Reliability Issues with PME and BME Ceramic Capacitors

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This work is a review of reliability issues specific for low-voltage precious metal electrode (PME) and base metal electrode (BME) multilayer ceramic capacitors (MLCC). A special attention is given to degradation and failures in capacitors with defects, in particular with cracks. Temperature and voltage reliability acceleration factors have been calculated based on approximation of distributions of degradation rates of leakage currents using a general log-linear Weibull model. Results show a substantial difference in behavior of BME and PME capacitors with defects. Mechanisms of degradation and failures in humid and dry environments and risks of overstressing capacitors during highly accelerated life testing (HALT) are discussed.

Key words: ceramic, capacitor, BME, PME, reliability, degradation, cracking.

1. INTRODUCTION

Two major reliability issues with low-voltage (rated to below 200 V) MLCC are: (i) degradation of insulation resistance (IR) associated with migration of oxygen vacancies (V_O^{++}), and (ii) failures related to cracking caused either by soldering or post-soldering stresses. The first one prevails for commercial BME capacitors, whereas the latter to PME capacitors that until recently were the only types of capacitors used for hi-reliability and in particular space applications. Insertion of BME capacitors into space systems requires a better understanding of degradation and failure mechanisms and their difference from the traditionally used PME capacitors.

2. RELIABILITY ACCELERATION FACTORS

Intrinsic degradation of IR in different types of BME capacitors had been studied using monitored HALT. Current degradation at initial stages was approximated with linear functions (see Fig.1) to determine the rate of degradation, *R*.

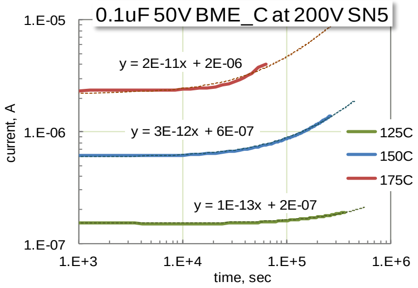


Fig.1. An example of degradation of leakage currents in BME capacitors at different temperatures.

Distributions of *R* at different voltages and temperatures were approximated with Weibull functions, and results of HALT were analyzed using a general Weibull Log-Linear model that allowed estimations of activation energy E_a and voltage acceleration constant, *n*, in the Prokopowicz-Vaskas (PV) model:

$$L = A \times \exp\left(\frac{E_a}{kT}\right) \times V^n ,$$

where *L* is the scale parameter of Weibull distributions, and A is a constant.

Results of analyses for different types of X7R capacitors rated to 50 V are shown in Table I and indicate voltage acceleration constant $n = 3.9 \pm 1.4$ for Mfr. A and 5.5 ± 0.2 for Mfr. C. These values are greater than those typically accepted for PME capacitors, $n \approx 3$. Average activation energies are 1.8±0.2 and 2.4±0.6 eV for manufacturers A and C respectively. E_a values are substantially greater than the values that are typically attributed to PME capacitors, 0.9 to 1 eV. The relatively large values can be partially explained by the fact that E_a is a sum of activation energies of leakage currents, E_{a_leak}, and migration of V_O^{++}, E_{a_migr}. Considering that E_{a_leak} is ~ 0.8 eV, E_{a_migr} is in the range from 1 to 1.6 eV, which is close to the range of activation energies reported for migration of oxygen vacancies.

Table I. Voltage acceleration constant and activation energy of degradation rate in BME capacitors rated to 50V.

Capacitor	*n*	E_a, eV
BME_A, 0.33, 1210	5.6	1.5
BME_A, 0.33, 0805	4	1.8
BME_C, 0.33, 0805	5.3	2.4
BME_A, 2.2, 1210	3.8	1.7
BME_C, 2.2, 1210	5.4	2.9
BME_C, 2.2, 1206	5.7	2.8
BME_A, 2.2, 1812	2.1	2
BME_C, 0.1, 0603	-	1.6

Based on modeling of HALT results, the probability of failures of BME capacitors at operating conditions was shown to be negligibly small in most cases. This means that the intrinsic degradation in BME capacitors does not pose a significant reliability risk and the major reason of failure is due to the presence of defects in the parts.

3. REVEALING DEFECTS IN MLCCs

Performance characteristics of low-voltage MLCCs (capacitance, dissipation factor, and IR) have insufficient sensitivity to the presence of local defects to reveal defective capacitors [1, 2]. However, similar defects affect breakdown voltages (VBR) of the parts. In low-voltage BME capacitors VBR is typically dozens or hundreds times greater that the rated voltage (VR). This allows revealing and screening of structural defects that result in thinning of the dielectric by the low-voltage tails in distributions of VBR (see Fig.2). However, revealing capacitors with cracks is a more difficult task because cracking does not necessarily reduces IR or VBR [3]. Considering that in low-voltage MLCCs VR ≪ VBR, dielectric withstanding voltage (DWV) testing that is carried out for PME capacitors at 2.5xVR, is not effective for BME capacitors.

