



NASA Electronic Parts and Packaging (NEPP) Program

Humidity Testing of PME and BME Ceramic Capacitors with Cracks

Alexander Teverovsky*, Jaemi Herzberger**

*AS&D Inc.

**NASA Space Technology Research Fellowship Student,
University of Maryland

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Alexander.A.Teverovsky@nasa.gov

Base-Metal-Electrode (BME)
Precious Metal Electrode (PME)

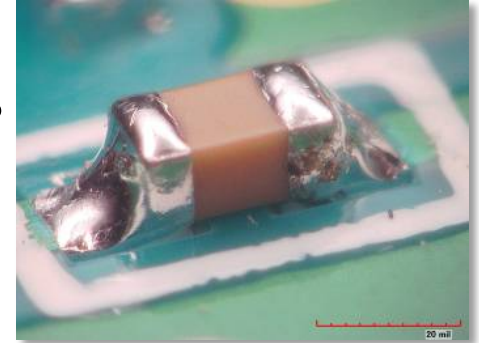
List of Acronyms

DCL	direct current leakage
DG	dendrite growth
ECM	electro-chemical migration
EIA	Electronic Industries Alliance
FA	Failure analysis
HSSLV	humidity steady state low voltage
IR	insulation resistance
MLCC	multilayer ceramic capacitor
PME	precious metal electrode
PWB	printed wiring board
RH	relative humidity
THB	temperature, humidity, bias

Purpose and Outline

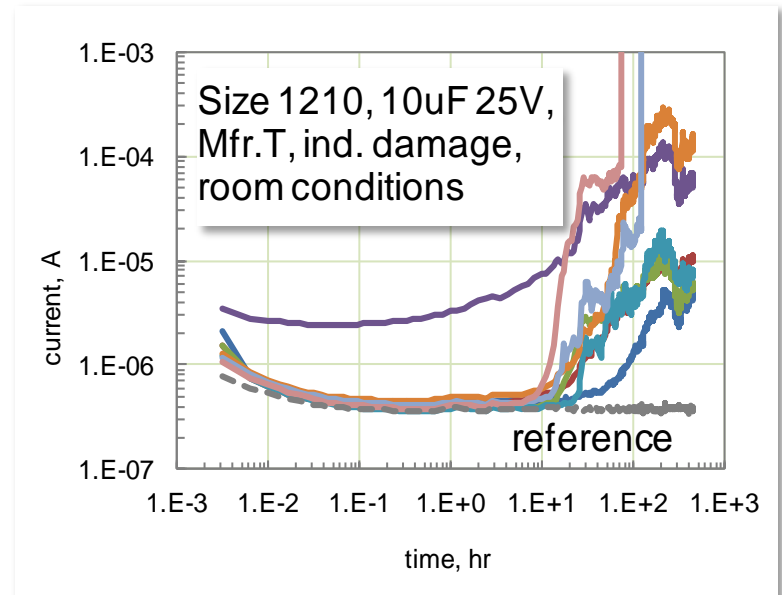
Purpose:

- ✓ Compare behavior of BME and PME MLCCs in humid environments.
- ✓ Evaluate the effectiveness of HSSLV testing for BME capacitors.

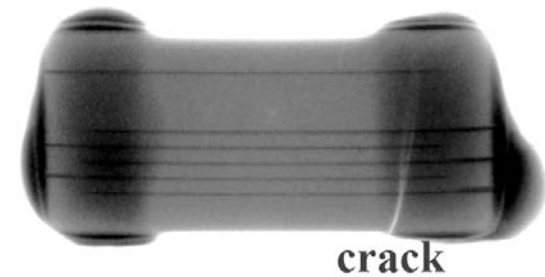


Outline:

- ❑ Introduction.
- ❑ Experiment.
- ❑ Degradation of DLC and failures during HSSLV testing.
- ❑ Factors affecting results of humidity testing.
- ❑ Results of FA.
- ❑ Discussion and Conclusion.

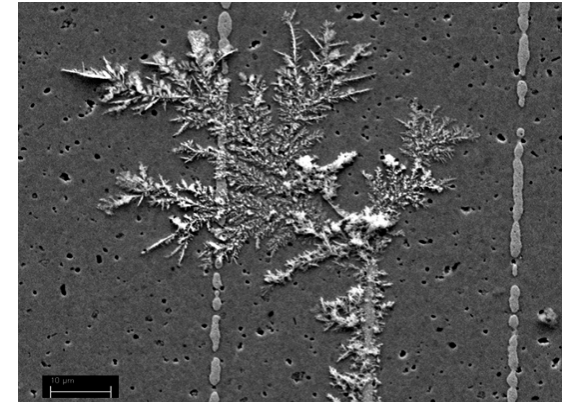


Introduction



- ❑ Most field failures of MLCCs are due to cracks.
- ❑ Moisture/ionic contaminants in cracks short electrodes directly or as a result of ECM and dendrite growth (DG).
- ❑ Ag is highly susceptible to DG
 - can be observed at 40% RH and 0.4V;
 - alloying with Pd reduces the probability of DG, but it still might happen due to Ag diffusion along the grain boundaries.

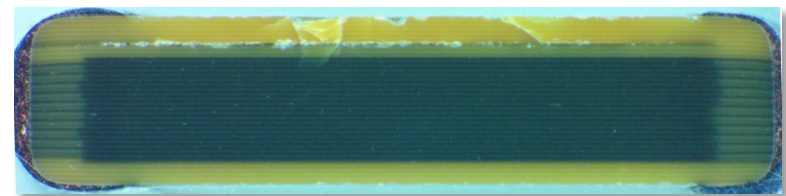
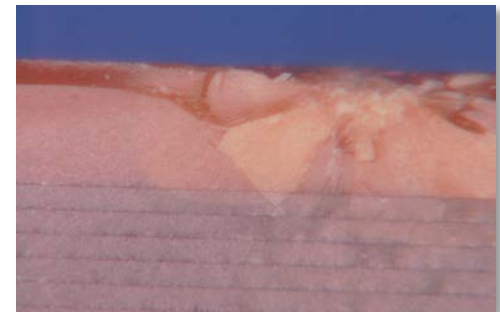
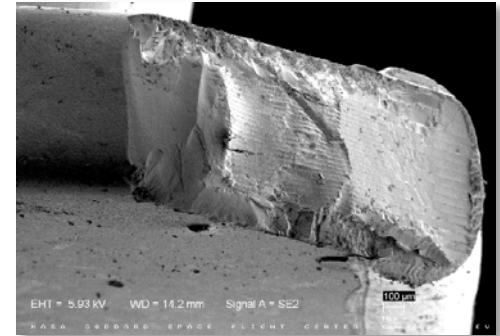
=> high risk of failures for PME capacitors.



- ❑ HSSLV testing has been proven effective in revealing structural defects/cracks in PME MLCCs.
HSSLV conditions: 85 °C, 85% RH, at 1.3 V \pm 0.25 V, applied through 100 k Ω resistors, for 240 hours.
- ❑ Is HSSLV testing effective for BME MLCCs?

