Low De-rating Reliable and Efficient Ta/MnO_2 Capacitors

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Introduction:

Solid Tantalum capacitors with MnO_2 cathodes (Ta/MnO_2 capacitors) were invented by Haring, Summit, and Taylor from Bell Telephone Laboratories about a half a century ago.[1] These capacitors combine record high charge efficiency CV/cc with stable capacitance (C) over temperature (T) and voltage (V) as well as low and stable d.c. leakage (DCL). Applications of Ta/MnO2 capacitors in special electronics like military, aerospace, and medical proved their high reliability in broad range of the operating conditions. The MnO_2 cathode, which is the major feature of the invention, plays critical role in providing stability and reliability to Ta/MnO_2 capacitors through efficient self-healing mechanisms. These mechanisms include replenishing of oxygen in the bulk of the oxide dielectric as well as blocking defect spots in the dielectric due to phase transformations from conductive MnO_2 to non-conductive low manganese oxides (Mn_2O_3, Mn_3O_4, and MnO).

During field applications, some failures of the Ta/MnO_2 capacitors occur, which can be expected even with low failure rate, taking into consideration the high volumes and the longtime of usage of these capacitors in special electronics. Some publications presented these failures as a result of the inherent instability of the Ta/MnO_2 capacitors coming from their basic structure and leading to catastrophic distraction of the circuit board with the failed capacitor. In this situation any electronic device using Ta/MnO_2 capacitors becomes potentially unreliable. Inevitably these publications created negative image of the Ta/MnO_2 capacitors and influenced decisions on applications of these capacitors, especially, in new designs. This paper distinguishes inherent properties of the Ta/MnO_2 capacitors from what comes from the art of their manufacturing and testing. The paper demonstrates that with right technology and special screening Ta/MnO_2 capacitors combine record high efficiency with extremely low failure rate even when used without de-rating.

Myths and Facts about Ta/MnO_2 Capacitors

Following are popular statements about Ta/MnO_2 capacitors presented in literature and well known to the end users:

- There is a mismatch in coefficient of thermal expansion (CTE) between Ta_2O_5 dielectric and MnO_2 cathode, which causes mechanical stress at the dielectric/cathode interface during high temperature manufacturing steps, assembly, and field applications. **This is a myth**. In reality CTE of Ta_2O_5 ($6.5*10^{-5}\ K^{-1}$) and CTE of MnO_2 ($\approx 5*10^{-5}\ K^{-1}$) are practically identical and can't cause mechanical stress at the dielectric/cathode interface.[2]
- Hard crystalline MnO_2 breaks soft amorphous Ta_2O_5 under mechanical stress, including vibration and stress during field applications. **This is a myth**. In reality hardness of crystalline MnO_2 (<1

GPa) is much lower than hardness of amorphous Ta_2O_5 (≈ 8 GPa). This makes it impossible for MnO_2 to damage the dielectric.[2]

- Failed Ta/MnO_2 capacitors burn due to oxygen released by MnO_2 cathode, which results in severe damage of the circuit board with the failed capacitor. **This is a myth.** Release of oxygen from MnO_2 at high temperature can cause short flash on the capacitor surface; however, it is immediately extinguished due to phase transformation of MnO_2 into low manganese oxides. These low manganese oxides don't have active oxygen and prevent oxygen coming from the surrounding atmosphere to support the burning. Fig. 1 shows typical image of the failed Ta/MnO_2 capacitor and its impact on the circuit board (from the Calendar published in 2011 by the High Reliability Laboratories Co.)

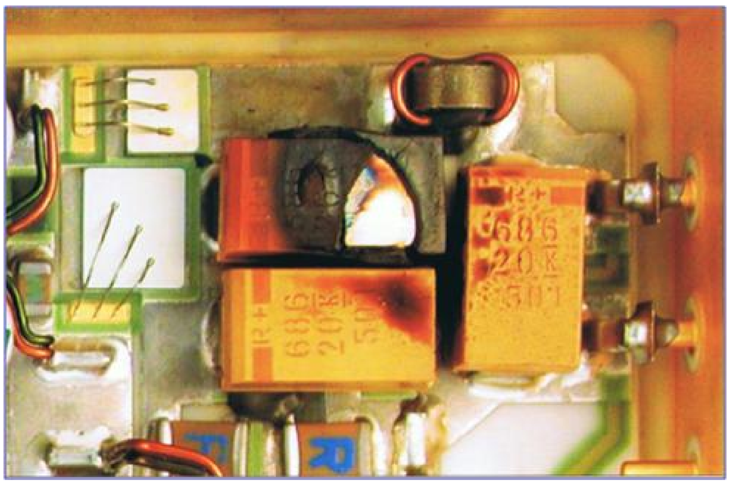


Fig. 1. Failed Ta/MnO_2 capacitor on a circuit board

As one can see from the Fig. 1, there is very little damage to the circuit board around the failed Ta/MnO_2 capacitor. This is contradictory to the severe damage expected in the case of the burning event. Fig. 2 presents typical cross-section of the failed Ta/MnO_2 capacitor, which can explain this contradiction.