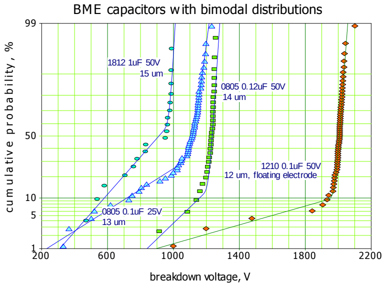


Fig.2. Examples of VBR distributions for BME capacitors showing low-voltage tails.

4. FAILURES IN CAPACITORS WITH DEFECTS

Defects that result in thinning of the dielectric enhance local migration of V_O^{++} due to increased electric field. As a result, degradation of leakage currents might increase substantially and cause infant mortality (IM) failures. Simulations [4] show that the same degradation processes that cause wear-out failures in capacitors without defects, can result in IM failures of the parts if defects are present. In this case, reliability acceleration factors determined for wear-out degradation can be also used to predict IM failures.

Modeling thermal runaway processes in capacitors with defects [4] shows that in the range of typical HALT conditions (temperatures from 125 to 200 ºC and voltages up to 10×VR), voltage increases the probability of catastrophic failures to a greater degree compared to temperature. However, the risk of overstressing during HALT by increasing test voltages is greater than by increasing temperature. Small size defects that would never cause failures at normal operating conditions can result in short circuit failures during testing at increased voltages, thus resulting in wrong acceleration factors and false reliability predictions.

BME capacitors with defects are more likely to fail parametrically, whereas catastrophic failures are more likely for PME capacitors that have much lower leakage currents and the probability of thermal breakdown. Failures in PME capacitors are likely due to the time dependent dielectric breakdown (TDDB) caused by generation of electron traps or thermochemical processes in the dielectric. Instant release of energy in the defective area during breakdown results in adiabatic overheating and local melting causing short circuit failures. Contrary to PME, degradation in BME capacitors occurs gradually and energy generated at the defect can be balanced by the heat dissipation thus preventing catastrophic failures.

5. MECHANICAL STRENGTH OF MLCCs

Cracking of MLCCs remains a serious problem for space systems. This problem increases substantially for large size capacitors and in cases when manual soldering is involved or the system experiences mechanical shock or vibration [5]. In any case, a fracture occurs when a sum of external and internal mechanical stresses exceeds the strength of the part. To reduce the probability of cracking, the level of stress should be reduced, e.g. by optimizing the assembly workmanship and rules for board design, and the strength of the parts increased by selecting the most mechanically robust capacitors. The latter might be achieved by selecting MLCCs based on the in-situ measurements of mechanical characteristics.

Modulus of rupture (MOR) was measured in-situ for different lots of capacitors using a flexural strength method per AEC-Q200-003 that determines tensile strength at the surface of the parts [6]. Results show that MOR values depend on the size of capacitors, and case size 1206, on average, have tensile strength that is approximately twice the value for 2225 capacitors. This means, that only the same size capacitors can be used for comparative analysis of the lots. Mechanical strength is a lot-related characteristic of MLCCs and variations of MOR from lot to lot might exceed 50%. Lots with higher strength are less susceptible to cracking.

Comparison of MOR values for BME and PME capacitors (Fig.3) showed no substantial difference. There is a trend of decreasing strength with increasing size of the parts for both PME and BME capacitors. This might be one of the reasons for the smaller case size capacitors being less prone to assembly related cracking. Considering that the same value BME capacitors have a smaller size than the corresponding PME, replacement of PME with BME capacitors might be beneficial to reduce cracking.

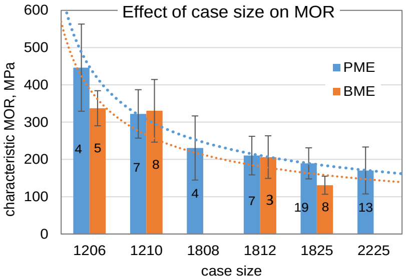


Fig.3. Characteristic values of Weibull distributions of MOR for different lots. Error bars correspond to standard deviations and the numbers to the quantity of tested lots.

6. CAPACITORS WITH CRACKS IN HUMID ENVIRONMENTS

Historically, moisture resistance of PME capacitors was evaluated using a humidity steady state low voltage (HSSLV) testing, when parts are stressed at 85 ºC, 85%RH and voltage of 1.3 V. Experiments showed that this testing can detect failures in PME capacitors with cracks, but it is not effective for BME capacitors, for which a temperature-humidity-bias (THB) testing, where parts are stressed at the same temperature and humidity as HSSLV test, but at a rated voltage, is more effective.