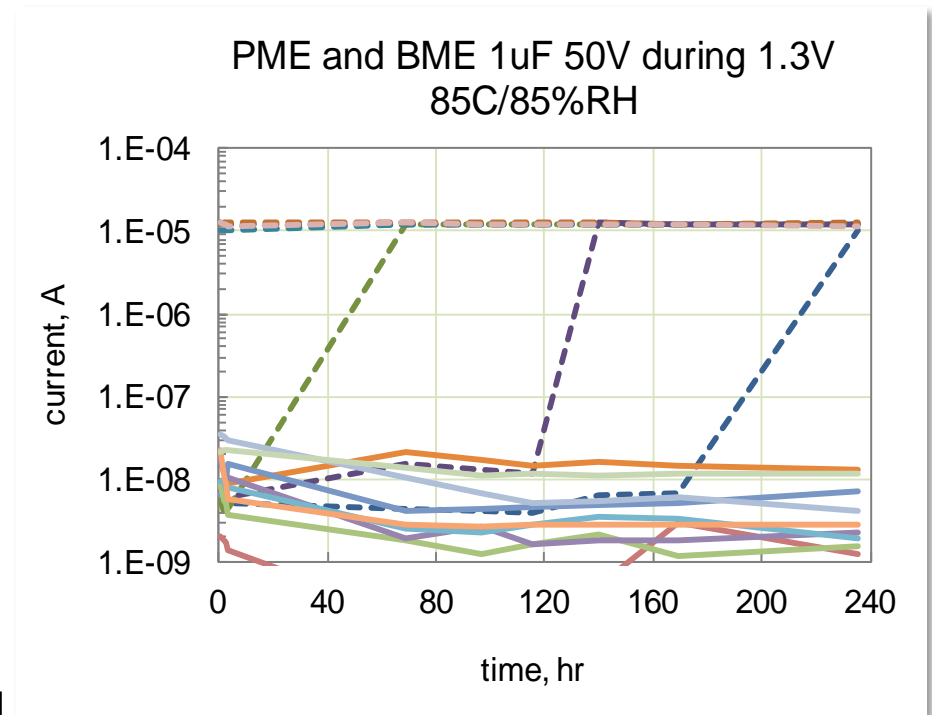
Experiment

- ❑ Large-size PME and BME capacitors (1210, 1825, 2220) with similar characteristics.
- ❑ Cutting, cleaving and indenting was used to simulated processes in capacitors with cracks.
- ❑ Damaged parts had initial characteristics within the specified limits.
- ❑ THB testing at different voltages and temperatures:
 - Humidity chamber (85°C/85% RH)
 - Dessicator (22°C/85% RH)
- ❑ Failure criterion: $DCL > 1 \mu A$.



HSSLV Testing of PME and BME MLCCs with Cracks. EIA size 2220 1 μ F 50V.

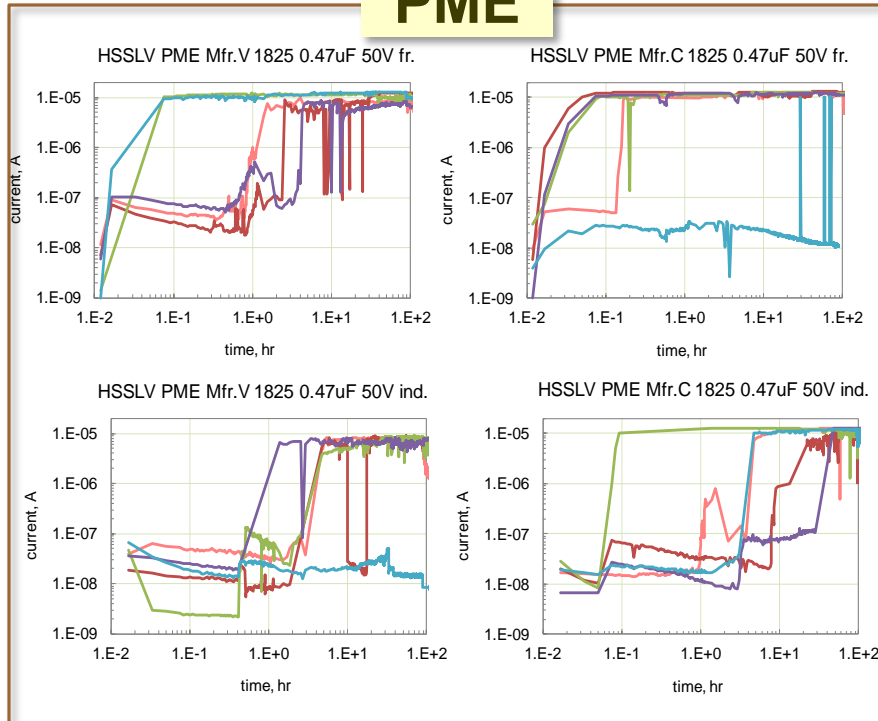
- ❑ Capacitors were damaged by Vickers indenter.
- ❑ PME:
all parts failed the testing eventually (dashed lines).
- ❑ BME:
none of 9 tested BME capacitors failed, and no degradation of the leakage currents was observed (solid lines).



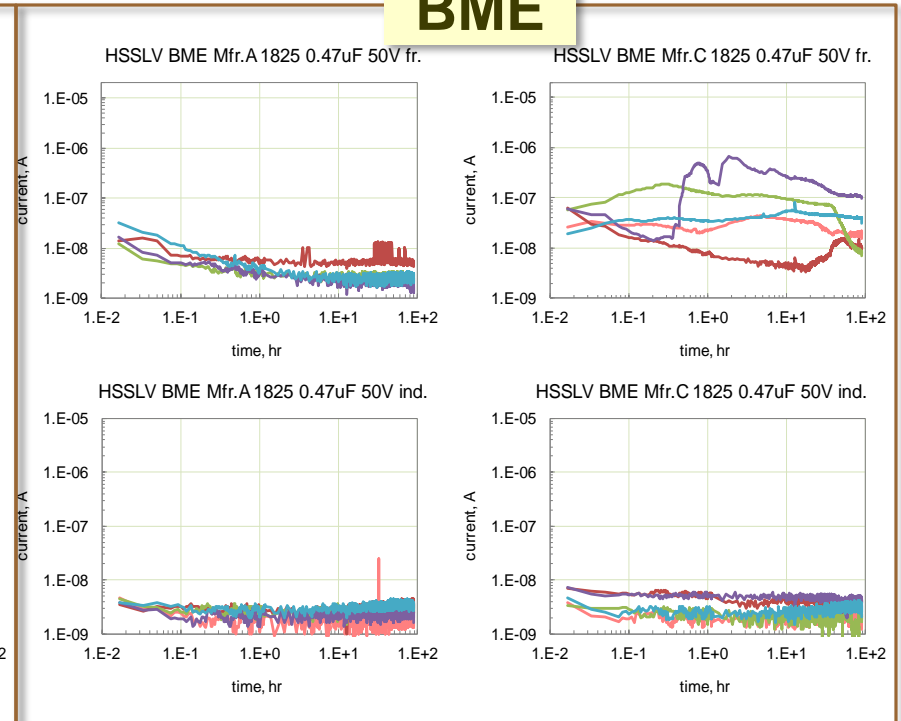
HSSLV Testing of PME and BME Capacitors. EIA size 1825 0.47 μ F 50V.