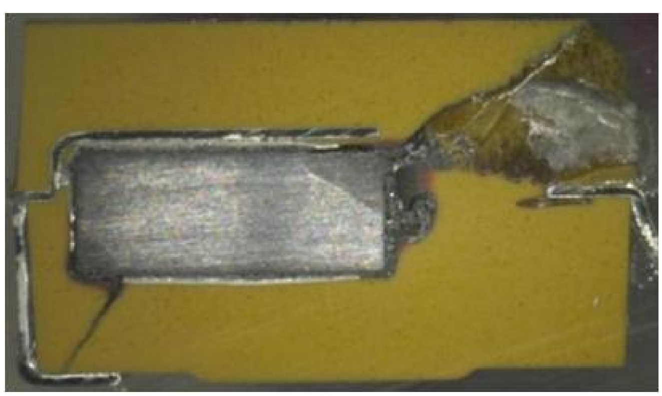


Fig. 2. Cross-section of the failed Ta/MnO_2 capacitor

According to Fig. 2, the ignition involved only a small area on anode surface and was immediately extinguished before propagating through the anode body. Small size low voltage Ta/MnO_2 capacitors typically don't ignite when failed since they don't have enough energy to achieve ignition temperature. It's obvious, that even small probability of ignition isn't acceptable in combustible atmosphere, where Polymer Ta capacitors can replace Ta/MnO_2 capacitors.

- Ta/MnO2 capacitors can't work reliably without 50% de-rating at temperatures T ≤ 85^o C. **This is a myth**. Moreover, de-rating can cause loss in reliability instead of expected gain in reliability

Pros and Cons of De-rating

Major degradation mechanisms in Ta/MnO_2 capacitors, which can cause parametric and catastrophic failures of these capacitors, are oxygen migration from the Ta_2O_5 dielectric into the Ta anode and crystallization of the amorphous matrix of the Ta_2O_5 dielectric.[3] Low voltage capacitors are more susceptible to oxygen migration since in these capacitors the thickness of the layer depleted with oxygen Ta_2O_{5-x} near the anode surface is comparable with the total thickness of the Ta_2O_5 film. High voltage Ta capacitors with thick Ta_2O_5 dielectric are more susceptible to crystallization due to higher internal energy of the amorphous dielectrics and lesser impact of the energy gain at the dielectric/anode interface.[3] Both degradation mechanisms, oxygen migration and crystallization, depend exponentially on the electric field in the dielectric **F = Va/t**, where **Va** – application voltage, **t** - dielectric thickness. From this consideration, probability of failure will decrease exponentially at lower **Va** or higher de-rating which is the ratio between rated voltage **Vr** and application voltage **Va**.

At the same time, there are factors that increase probability of failure due to de-rating, especially, in high voltage capacitors. The major factor for the reliability loss with de-rating is that high voltage capacitors with thick amorphous dielectrics are more susceptible to crystallization than the lower voltage capacitors with thinner dielectrics. Fig. 3 demonstrated this effect by comparing SEM images on the Ta_2O_5 dielectrics formed at formation voltage V_f = 110 V (t = 220 nm) and V_f = 180 V (t = 360 nm).

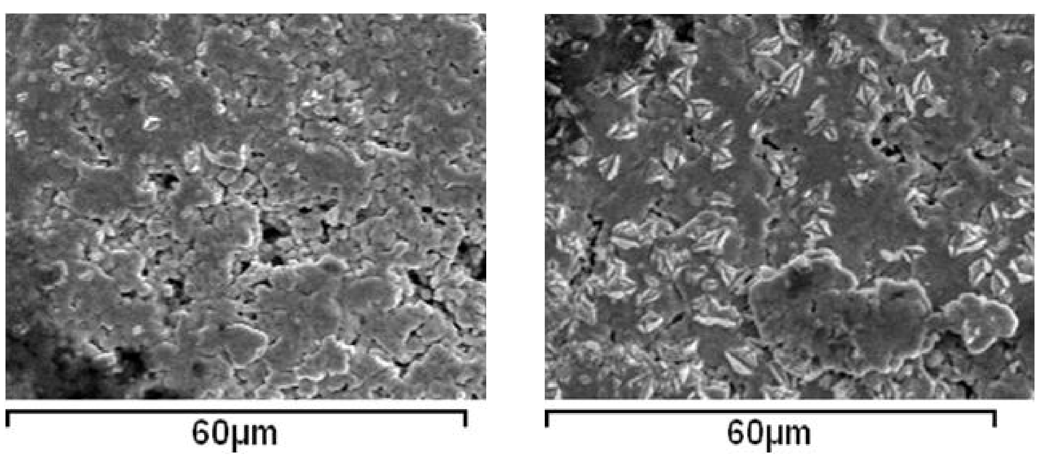


Fig. 3. SEM images of the Ta_2O_5 films with V_f = 110 V (left) and V_f = 180 V (right)

