

Failures in Base Metal Electrode (BME) Capacitors

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Introduction

A new failure mechanism has been discovered for today's latest high volumetric efficiency multilayer chip capacitors. Over the past couple of years, the drive for lower costs has been promoted by the replacement of silver palladium electrodes by nickel. Diligent qualification procedures predicted very long life. However, experience has uncovered an Achilles heel. The capacitors fail when exposed to high (> 85%) humidity un-powered for extended periods.

This paper provides an overview of salient details of the construction of ceramic multilayer capacitors. Reviewing the literature and intuiting the possible bad actors form candidate hypotheses. An experimental and analytical procedure for quantifying the merit of each hypothesis is proposed.

Data at Hand

An alarming failure rate for nickel BME MLCC's exposed high relative humidity has been reported to the authors. At this time, experiments to duplicate these failures are underway. Therefore, no conclusive proof is available to confirm or refute this failure mode at this time. The experimental planning required a literature review and the formation of hypotheses. These efforts are described briefly in this paper.

Development of the Ceramic Multilayer Capacitors

The capacitor, as a device, has undergone a transformation from its earlier major use as for energy storage in power regulation. The use of ceramic multilayer capacitors has blossomed to hundreds of billions per year [1] due both to their low cost, shrinking form factor [2] and to the ever-growing need for improving digital signal integrity compromised by the continuing increase in operating frequency of digital electronics. As capacitors have grown to

become the highest count component type on populated boards, they also have been labeled as the most common cause of failure [3].

The multilayer ceramic capacitor (MLCC) is based on a simple interleaved electrode construction. Since capacitance depends linearly upon the dielectric constant and linearly upon the plate area but upon the inverse square of the dielectric thickness [4], the primary design goals are minimizing the dielectric thickness and then maximizing the dielectric and plate areas. Of course, keeping electrode plates thin also makes for a thin overall capacitor assembly stack. Therefore, need for a better dielectric has fostered a flurry of successful development activity over the last three decades.

Because ceramics are produced by firing a "green tape" (ceramic powder in a wax carrier), the ceramic sintering temperature (~1100 to ~1700 K) must be compatible with the melting temperature of the electrode material, since both the electrodes and the dielectric are fired simultaneously (co-fired) in the assembly. The melting temperature of silver is 1294 K; the melting temperature of nickel is 1728 K; the melting temperature of palladium is 1828. Platinum, an alternative electrode material, melts at 2041 K. Secondly, chemistry (primarily oxidation reactions) during firing drives material selections and determines allowable gases in the sintering oven atmosphere. Finally, since ceramics are minerals, aspects of geology, mining and commodity markets further constrain material selection.

Ceramic Dielectrics

The primary ceramic capacitor dielectric material is barium titanate (BaTiO_3). It was first discovered in 1940, and its ferroelasticity was discovered in 1945. It demonstrates a dielectric constant in the range of 1000 to 5000 depending on realized morphology, viz. grain size. Structurally, BaTiO_3 is a perovskite. The

perovskite structure is remarkable; perovskite may be the most common mineral crystalline structure in the earth. BaTiO₃ goes through a series of phase changes over temperature and pressure. The tetragonal configuration, between 273 K and 403 K, is the configuration of practical importance. [5, 6, 7]

The dielectric constant of pure BaTiO₃ suffers spikiness at the phase change temperatures especially at the curie point (403 K). Therefore, there are many concoctions of additives to stretch out or, using industry terminology, relax these transitions [8]. These additives fall into the classes of isovalent substitution (strontium, lead, calcium, and others), donor ions (niobium, tantalum, tungsten) or acceptor ions (manganese, cobalt, and others). All three categories replace atoms in the crystal. Another option is the introduction of impurities like magnesium or aluminum. Each of these strategies may introduce problems. Possible quality issues faced in the past from the introduction of these material modifications include aging, reduction in dielectric strength and onset of semiconducting behavior [9].

Other ceramics also have been used for dielectrics. These include strontium titanate, lead titanate, lead magnesium niobate (PMN), lead zinc niobate, lead iron niobate-lead tungstate and others.

Industry Standard

There is an industry standard for standard MLCC sizes and performance metrics. The Electronic Industries Association (EIA) Standard 198 describes class II capacitors in terms of temperature range and capacitance variation range [5]. Therefore the common designation Y5V implies -30 C to 85 C with a change of capacitance in the range of +22% to -82%, and the common designation XR7 implies -55 C to 125 C with a change of capacitance in the range of ±15%.