- ✓ 2 types of PME and 2 types of BME from different manufacturers.
- ✓ 10 samples in each group, 5 indented and 5 fractured.

PME



BME



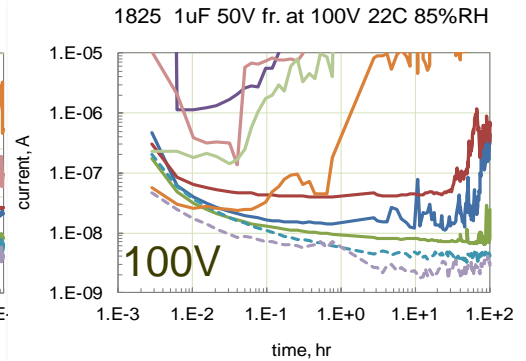
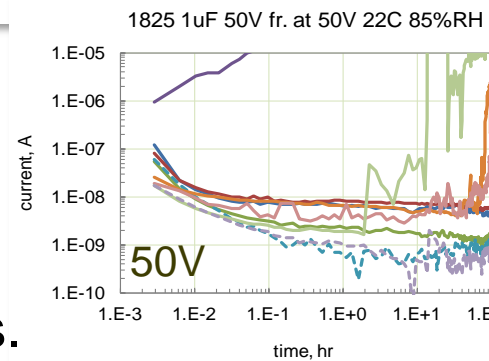
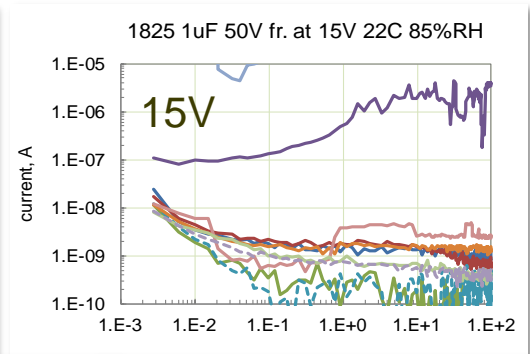
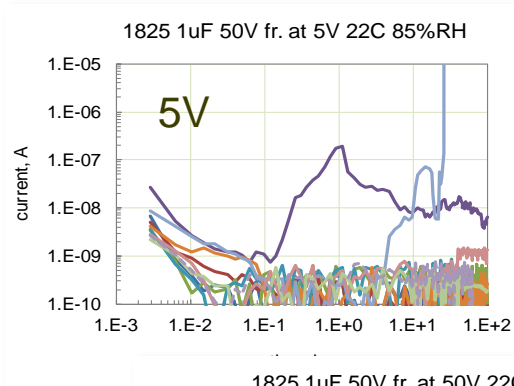
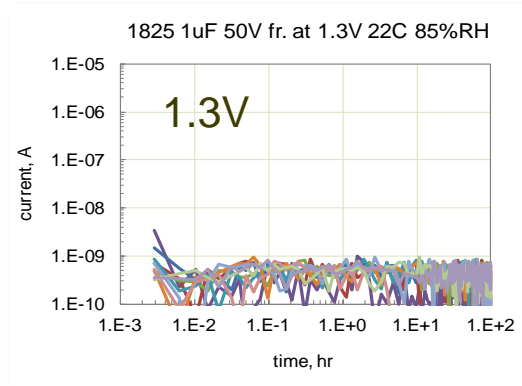
- ❑ PME: All failed during 100-hour testing.
- ❑ BME: No failures; some degradation for fractured BME_C capacitors.
- ❑ Intermittent failures at 1.3V in large-value PME capacitors.

Failures during HSSLV Testing

#	Part	Mfr	Electrode	damage	F/QTY
1	2220, 1 μ F, 50V	A	PME	indenter	5/5
				fracture	4/4
2	1825, 1 μ F, 50V	A	BME	indenter	0/14
				fracture	4/15
3	1825, 1 μ F, 50V	C	BME	indenter	0/4
4	1825, 0.1 μ F, 100V	P	PME	indenter	5/5
				fracture	4/4
5	1825, 0.47 μ F, 50V	C	PME	indenter	14/14
				fracture	5/5
6	1825, 0.1 μ F, 100V	C	PME	fracture	5/5
7	1206, 10 μ F, 16V	M	BME	Indenter	1/6
8	1206, 22 μ F, 6.3V	M	BME	Indenter	1/7
9	1206, 4.7 μ F, 25V	C	BME	indenter	1/6
10	1210, 10 μ F, 25V	M	BME	indenter	0/9
11	1825, 0.47 μ F, 50V	V	PME	Indenter	14/14
				fracture	5/5
12	1825, 0.47 μ F, 50V	C	BME	Indenter	5/14
				fracture	0/5
13	1825, 0.47 μ F, 50V	A	BME	indenter	3/14
				fracture	0/5

- ❑ All PME MLCCs with cracks, failed the testing.
- ❑ Only 16% out of 93 BME MLCCs with cracks failed.
- ❑ Majority of BME failures occurred in fractured capacitors, parts that were manually soldered to the PWB, or with substantial damage (chip-outs) caused by indenter.
- ❑ IR in failed BME capacitors was ~4 orders of magnitude greater than in PME capacitors.

