperatures found in electronic equipment. Figure 3 shows its small-signal dielectric constant as it depends upon grain size and
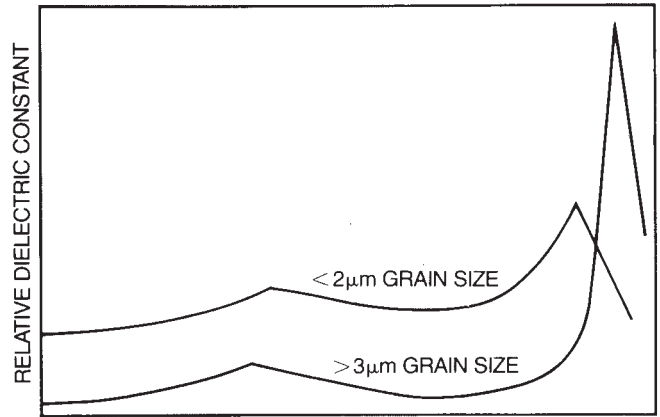

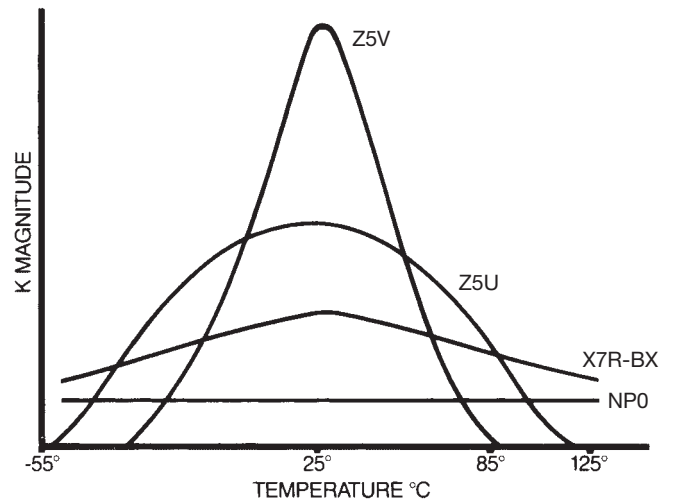Figure 3. Small-signal dielectric constant varies with temperature

Figure 4. Changes in dielectric constant (K) with temperature for various ceramic dielectrics

DESIGNATION	CLASS	TEMPERATURE RANGE °C	TEMP-CAP CHANGE	DIELECTRIC CONSTANTS UP TO	BaTiO₃ CONTENT %	OTHER INGREDIENTS	GRAIN SIZE
"Temperature Compensation"	1	-55 to +125					
NP0			±30 ppm	75	10 to 50	CaTiO₃TiO₂ rare earth oxides, etc.	~1 μm
Intermediate K							
BX, X7R	2	-55 to +125	±15%	3000	90 to 98	Donor dopants, Sintering aids	~1 μm
High K	2	+10 50 +85					
Z5U			+22% 56%	8000	80 to 94	Curie Point Shifters, Electrical Dopants, Sintering aids	3-20 μm
Z5V			+22% 82%	18000	80 to 94		

Table I. Barium titanate based dielectrics for MLCs

temperature. Figure 4 shows the temperature behavior of the different types of dielectric materials that are based on barium titanate. Table I reviews this behavior in more detail.

"Temperature-compensating" materials used as MLC dielectrics have between 15 and 50 percent barium titanate. Their temperature coefficients can range from +150 ppm/°C with a dielectric constant of 30, to a temperature coefficient of - 2200 ppm/°C with dielectric constants of a few hundred. These formulations usually have Q's in excess of 1000 and are called Class 1 dielectrics. In early formulations, oxides with positive and negative temperature coefficients, such as

barium titanate, calcium titanate, strontium titanate, and magnesium titanate, were mixed to obtain the desired temperature behavior.