Electrode Economics

The terminology used for metals brings a combination of a historical, trade and mining points of view into the lexicon. Nonferrous metals are lumped into 3 categories: precious metals, base metals and alloys. Precious metals are customarily called “noble” metals in the metal working trade [10], noble being a reference to the economic resources of nobility rather than to the noble gasses. The precious metals consist of gold, silver and the platinum metals group. The platinum metals group includes ruthenium, rhodium, palladium, osmium, iridium and platinum. These

materials are lumped together, because they are found together in ore [11].

The price of palladium began to raise in January of 1997 from a relatively stable price around \$ 125 per troy ounce to a peak of almost \$1100 per troy ounce in early 2001 (1 troy ounce = 0.0311 kg) [12]. This price was not representative of a whole scale investor community switch to from other assets to the metals market, because the price of gold, in contrast, was stable through the same period. This price increase in palladium was due to the combination of shrinking supply and rising demand.

Russia is the largest palladium supplier (52% of U.S. imports 1997 to 2000 and 51% of the world’s production in 2001 [11]), and the instabilities in Russia have been problematic. Palladium shipments were suspended in 1997 due to the abolition of the Russian Committee for Precious Metals and Stones (Roskomdragmet) in December 1996. The attractive price will make additional potential sources of palladium in Canada and Africa available over the long haul [13]. Other major sources of the world’s supply of palladium in 2001 were South Africa (33%), U.S. (7%), Canada (5%) [13]. The price of palladium has returned to the \$300 per troy ounce range.

On the demand side, the automotive industry’s use in for catalytic converters accounts for 50% of the palladium use [12]. One of the non-BME electrode alloys used in MLCCs has been an alloy of 85% silver and 15% palladium. Capacitors account for the lion’s share (75%) of the electronics industry’s demand for the element. Future demand due to the growth of fuel cells in electronics may put new demand on the palladium supply [14].

The price of palladium has forced a switch to BME in ceramic capacitors beginning in 1998. The change at AVX was 80% completed by March 2002. A full industry transition to nickel has been underway. This required investment in new kilns and modified manufacturing processes. [15]. The melting temperatures for the pure metals silver, palladium, nickel are 962 C, 1554 C and 1453 C respectively. MLCC manufacturers may also try to change the ratio of silver to palladium or substitute platinum for palladium.

Thermodynamics

The chemical thermodynamics expression of oxidation potentials during sintering is captured in the Ellingham

Diagram [16]. The literature includes a nice representation of the Ellingham Diagram for this situation. The chart compares the relative reaction potentials in terms of the common logarithm of the partial pressure of oxygen against the inverse of absolute temperature. Rather than repeat a lengthy tutorial describing the chart, the point is that metallic nickel and Ti_2O_3 are not compatible in air at the firing temperatures. Dopants must be introduced into the dielectric or the gas mixture must be modified to prevent the formation of TiO_2 . The companion presentation will provide more discussion.

Moisture Related Hypotheses

Several papers indicate that moisture has long been a known problem in capacitors. The paper by Baker and Freiman conducts an experiment on wet and dry dielectrics to determine the relative strength and characterize their crack growth [20].

The most likely set of hypotheses is that water is causing problems that were not evident with the silver-palladium electrodes but are not evident with nickel electrodes. Reasons why moisture might cause a problem could be (1) adsorption of water formation on the nickel surface causing swelling, (2) morphology of the electrode permitting diffusion and condensation causing swelling, (3) moisture stress corrosion cracking at the interface of the electrode and the dielectric [21], (4) stresses due to volumetric swelling of the dielectric due to moisture absorption (appearing to be a reduced strength), (5) chemical changes in the dielectric material properties in the presence of moisture.

To address the rationale for the first hypothesis (1), metals exposed to the atmosphere form a layer of water on the surface. This formation is called “surface hydroxylation”. Metal-oxygen bonds form which result in disassociation of the water molecule into a surface of hydroxyl (O-H) groups. Several layers build up upon this first layer into a thin coating of water. The thickness of the layer is usually referred to in equivalent monolayers of thickness for convenience. The number of monolayers formed increases with the relative humidity in the atmosphere and the number of lattice defects in the metal surface [18]. The water that forms almost immediately on metals in air provides a source for chemical reaction due to other species in the air. This water layer can grow to 40 nm [19].

The switch to nickel was not done in isolation. The continuing evolution of capacitor size and performance not doubt caused both reductions in the thickness of the nickel and the dielectric relative to the previous silver-palladium. If there are voids in the capacitor to promote wicking action, then this could be a culprit.

For convenience, hypotheheis (5) will be discounted at least temporarily. Small cracks in materials attract water by surface tension, a capillary action. The water in these cracks may contain solutes of the elements such as Strontium [21] added to the ceramic. However, one must initially suspect that this water is a result of the crack initiation rather than a causal link to the crack formation.