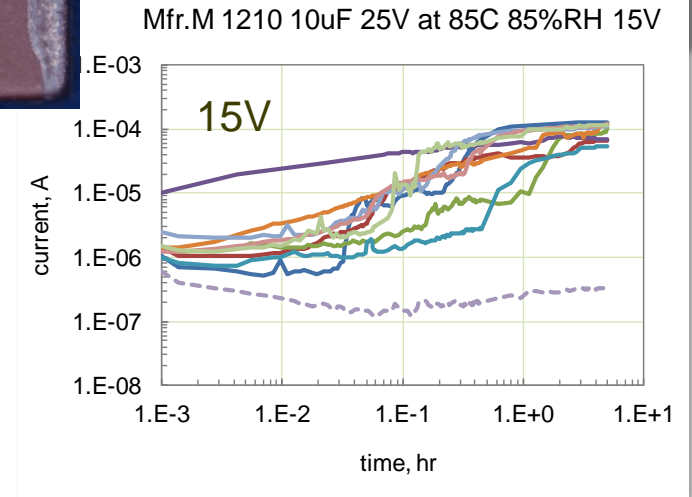
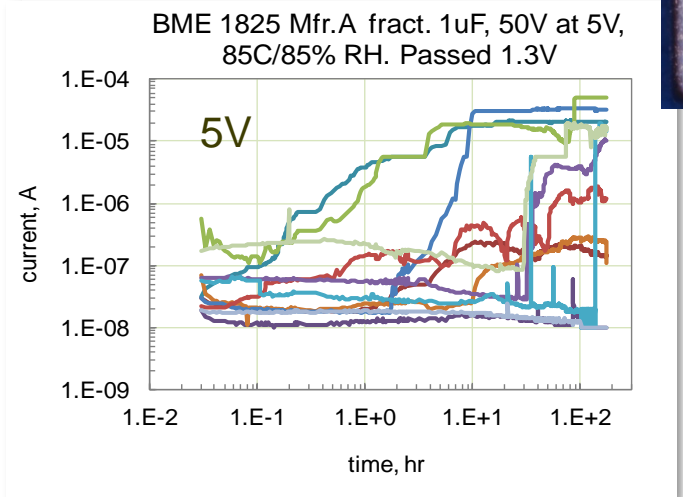
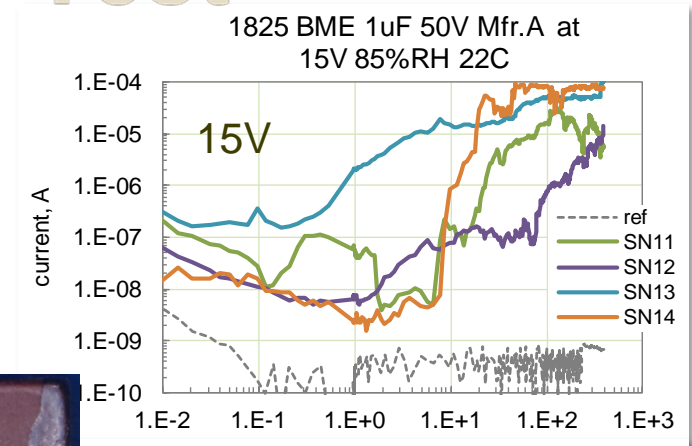
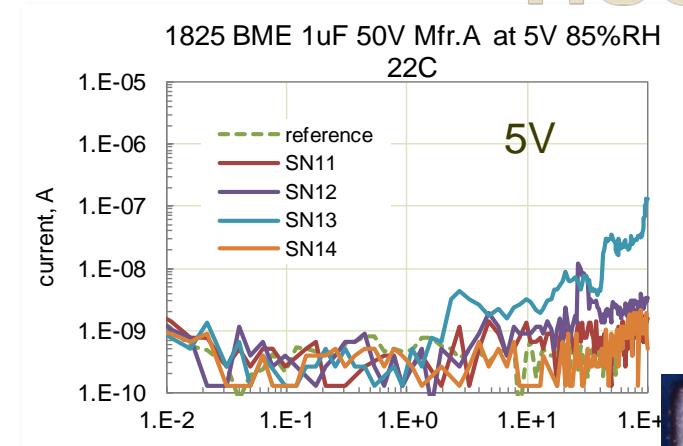
Effect of Voltage on Humidity Testing



- ✓ Step-stress testing: 100hr steps at 22°C/85% RH.
- ✓ Fractured BME MLCC 1 μ F, 50V, Mfr.A and Mfr.C.
- ✓ Reference parts –dashed lines.

- ❑ No failures at 1.3V, the number of failures increases with voltage.
- ❑ All Mfr.C capacitors had catastrophic failures after 100 hrs at 100V, whereas half of Mfr. A capacitors did not fail.
- ❑ At $V \geq 50V$ degradation in BME_A increases with time of testing.
- ❑ BME_A capacitors had ~twice the dielectric thickness of BME_C.

THB Testing of Capacitors that Passed HSSLV Test

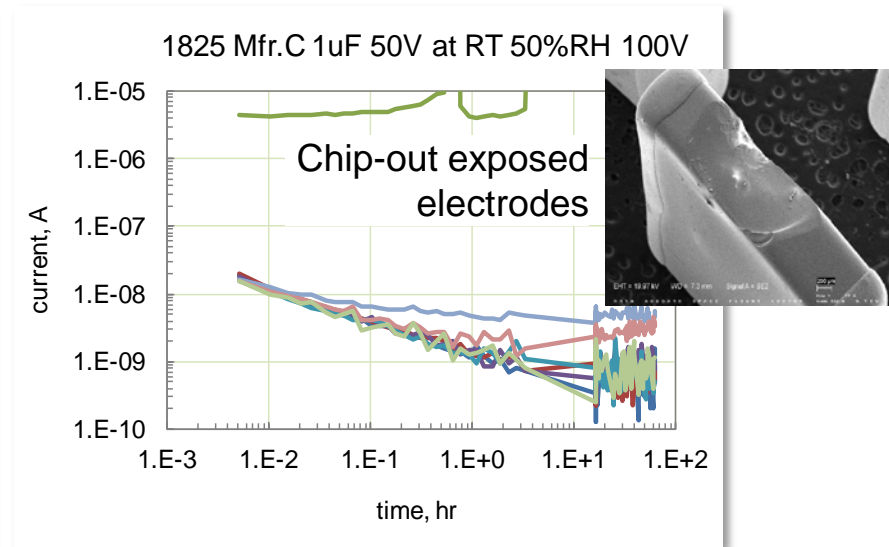
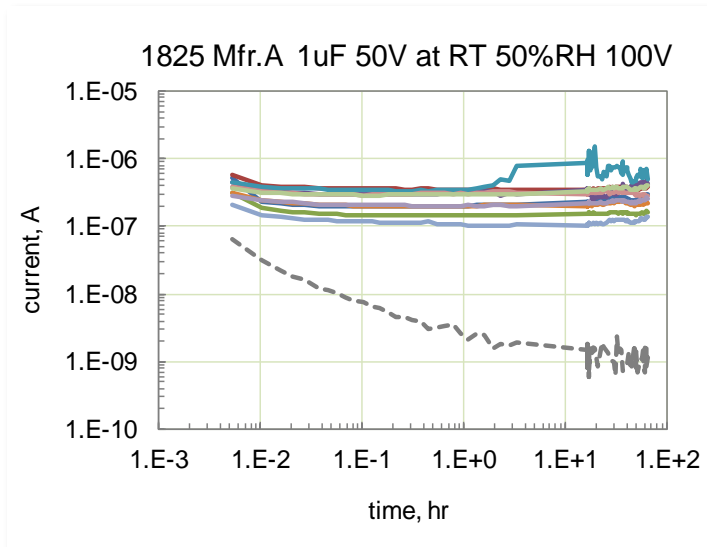


❑ The presence of cracks can be revealed by THB testing at $V \gg 1.3V$.

Effect of Cover Plate

- ✓ Two types of 1825, 1uF, 50V capacitors with similar damages caused by indenter passed HSSLV testing.
- ✓ DCL at 100V was monitored after the testing.