The most popular formulation in this class is "NP0" material (± 30 ppm/°C from - 55°C to +125°C). Modern NP0 formulations, as pioneered by Bolton (1), contain a large proportion of neodymium, samarium and other rare earth oxides and have dielectric constants of 70 or more. These materials are quite voltage stable and have their minimum dielectric thicknesses determined largely by physical constraints of manufacturing and flaw size, rather than by dielectric performance requirements.

Intermediate dielectric-constant ceramics are modified barium titanates, sintered to a small grain size (less than 2 µm). These are Class 2 materials, sometimes called "temperature-stable" ceramics. These ceramics provide significantly more stable temperature behavior than large-grain barium titanate (see Figure 3).

Stability is increased further by making the ceramic with a controlled inhomogenuity. To attain this, $BaCO_3$ is first pre-reacted (calcined) with TiO_2 to barium titanate powder. This drives off about 15 percent CO_2 that would impede densification if present during sintering. When such pre-reacted barium titanate is mixed with a donor-dopant and then sintered, only a small amount of the donor diffuses into the original barium titanate grains. The sintered ceramic then contains regions of very low donor concentration at the original grain cores, but there is considerable solubility of the dopant in the regions surrounding the cores where grain growth takes place (Figure 5). A STEM photomicrograph of such a structure is seen in Figure 6. With sufficiently high doping levels, secondary crystallization can be completely inhibited.

The sintered ceramic then shows two dielectric-constant peaks (Figure 7), one at about 125°C from the undoped grain cores, and a second at lower temperatures, resulting from the heavily doped grain grown region (3). The volume ratios of the two regions are determined by the crystallite sizes of the original powder and by the grain size of the sintered ceramic.
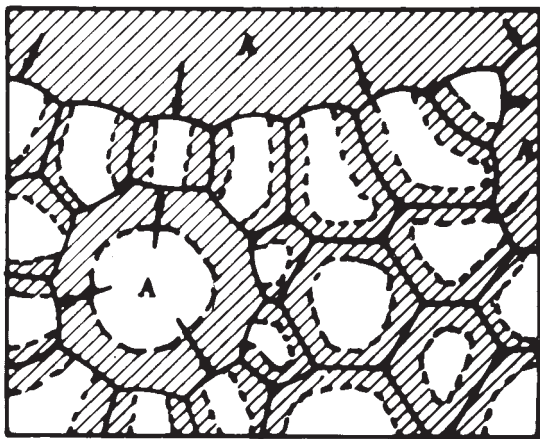

Figure 5. Schematic of polycrystalline structure. Secondary recrystallization and grain growth proceed from areas A. Cross-hatched areas contain dopant. Clear outlines show original grain cores. (Adapted from W.O. Kingery) (2)
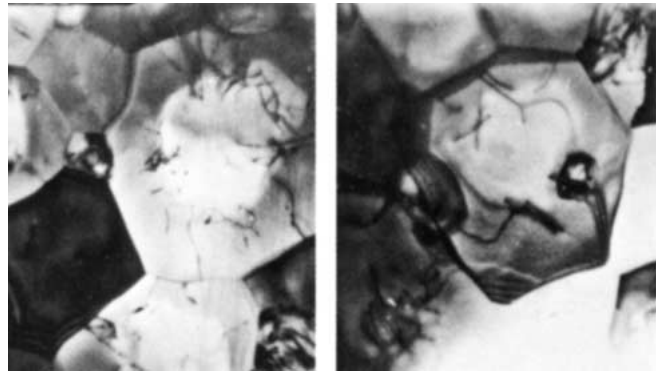