Investigation

The study of these hypotheses is currently underway. A number of experimental steps are required. First, this laboratory has purchased bulk off-the-shelf MLCCs. The initial focus is on the 0805 size.

For failure analysis, access to the electrode plates and bulk material is required. The capacitor industry often designs special test capacitors and coupons to avoid the need to destructively open up capacitors in failure analysis [20]. Inspection in this case will require opening capacitors, “delidding”. The section below discusses the delidding issues. Delidding hardware has been fabricated. Initial delidding has yielded good results, but modification to perfect the tool is still underway. A detailed update will be provided in the presentation.

Inspection of the bulk capacitor cracking, electrode and electrode to dielectric interfaces surfaces will be by optical microscope, scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). An initial inspection by microscope, SEM and EDS of MLCC cracks from the field already has been inspected.

Two bulk test plans are underway to provide samples for failure analysis. Equipment is being set up to subject capacitors to saturated air at room temperature with real time monitoring of capacitance. In addition, die penetrant will be used (with the inspection tools) to aid in determining the moisture diffusion path.

Analytical models will tie the observations and hypotheses together. A very crude finite element (FEA) appears below. A colleague in the Laboratory

with assumed geometry and properties has already run an FEA. This preliminary model did show extraordinary sensitivity, high stresses, to swelling. More detail on the FEA plans will appear below.

Inspection methods

In this case already having a cracked capacitor, inspection the electrode surfaces both optically and by spectroscopy is a necessary step in finding the root cause of the crack. One of the issues in failure analysis of MLCC's is their construction. The MLCC is a very small item made of a sandwich of metal and brittle ceramic. The MLCC is difficult to manipulate by hand due to its size. Many researchers have worked on methods of identifying failed capacitors in situ using a variety of noninvasive methods to aid in manufacturing including acoustic resonance [22]. Several methods of opening the capacitor are being evaluated.

Chisel

The simplest method is to promote cracking along the fracture line by simply using a pointed probe in as a chisel. Two chisel type methods are being attempted. The first is simply using a Scriber (General Tools No. 88CM) to apply force to the crack by hand. The shattered looking capacitor is shown on the following photo. The greatest difficult is the small size of the capacitor itself.

Stationary Indenter

A simple indenter device can promote the fracture without loosing the capacitor. The following photos show a simple U type assembly with cone point set screw and a retaining/positioning plate.

Ballistic shearing

A ballistic shearing process offers the potential to open a capacitor at a desired plane without causing unwanted shearing or cracking adjacent to the plane. This shearing feature is due to the fact that a supersonic impact, by definition, only disturbs the surrounding materials during penetration in the region that the strain wave reaches duration of the impact. The effect can be observed in the clean holes caused by high velocity riles in vandalized road signs, as are common in some western states.

The speed of sound in a solid is given by the square root of the bulk modulus divided by the density.

Using approximate properties for alumina of $E = 300$ GPa and $\rho = 3700$ kg/m³ [34], the solution yields a velocity of 9 km/s. It is impractical to make a device to reach these speeds, because this velocity is on the order of the velocity of a detonation wave.

Mechanical Shearing

Another device has been designed to shear the capacitor at a predetermined plane. If the tensile strength of alumina is on the order of 200 MPa, then the sheer strength is roughly 100 MPa. The cross section of an EIA 0805 capacitor offers across section 2mm by 1.25mm. Therefore a force of 250 N is required. Small screws easily provide this force.

Chemical Removal

Chemical etching for removal of the capacitor layers was rejected from consideration to avoid stripping chemical residues from the electrodes.

Fabricating test items

The ideal approach would be to get access to the fabrication facility. Defective parts could be made to test the hypotheses. Some would be mechanically easy to separate. Some would have flaws induced. However, this method requires sponsorship by a ceramic vendor. If the study proceeds to prove out a new failure theory, there is little doubt that the vendors will perform these tests themselves.

Finite Element Modeling

Commercial finite element analysis (FEA) will predict the detailed strain fields within the dielectric layers based on the geometry, material properties, loading (swelling) and boundary conditions. Assumptions derived from visual and spectroscopic observations of the failed samples will be factored into the models. A moisture diffusion model may also be included if the die penetrant testing shows this necessary. Similar analysis of MLCC's is available in the literature [23]. Material properties of BaTiO₃ are also available [24].

Conclusion

Unpowered MLCC cracking when exposed to high relative humidity has been reported. Work is underway to quantify the observations of unpowered MLCC's failing due to cracks when exposed to high humidity.