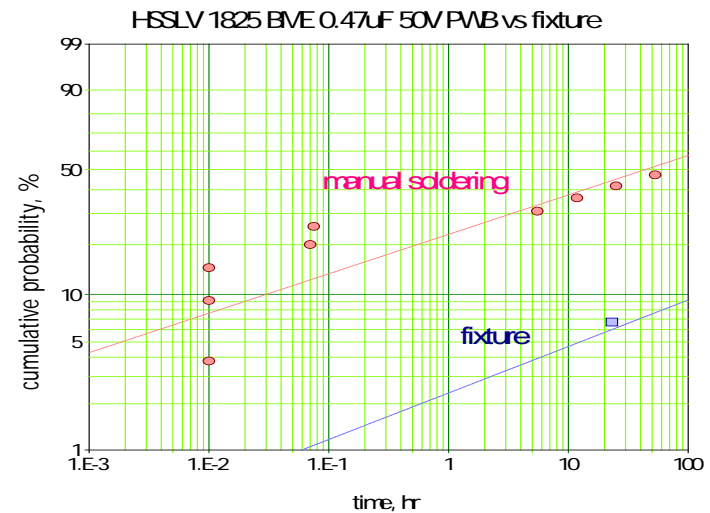
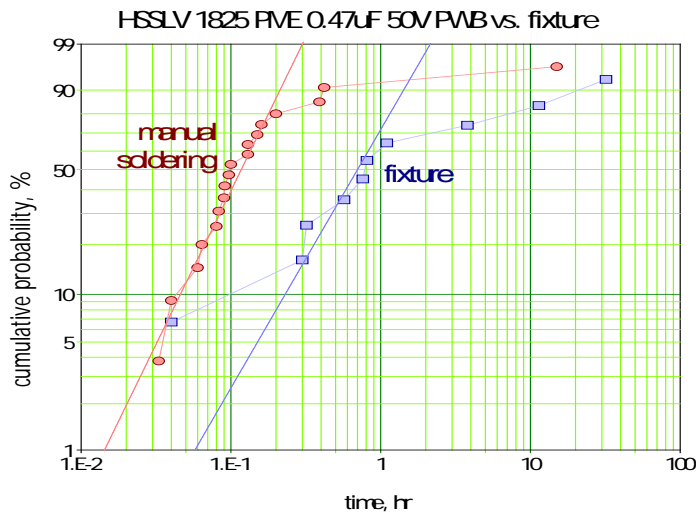
	H, mm	t, um	CP, um	EM, um
BME_C	1.05	12.5	340	290
BME_A	1.32	22.5	110	210



❑ Capacitors with larger cover plates are less likely to fail when cracks are formed at the surface.

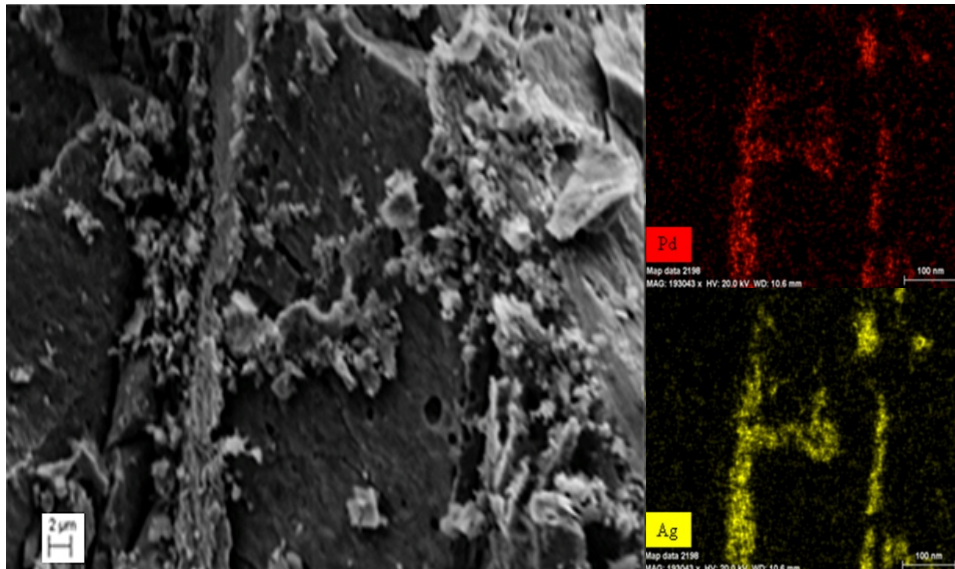
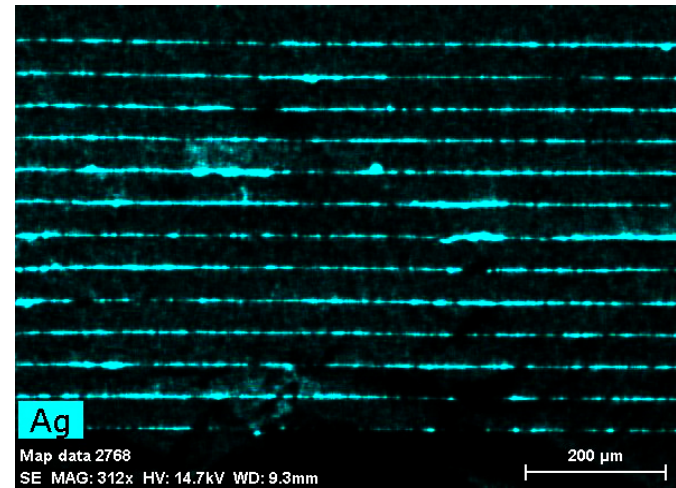
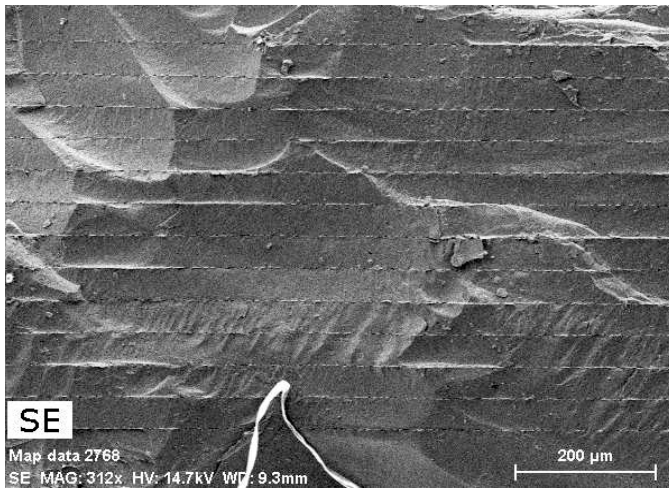
Effect of Manual Soldering

- ✓ Two groups of PME and BME 1825, 0.47 μ F, 50V capacitors with similar cracks introduced by indentation were tested in fixtures and after soldering onto a polyimide PWB.
- ✓ No preheating; a soldering iron was set to 320 °C.