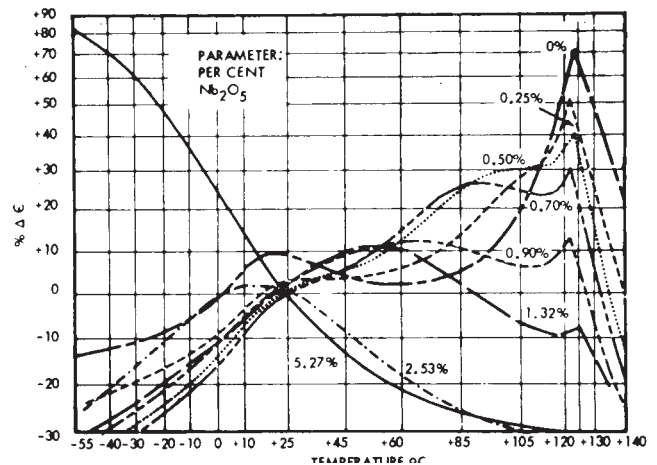Figure 6. STEM photomicrographs of intermediate dielectric-constant ceramic material

Figure 7. The sintered ceramic shows two dielectric-constant peaks

"X7R" formulations are the most popular intermediate dielectric-constant materials. They contain additional ingredients, such as calcium zirconate, or even small amounts of acceptors. Their temperature variation of capacitance is within 15 percent from - 55ºC to +125ºC.

Class 2 high dielectric-constant materials are relatively homogeneous barium titanate formulations that have grains grown to more than 3 µm. Their high K stems from the addition of substituents with the same valences. These shift the Curie point to the room temperature region. Sr(2 +) or Zr(4 +) are often used, making peak dielectric constants as high as 18,000 available. Such materials can lose up to 50 percent of their dielectric constant at 50°C, but find general applications in computers and other commercial low-power electronic equipment requiring a limited temperature range.

For "Z5U" requirements (capacitance loss of less than 56 percent at 80°C) calcium is most often added in the form of calcium zirconate. The resultant dispersion in the dielectric characteristics widens the K versus temperature curve, and controls the maximum capacitance loss at 85°C. Room temperature dielectric constants of more than 8000 are then seen. These materials also contain inhomogenuities in the form of unreacted, relatively pure, grain cores.

A polished cross-section of a Z5U multilayer capacitor exhibits a higher etching rate in the multi-component
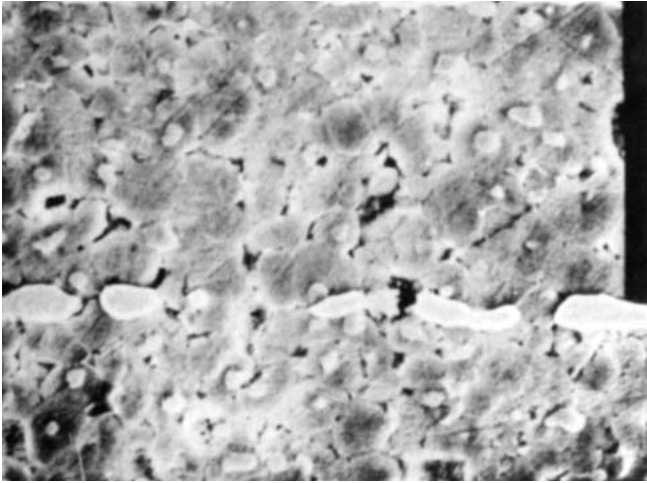
Figure 8. Cross-section of Z5U ceramic dielectric (etched)

grain grown region than in the grain cores. As a result, "bumps" are seen in the center of the grain cores (Figure 8). Microprobe examination verified the expected relative purity of the grain cores. The volume ratio of these grain cores is negligible and the temperature dependence of the dielectric constant is not noticably affected.

Commercial "high-K" formulations also contain Curie-point shifters, donor and acceptor dopants. These are used primarily to improve dielectric stability. This is particularly important when sintering is to take place in atmospheres of low oxygen pressures: enough acceptors are needed to "neutralize" the oxygen vacancies that are formed. On the other hand, dopants with different valences usually cause grain growth inhibition. This can be detrimental in high-K dielectrics, since the dielectric constant is often proportional to the grain size. Consequently, sintering aids, such as silicates, are often used to enhance densification and grain growth.