References:

1. Smyth, D., Multilayer Ceramic Capacitors with Base Metal Electronics, Proceedings of the 12th IEEE International Symposium 2000, pp. 369-373 V1.
2. Prismark, (December 2000) "Pushing the Shrinking Envelope, A Status Report on Embedded Passives in PCBs", <http://aept.ncms.org/0101%20Prismark%20embedded.pdf> (10 October 2002).
3. Chen, W., Li, L., Qi, J., Wang, Y., Gui, Z., Influence of Electroless Nickel on Multilayer Ceramic Capacitors and the Implications for Reliability in Multilayer Ceramic Capacitors, J. Am. Ceram. Soc., 81 [10] 2751-52 1998.
4. Ochi, A., Saito, S., Utsumi, K., Yonezawa, M., "Small Y5V Chip-Capacitors with Very Large Capacitance, IEEE.
5. Burn, I., Ceramic Capacitor Dielectrics, Engineered Materials Handbook, Vol. 4, Ceramics and Glasses, ASTM 1991.1.
6. Dutch, S. "Perovskite Structure" <http://www.uwgb.edu/dutchs/PETROLOGY/Perovskite%20Structure.HTML> (23 October 2002).
7. Yacoby, Y., Girshberg, Y., Theory of Ferroelectric Phase Transitions in Pure and Mixed Perovskites, Mat. Res. Soc. Symp. Proc. V. 718.
8. Chen, G., Low Firing Y5V Relaxor Multilayer Capacitors, IEEE Transactions on Components, Hybrids, and Manufacturing Technology, V. 12, N. 1, March 1989.
9. Hennings, D., Multilayer Ceramic Capacitors with Base Metal Electronics, Proceedings of the 12th IEEE International Symposium 2000, pp. 135-138 V1.
10. Harper, C., Passive Electronic Component Handbook, 2nd Ed., Mc-Graw Hill, 1997.
11. Hillard, H., Platinum-Metal Groups, U.S. Geological Society Survey, Mineral Commodity Summaries, January 2002, <http://www.usgs.gov/minerals/> (22 October 2002).
12. Zysk, E., Precious Metals and Their Uses, Metals Handbook, 9th Ed., V. 2, Properties and Selection: Nonferrous Alloys and Pure Metals, 1979.
13. Forrester, H. (9 July 1998) "Russian bank deal seen raising platinum export outlook" http://www.findarticles.com/cf_1/m3MKT/n130_v106/20976994/p1/article.jhtml?term=Russia (21 October 2002).
14. Gui, Z., Wang, Y., Li, L., Lead-Based Relaxor Ferroelectric Ceramics for High Performance Low Firing MLCs, unknown IEEE 1996.
15. Market Statistics, What's Going On with the Price of Palladium, Passive Component Industry, March/April 2000. http://www.ec-central.org/magazine/PDF/art_8_mar_apr_00.pdf (21 October 2002).
16. Gaskell, D., Metallurgical Thermodynamics, Second Edition, 1981.
17. Sakabe, Y., Reynodls, T., "Base-Metal Electrode Capacitors, American Society Ceramic Bulletin, V. 81, N. 10, October 2002.
18. Leygraf, C., Graedel, T., Atmospheric Corrosion, Wiley-Interscience, 2000
19. Leygraf to Donahoe (18 October 2002) "Re: Questions for J. Electrochem. Soc. May 1995.
20. Baker, T., Freiman, S., Fracture Behavior of Ceramics Used in Multilayer Capacitors, Mater. Res. Soc. Symp Proc, 72, 81-90, 1986.
21. Lane, M., Snobgrass, J., Dauskardt, R., Environmental Effects on Interfacial Adhesion, 2001.
22. Erdahl, D., Ume, I., "Online-offline laser ultrasonic quality inspection tool for multi-layer chip capacitors", Proceedings 52nd Electronic Components Technology Conference, 2002.
23. Wereszczak, A., K. Breder, M. K. Ferber, R. J. Bridge, L. Riester, and T. P. Kirkland, "Failure Probability Prediction of Dielectric Ceramics in Multilayer Capacitors," In press, Proceedings of the International Symposium on Multilayer Ceramic Devices, Transactions of the ACerS, 100th Annual Meeting and Exhibition of the American Ceramic Society, Cincinnati, OH, 1998.
24. Uludogan, M., Cagin, T., Goddard, A. "Ad Initio Studies on Phas Behavior of Barium Titanate" http://www.wag.caltech.edu/home-pages/tahir/PDF/BaTiO3_pap.pdf (23 October 2002).