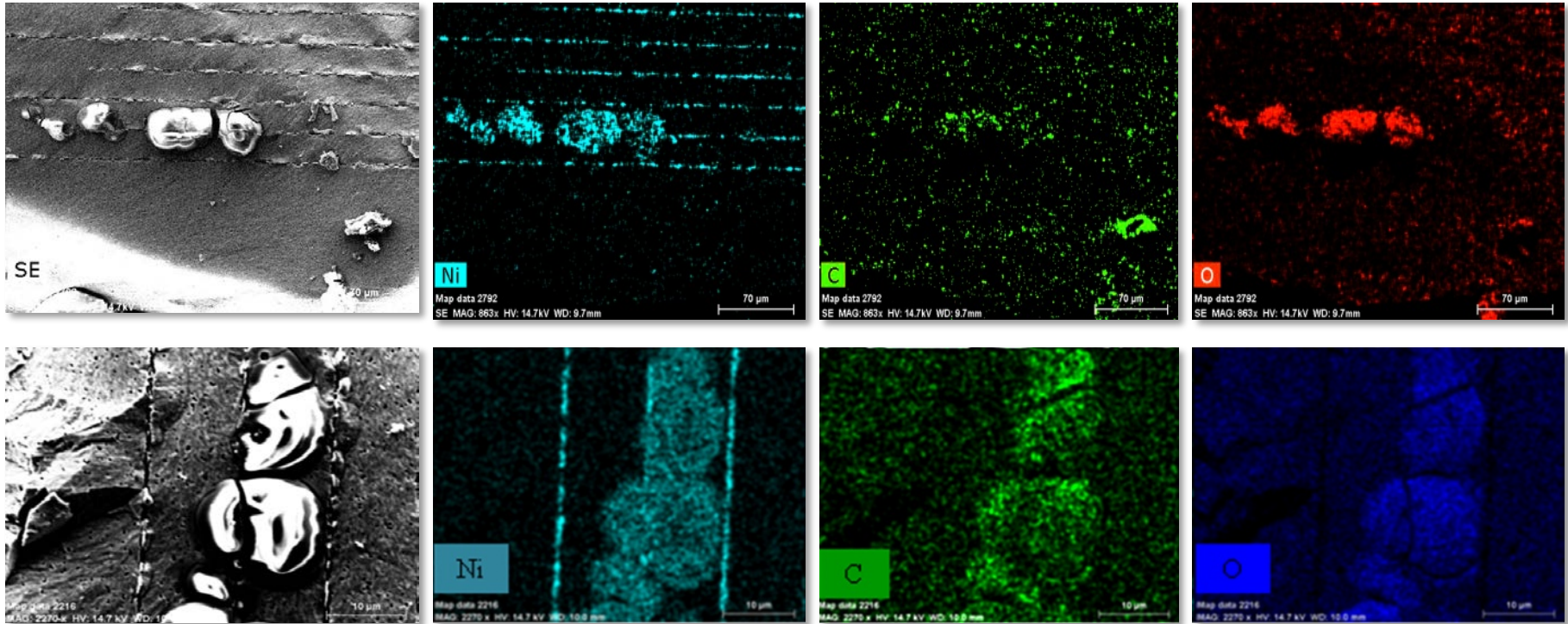
- ❑ All PME caps failed; however, soldered parts failed much earlier.
- ❑ Half soldered BME caps failed, whereas only 1 of 10 samples failed in the group that was mounted in the fixture.
- ❑ Manual soldering have a detrimental effect on MLCCs with defects.

Failure Analysis of PME Capacitors



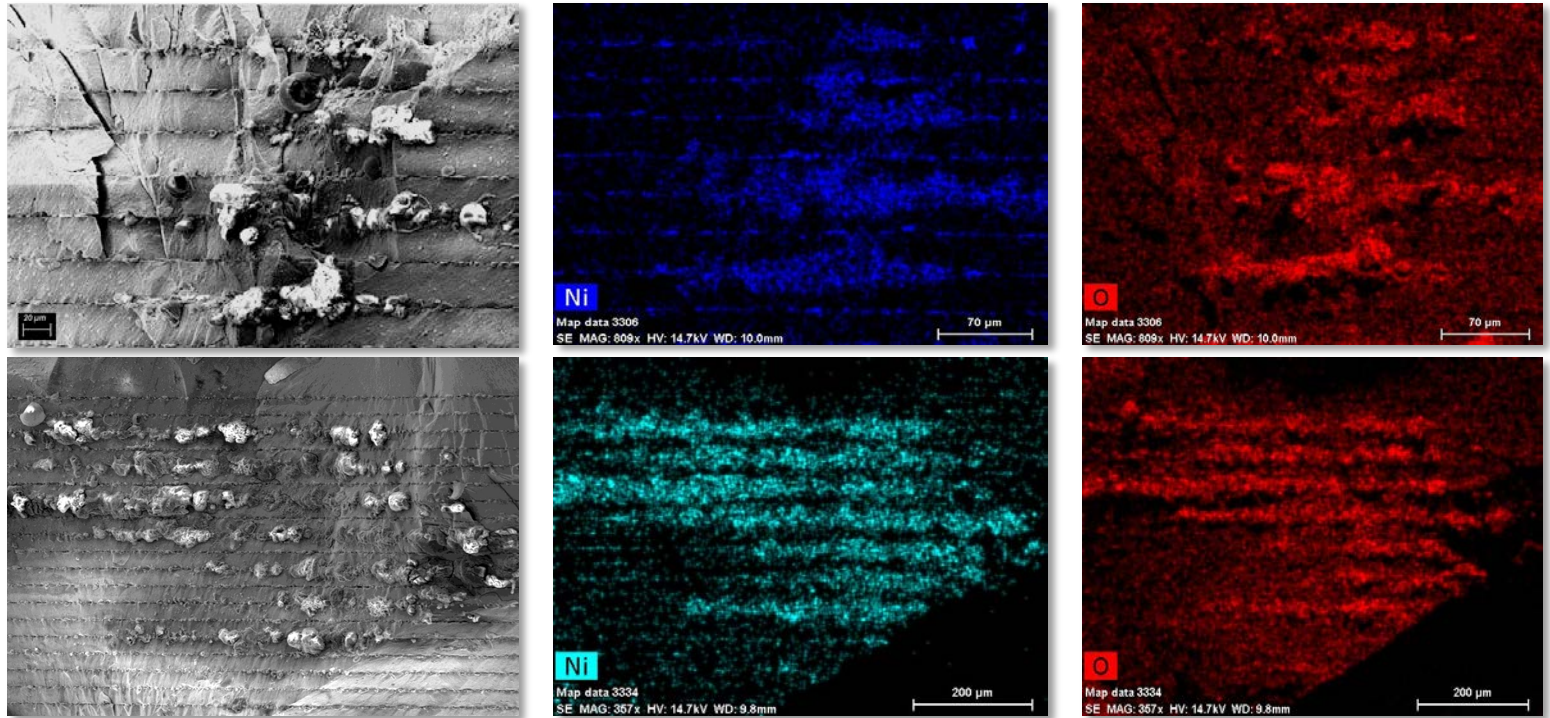
- ❑ Silver deposits were detected on the surface between electrodes.
- ❑ Ag or Pd dendrites were not found, but their formation is possible.