In the past five years, some high dielectric-constant ceramic dielectric formulations have been developed that utilize lead-iron-tungstate and niobates. These may sinter at temperatures as low as 1000°C.

Electrode Material

The electrode material must yield a conductive film that is continuous after firing and does not diffuse into, or react with the ceramic dielectric. This requires the use of non-oxidizing metals or alloys with high melting points. Palladium was one of the earliest materials used. Palladium reduces during heating to allow film formation, and its surface oxidizes during cooling (below 870°C). This causes it to bond to the ceramic. Alloys containing gold and platinum are also used.

For cost reduction, increasing amounts of silver are added to the electrode alloys. This also lowers the melting point of the alloy. The development of lower firing formulations allows the use of more silver, which results in electrode cost savings.

The use of nickel electrodes reduces still further the electrode cost, but the requirement for a low oxygen pressure firing atmosphere (to keep the nickel from oxidizing) dictates significant changes in ceramic composition and processing. The use of tin-lead electrodes is another low-cost approach to reduce the electrode cost of multilayer capacitors. When utilizing this alloy, the capacitors are sintered with a fugitive electrode material, producing voids in the intended electrode regions. These voids are then impregnated with the low melting alloy to form the internal electrodes.

Low-Firing Formulations

Firing temperatures below 1170°C are required to use electrode alloys containing 70 percent or more of silver. Reduced firing temperatures are attained through additions of relatively large percentages of bismuth compounds or of reactive glass frits. These tend to liquidfy during sintering and often have a high solubility for the barium titanate. During cooling, epitaxial recrystallization often occurs on the nondissolved barium titanate grains.

Figure 9 displays electron back-scattered images of a bismuth-containing barium titanate, revealing higher bismuth concentration in the grain shells than that found in the grain cores. These systems yield dielectric
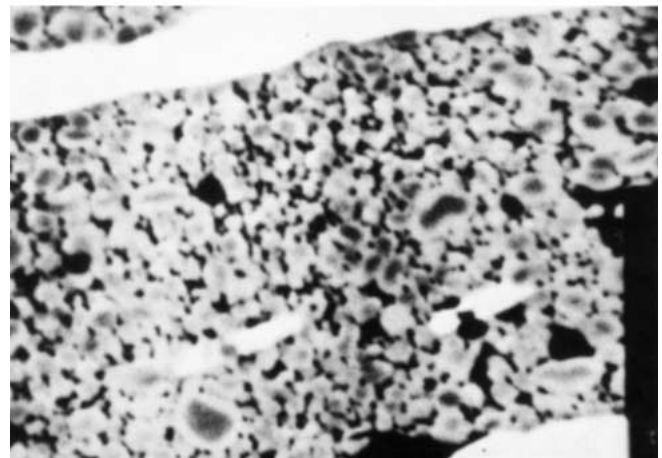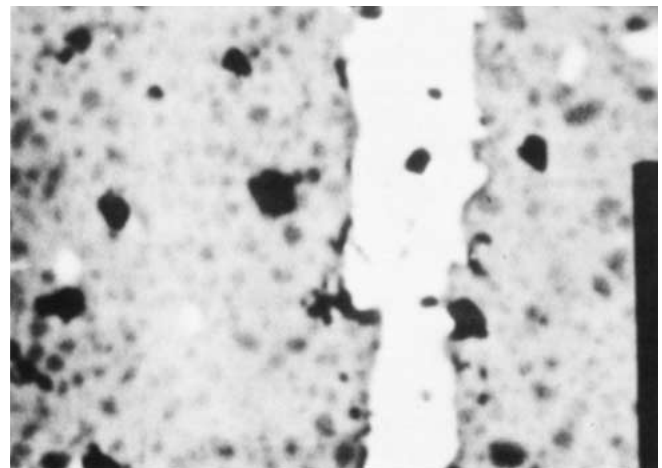

Figure 9. Scanning electron microscope back-scattering images of polished (top) and etched (bottom) samples of bismuth containing barium titanate

constants that are closer to that of barium titanate than those in which a distinct, uncrystallized solidified liquid phase is present after cooling.