Extensive testing of PME and BME capacitors with introduced cracks (using Vickers indenter, fracturing, or cross-sectioning) in humid environments [7] showed that the probability of failures for PME capacitors with cracks is greater than for BME capacitors. All 57 tested PME MLCCs with cracks failed humidity testing whereas only 16% (out of 93 samples) failures were observed for similar value BME MLCCs with cracks. Failed BME capacitors had much greater IR than PME capacitors. The difference in resistance to humidity testing is due to the specifics of electro-chemical behavior of Ni and Ag/Pd electrodes and properties of formed products (conductive Ag-based deposits for PME and isolative Ni/C/O compositions for BME capacitors). Fig.4 shows examples of deposits on the surface of fractured BME and PME capacitors.

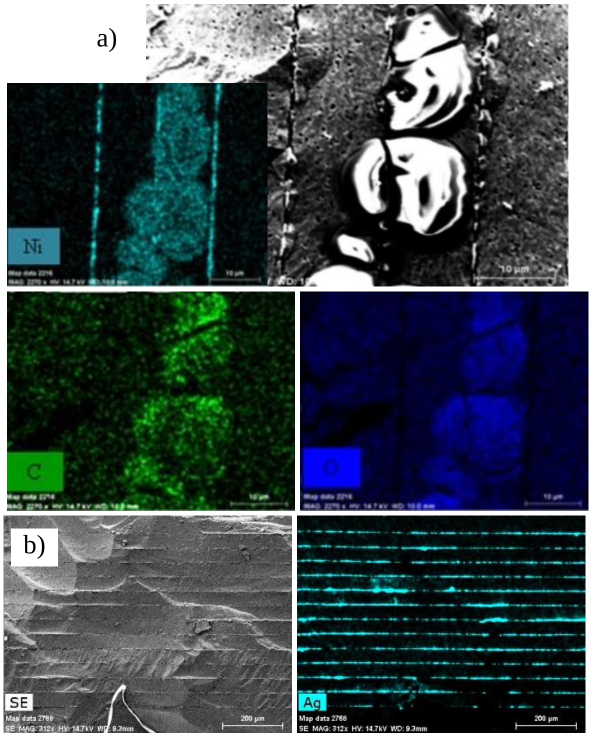


Fig. 4. SEM images and EDS mapping of fractured capacitors. a) BME, case size 1825, 1 µF, 50 V, capacitor, after testing at 22 °C, 85% RH, and 15 V for 300 hours. b) PME, case size 1825, 0.1 µF, 100 V capacitor, after testing at 22 °C, 85% RH, and 5 V.

High leakage currents in failed PME capacitors were due to formation of deposits caused by electro-chemical migration (ECM) of Ag. Silver oxide deposits are conductive (resistivity of Ag2O/Ag2O3 varies from 10^{-5} to 10^{-3} Ω-cm) and even a thin, 10 nm thick, Ag-oxide film in a 100 µm wide crack with a 10 µm spacing would have resistance from 1 to 100 Ω. For this reason, drying of the failed PME MLCC might not cause any substantial increase of IR.

Some degradation of IR in BME capacitors is due to formation of amorphous deposits at the anode electrodes as a result of Ni ions interaction with water and CO_2 that forms complex anions moving back to the anode. Drying of these deposits can increase IR substantially.

Pure stoichiometric NiO crystals are perfect insulators (~10^{13} Ω-cm), and doped/non-stoichiometric oxides still have high resistivity (10 to 10^{6} Ω-cm). For this reason, composites that are formed on BME capacitors do not degrade IR substantially and do not cause failures.

Testing of cross-sectioned MLCCs having a thin 2 - 4 µm layers of water (water layer testing technique [8]) showed that metals most susceptible to ECM and dendrite growth are Pb > Sn ≈ Ag for PME, and Pb > Sn ≥ Cu, for BME capacitors. Pb, Sn, Ag and Cu ions are generated by anodic dissolution of the frit, termination finish, and solder. Although the products of Ni migration have high resistivity, anodic dissolution of Sn, Pb or Cu from terminations might provide materials to form conductive deposits or dendrites in cracks located close to terminations (see Fig.5).

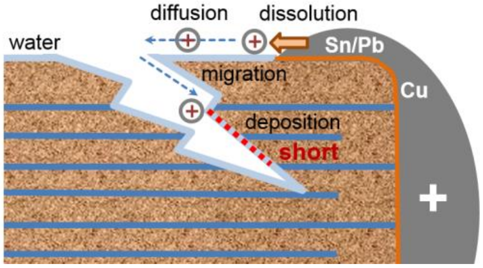


Fig.5. Schematic of failures in BME capacitors with cracks caused by ECM of termination metallization.