Failure Analysis of BME Capacitors



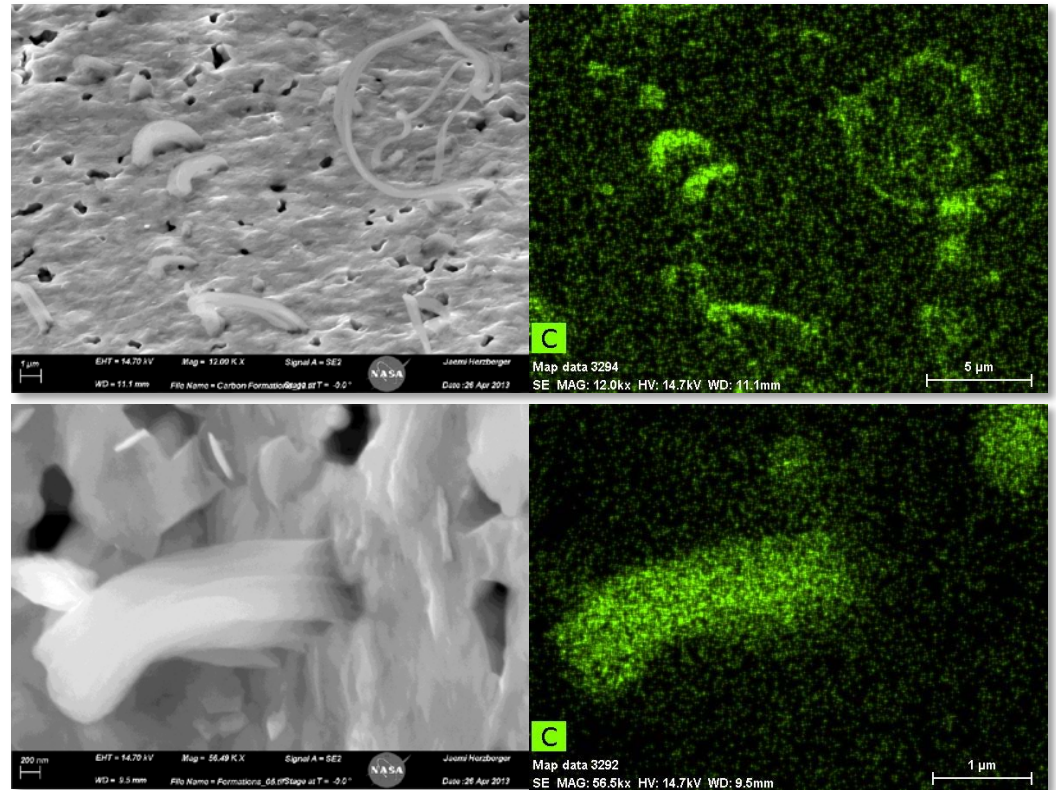
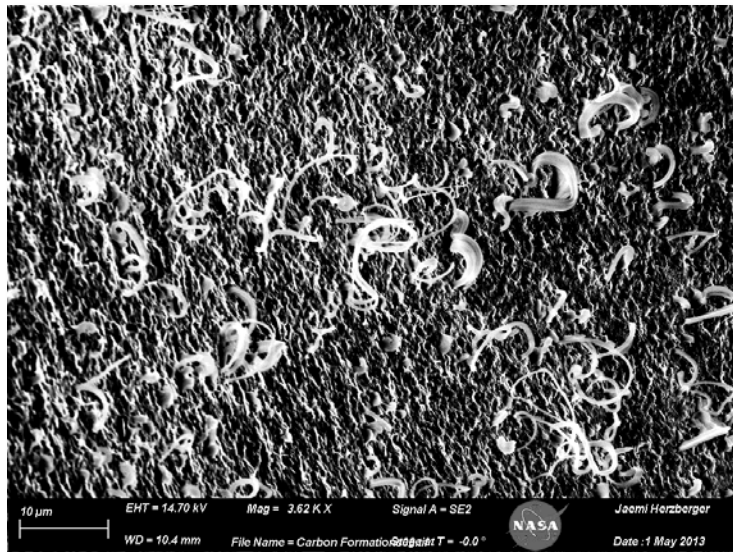
- ❑ Bulbous, amorphous formations contained Ni, C, O.
- ❑ Formed composites had poor electrical conductivity.
- ❑ The composites formed mostly at the anode electrodes.

FA of BME Capacitors, Cont'd



- ❑ Extensive areas on the surface covered by Ni/O formations, spanned many anode and cathode electrodes.
- ❑ In dry condition IR > 30 MΩ (formations are not conductive).
- ❑ Formations are similar on parts from different manufacturers.

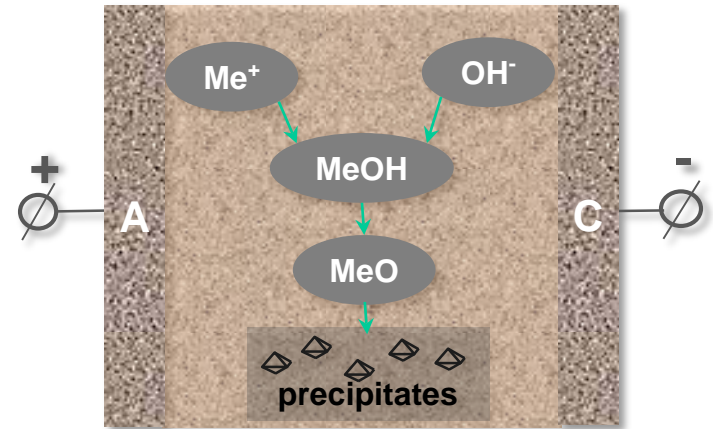
Carbon Filaments



- ❑ Carbon filaments detected in numerous locations on the fractured surface of BME MLCCs from several manufacturers after humidity testing.
- ❑ Curl morphology, diameter $\sim 1 \mu\text{m}$, length up to dozens of micrometers.
- ❑ Filaments likely grew from the micro-voids in the ceramic.

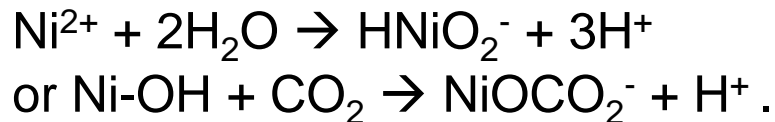
Discussion - Failures in PME MLCCs

- ❑ All PME capacitors with cracks failed HSSLV testing.
- ❑ Failures were due to formation of deposits caused by ECM of Ag.
- ❑ Silver oxides are conductive (resistivity of $\text{Ag}_2\text{O}/\text{Ag}_2\text{O}_3$ varies from 10^{-5} to $10^{-3} \Omega\text{-cm}$).
- ❑ In a $100 \mu\text{m}$ wide crack with a $10 \mu\text{m}$ spacing, even a thin, 10 nm thick, Ag-oxide film would have resistance from 1Ω to 100Ω .
- ❑ Even tiny areas of Ag-oxide can cause substantial IR degradation and failures.
- ❑ Drying did not cause a substantial reduction of IR in failed PME MLCCs.