This particular type of nonhomogenuity exists only after firing in a relatively narrow temperature-time regime. With longer sintering times the inter-granular liquid may drain from the dielectric and accumulate near the electrodes (4) (Figure 10). The bismuth may also diffuse into the grains and result in a uniform bismuth distribution, particularly at higher sintering temperatures.

Three types of bismuth distribution have been verified using STEM techniques (Figure 11). The enhanced bismuth distribution at the grain boundaries (curve "A") gives the highest resistivity ceramic. Depletion of bismuth in the grain boundary regions, either by drainage (curve "B") or by diffusion into the ceramic (curve "C") gives lower resistivity and less stability on life test. The presence of the bismuth gradient can be verified by the sharp grain boundary etching of the material as is shown in the figure.

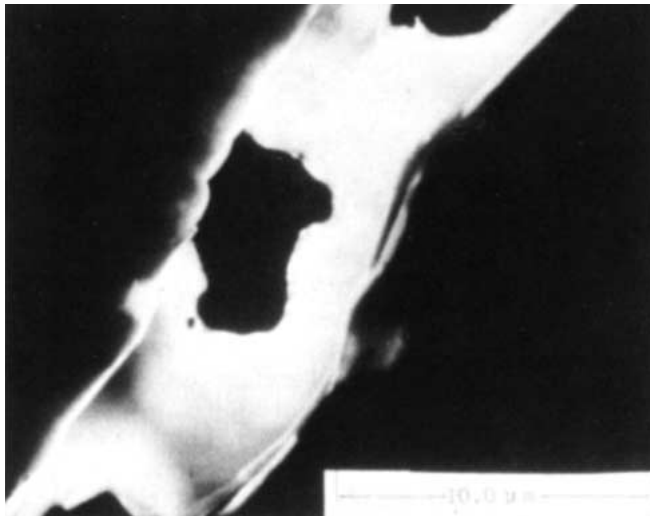Figure 11. Three types of bismuth distribution

Figure 10. Annular dark-field STEM image showing electrode-ceramic interface with bismuth-rich layer

These fluxed formulations also contain donor dopant gradients. These are not affected by changes in the bismuth distribution, resulting in a relatively reproducible capacitance-temperature behavior.

Multilayer Capacitor Manufacture

The processes used in the manufacture of multilayer ceramic capacitors require a high degree of sophistication to insure high-yield, large-scale, low-cost production. The characteristics of the raw materials must be controlled closely, otherwise many of the electrical and physical parameters and in the finished product will be affected.

In the raw $BaTiO_3$, the Ba/Ti ratio critically affects the grain growth kinetics and the defect structure. The effective stoichiometry is affected by impurities present and by their site occupancy ratio. Many trace elements,
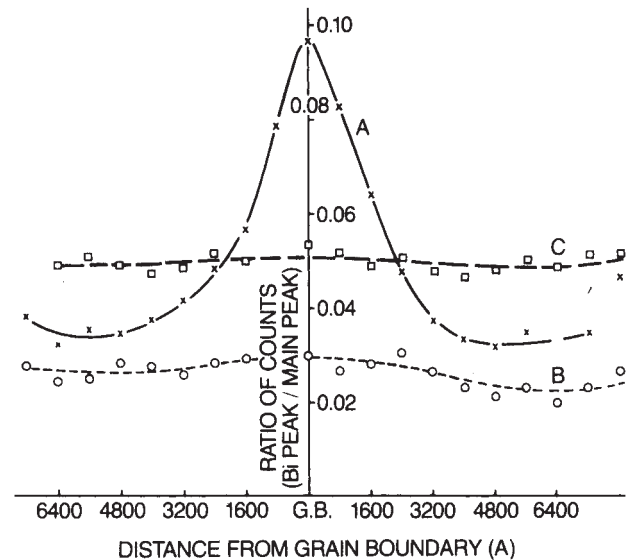
such as aluminum, sodium, iron or potassium, can substitute in the lattice as acceptors, contributing to electronic defects in the structure. These impurities must be controlled so that their partial evaporation during sintering does not cause lack of control.