7. CAPACITORS WITH CRACKS IN DRY ENVIRONMENTS

Results of monitored HALT using different types of BME capacitors with cracks showed that currents start increasing after a certain induction period of time, gradually rise up to two-three orders of magnitude to a maximum, and then are stabilizing and even decreasing with time of testing [4]. Contrary to that, no degradation in PME capacitors was observed until the point at which currents sharply increase indicating a short circuit failure. Also, failures of PME capacitors with cracks occurs at much higher levels of stress compared to BME capacitors. Typical results of HALT in MLCCs with cracks are shown in Fig.6.

Capacitors with greater intrinsic degradation are more susceptible to degradation in the presence of cracks. These parts have also a more significant reduction of breakdown voltages after HALT.

Contrary to humid environments, leakage currents in BME capacitors with cracks in dry conditions can degrade more noticeably compared to PME capacitors, but unlike PME capacitors, this degradation does not typically cause catastrophic failures. This behavior can be explained assuming accelerated transport of oxygen vacancies along the cracks.

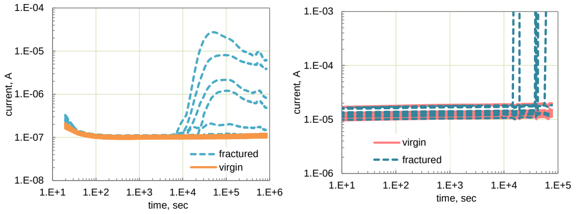


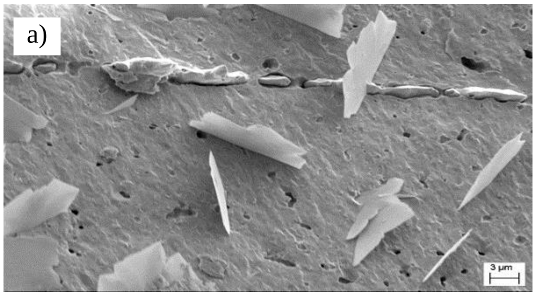
Fig. 6. Typical variations of currents with time in virgin and fractured capacitors during HALT. a) BME 0.33 μF 50 V, case size 0805 at 125 ºC, 100 V. b) PME 1 μF 50 V, case size 2225 at 165 ºC, 200 V.

8. STRUCTURAL ANOMALIES IN MLCCs

Two types of anomalous structures were observed during SEM examinations of fractured capacitors after exposure to humid environments: thin platelets on the surface of PME and filaments on the surface of BME capacitors (see Fig.7).

Energy dispersive spectroscopy (EDS) revealed the presence of lead, carbon, and oxygen in the composition of the platelets suggesting formation of hydrocerussite-like, Pb3(OH)2(CO3)2, structures. Only carbon was detected in the composition of the filaments that had curl morphology with a diameter ~1 μm, and length up to dozens of micrometers. The source of carbon is likely remnants of the binder burning process, and formation of the filaments is catalyzed by metal (Ni) that is used for electrodes. The thickness of the platelets was ~ 0.1 μm and the size ~ 10 μm. Both types of structures appeared to grow from the pores in the ceramic and are likely related to high mechanical stresses in the material.

The fractured surface of MLCCs is chemically active and in humid environments can facilitate formations of lead carbohydrates, or carbon filaments. The processes of growth, physical nature, origin, and significance for reliability of these anomalies require additional analysis.



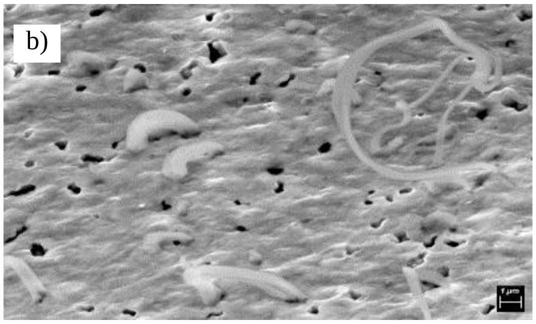


Fig. 7. Anomalous structures on the surface of fractured capacitors observed after humidity testing.
a) hydrocerussite-like platelets, Pb3(OH)2(CO3)2, on the surface of 0.1 μF 100 V PME MLCCs. b) carbon filaments on the surface of BME MLCCs.

9. ACKNOWLEDGMENT

This work was sponsored by the NASA Electronic Parts and Packaging (NEPP) program. The author is thankful to Michael Sampson, NEPP Program Manager, for support of this investigation, Bruce Meinhold, ASRC Federal Space and Defense, Group Lead, for a review and discussions.

10. REFERENCES

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