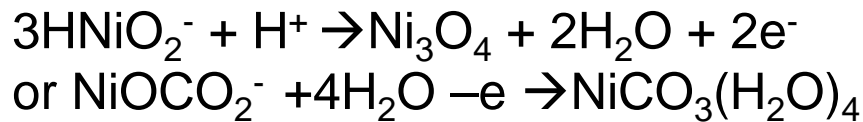


Discussion - Failures in BME MLCCs

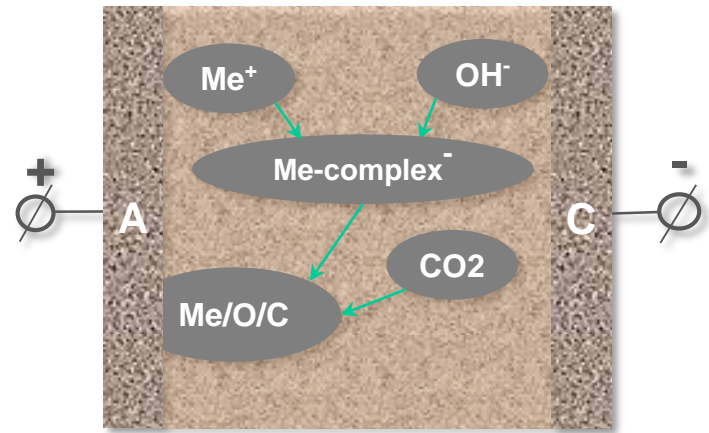
- Formation of amorphous deposits at the anode electrodes:
Ni ions interact with water/CO₂ forming complex anions that move back to the anode.



- At the anode nickel carbonates and oxides are formed:



- Pure stoichiometric NiO crystals are perfect insulators (~10¹³ Ω-cm); doped/non-stoichiometric oxides still have high resistivity (10 to 10⁶ Ω-cm).
- Formation of highly resistive composites does not degrade substantially IR and does not cause failures.



Failures in BME MLCCs

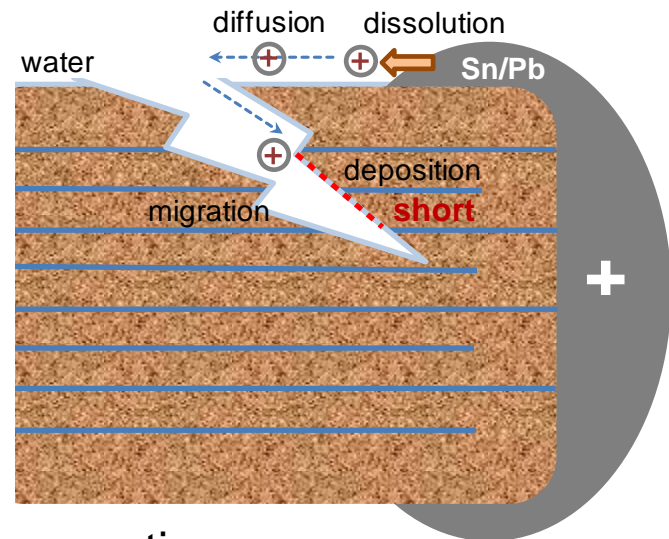
- ❑ Effect of voltage.
 - ECM at higher voltages happens faster and likely results in formation of deposits with a lower resistivity.
 - Extensive growth of Ni/O/C compositions results in further crack propagation.
- ❑ Short circuit failures (IR in kΩ range), occurred mostly in fractured capacitors.
 - Generation of ions by the anodic dissolution of metals used in the terminations (Cu, Sn, Pb).
 - Diffusion and migration in the crack.

Diffusion coefficient of metal ions in water, $D \sim 5 \times 10^{-10}$ to 9×10^{-10} m²/s

at $t \sim 1$ min, $L > 7$ mil.

$$L = \sqrt{D \times t}$$

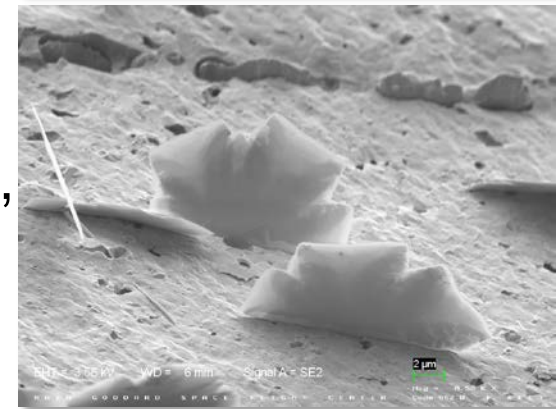
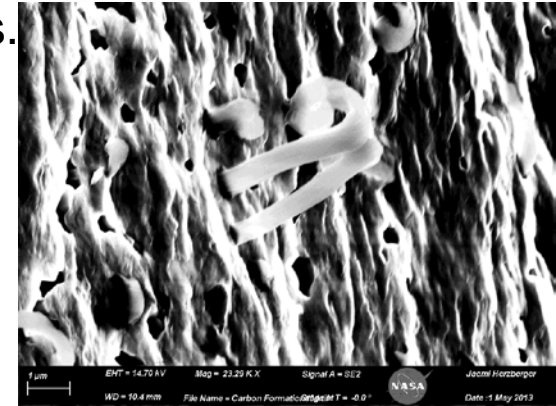
In a layer of adsorbed water the processes would be slowed, but still might happen during operation.



❑ Cracks at terminations might cause short circuit failures.

Discussion - ECM in MLCCs

- ❑ Carbon filaments.
 - Known to grow on catalyst surfaces and some metals (fastest growth on Ni) when heated in the presence of carbon-containing gases.
 - The carbon is transported by surface diffusion.
 - The presence of carbon is most likely due to the remnants from the binder burning process, and the catalytic metal (Ni) is used for electrodes.
- ❑ The ceramic is highly mechanically stressed, and diffusion processes are enhanced by the presence of grains and micropores.
- ❑ The surface of ceramic is chemically active and might result in growth of hydrocerussite-like, $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$, platelets.
- ❑ The processes of growth of carbon filaments and crystalline platelets requires additional analysis.



Conclusion

- ❑ In humid environments the probability of failure for PME capacitors with cracks is greater than for BME capacitors.
- ❑ The difference is due to the specifics of electro-chemical behavior of Ni and Ag/Pd and formed products (conductive Ag-based deposits for PME and isolative Ni/C/O compositions for BME capacitors).
- ❑ HSSLV testing is effective for PME MLCCs but fails revealing cracks in BME capacitors. For BME capacitors THB testing at 85 °C, 85% RH, and VR for 240 hours is recommended.
- ❑ MLCCs with larger cover plates have a lower probability of failures in cases where cracks originate from the surface of the part.
- ❑ Manual soldering of MLCCs containing preexisting cracks increases the probability of failure substantially.
- ❑ The fractured surface of BME MLCCs is chemically active and in humid environments can facilitate formations of Ni carbohydrate compositions, lead carbohydrates, or carbon filaments. These processes require more study and analysis.