Physical characterization of the raw material is just as important as definition of the chemistry. One aspect of this is homogenuity, or how much of the material is present in fully reacted, stoichiometric form. The amounts of nonstoichiometric compounds as well as of residual precursors can be determined by chemical analysis. These factors are controlled in $BaTiO_3$ by maintaining homogeneity of mixing and of temperature before and during calcining. In addition, crystallite size, aggregate size, aggregate hardness and surface area affect processing and ceramic characteristics.

Prior to formulation preparation the ingredients are precisely weighed and documented. The powders are mixed and milled for proper homogenization and reduction of aggregation. During milling, some shattering of crystallites and dislocation may be introduced. Variations in pH, viscosity, temperature and medium wear will affect the results of this milling process.

The milled product is mixed with a suitable binder solution (PVA or an acrylic resin) into a dielectric "slip." The physical properties of this slip, its rheology and surface tension, control the physical parameters of the "green" ceramic.

For preparation of the dielectric layers with "direct-laydown" or "wet" techniques, the dielectric layers may be deposited on a substrate by screening, curtain coating, or spraying. Alternatively, in the tape or "dry" process, self-supporting tapes are cast using doctor blading or similar techniques. Maintenance of proper dispersion of the powder in the slip is necessary to insure maximum packing when the deposited slip is dried. Where tapes are prepared, these can be rolled on reels for storage and testing.

In either process, electrode material is screened onto the dried ceramic dielectric. The metals used as electrodes are usually in the form of precipitated submicron powders, which are intimately wetted and mixed with organic screening media. The latter is made up from a binder-solvent solution that is compatible with the organic constituents of the dried dielectric. The medium is designed to provide the ink with the proper screening viscosity, and the binder in it serves to hold the metal in place after the solvent is dried.

Proper dispersion of metal particle aggregates as shown in Figure 12 helps to provide a homogeneous screened film. This is required to minimize the amount of metal that gives a continuous fired film. The metal can be dispersed in its virgin state by careful milling, or after it is made into high-viscosity ink. The high-viscosity media allows the application of higher shear forces and dispersion of the metal before flattening of the particles takes place.
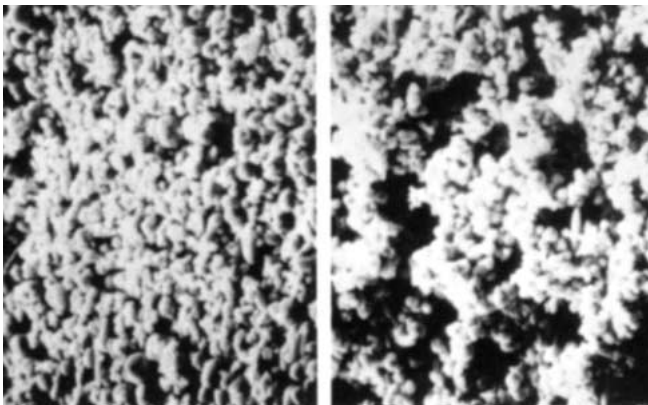

Figure 12. Dispersed and aggregated metal powder

Assembly of Multilayers

When tape is used, it is cut into individual sheets which are screened with electrode ink through a multiple set of electrode patterns. The sheets are then stacked and laminated into a solid "pad." Lamination temperatures and times are adjusted carefully to produce physically integral and crack-free pads, while protecting the thermoplastic properties of the tape.

The first step in the heat treatment of the "green" ceramic parts is the "burnout" of the organic constituents. This step must be performed gradually, as excessive initial heating rates result in rapid gas evolution. This can easily destroy the physical integrity of the parts. High heating rates can be caused by exothermic burning of the organic binder, and may be increased further by catalytic action of the metal film. Close control over the rate of temperature increase and over the atmospheric conditions are therefore necessary during this process.

During sintering, the most important parameter is reproducibility: time dependent changes in firing conditions, as well as variations caused by location of the parts in the kiln, must be minimized.

It is often possible to adjust the doping levels of the dielectric material to give the required performance with relatively fast cooling rates. Consequently, cooling rates are often limited by the thermal shock resistance of the refractories. Continuous kilns of the car, pusher, or walking-beam type are presently the most popular configurations for firing multilayer capacitors. Figure 13 shows multilayer capacitors being fired on zirconia slabs. Bulk loading is another popular firing configuration.

Figure 13. Firing MLCs on zirconia slabs

Fired chips are terminated in the electrode pick-up regions with a metal paint. This paint usually contains silver or palladium-silver mixes with approximately 5 to 10 percent glass frit, and 25 to 35 percent organic binder-solvent mix. With proper viscosity control, this termination paint is applied to chips as small as .04 in. x .05 in., onto closely defined "land" areas. For efficiency, this must be done rapidly, requiring considerable mechanical and process know-how. In one configuration more than 1000 chips are loaded simultaneously into cavities of a metal plate and passed under a paint-coated roller (see Figure 14). Most termination paints are fired at about 800°C.
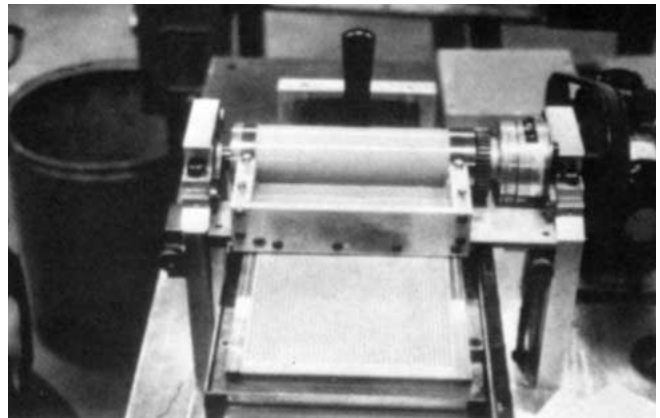

Figure 14. Applying metal paint for electrodes

At this point, the first electrical tests can take place. Figure 15 shows a typical chip capacitance tester.

Assembly is performed by soldering onto these land areas in various radial or axial lead configurations. Thermal shock as well as leaching out of the silver can be encountered during soldering. These effects are prevented

Figure 15. Testing capacitance of MLC chips

by gradual preheating and be close control over the time-temperature cycle of the solder-dipping process.

Multilayer capacitor chips can be encapsulated by dipping, molding, or sealing in glass cases. They may also be used un-encapsulated. Encapsulation materials must be selected with care to avoid degradation of the properties of the multilayer chip, since organic materials are less humidity resistant than the dense ceramic. With too little encapsulation adhesion, moisture traps and electrical leakage paths can be formed. Too much adhesion and encapsulation strength can cause excessive tensile stress in the ceramic during temperature cycling.

For application on hybrid circuit boards, bare chips are often used. These are usually mounted with reflowed solder or connected with conductive epoxy.

The requirements for automatic machinery, test equipment, floor space and labor in the post-firing steps are significantly greater than those required for handling materials and parts in multiples in the earlier phase of processing. Also, quality control and final testing, including life testing, is a very significant effort due to the large number of individual parts involved.

The economical mass production of multilayer ceramic capacitors requires basic understanding and implementation of materials and process technology, both in inorganic and organic chemistry. The application of electronic principles and know-how, as well as a high level of expertise in mechanical-equipment design, are also essential. Combining these disciplines successfully results in the manufacture of a highquality economical electronic component.

References

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