As one can see from Fig. 3, thinner dielectric has just a few small crystals, while thicker dielectric has high density of much larger crystals damaging the dielectric structure. The 50 V Ta/MnO_2 capacitors were manufactured with these dielectrics and put on Life test at rated voltage and T = 85^o C. Fig. 4 shows DCL distributions in these capacitors before the test (0 hours) and after 250 h of the Life test.

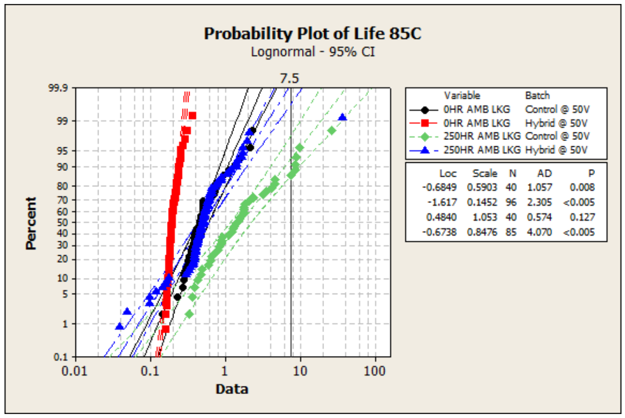


Fig. 4. DCL distribution before and after 250 h Life test at 50 V and 85° C in Ta/MnO$_2$ capacitors with V$_f$ = 110 V (hybrid) and V$_f$ = 180 V (control)

According to Fig. 4, capacitors with thinner dielectric had lower initial DCL; however, DCL in both types of capacitors was unstable, shifting to the higher values during the test and causing parametric failures even during this relatively short Life test. In case of the capacitors with thicker dielectrics, DCL instability can be attributed to the large density and size of the initial crystals, while in case of the capacitors with thinner dielectrics, DCL instability can be attributed to higher electric field stimulating crystal growth during the test.

Presented on Fig. 3 and Fig. 4 results evidence that de-rating of Ta/MnO$_2$ capacitors (in this case increasing the dielectric thickness for given application voltage) can have low effect or even negative effect on the reliability. At the same time, de-rating always causes rapid decrease in volumetric efficiency CV/cc, the major selling point of the Ta/MnO$_2$ capacitors. As an example, Fig. 5 shows Ta/MnO$_2$ capacitors D-case 4.7 uF – 50 V and A-case 4.7 uF – 25 V having the same capacitance 4.7 uF and approximately 50% difference in the dielectric thickness (similar to 50% de-rating).

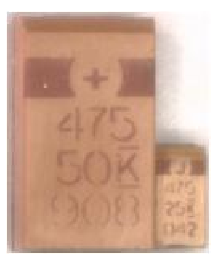


Fig. 5. Ta/MnO$_2$ capacitors D-case 4.7 uF – 50 V (left) and A-case 4.7 uF – 25 V (right)

Volume and mass of these capacitors relate as approximately 10:1. This is because coarser Ta powder is required to grow thicker dielectrics, which causes capacitance loss not only due to increase in the dielectric thickness, but also due to decrease in specific surface area of the anode. That's why to keep capacitance constant, ten times larger anode is required with 50% de-rating. Large size of the Ta/MnO_2 capacitors with 50% de-rating is also detrimental to their reliability since these capacitors have less efficient heat dissipation and, therefore, are more susceptible to ignition when failed.

F1 Technology and Simulated Breakdown Screening (SBDS)

F1 technology and simulated breakdown screening (SBDS) allow manufacturing of highly reliable and efficient Ta/MnO_2 capacitors with low (no) de-rating. The principle of the F1 technology is based on the fact, that density and size of the crystalline inclusions in amorphous matrix of the Ta_2O_5 film is directly proportional to the density of the crystalline seeds on anode surface prior to anodizing.[3] These seeds are originated by impurities on anode surface, typically carbide inclusions coming from residuals of organic lubricant used for pressing of Ta powder and oxide inclusions coming from native oxide dissolving in Ta particles during the powder sintering. Fig. 6 shows pores and cracks in the oxide dielectric formed on surface of Ta anodes enriched with carbon and oxygen.

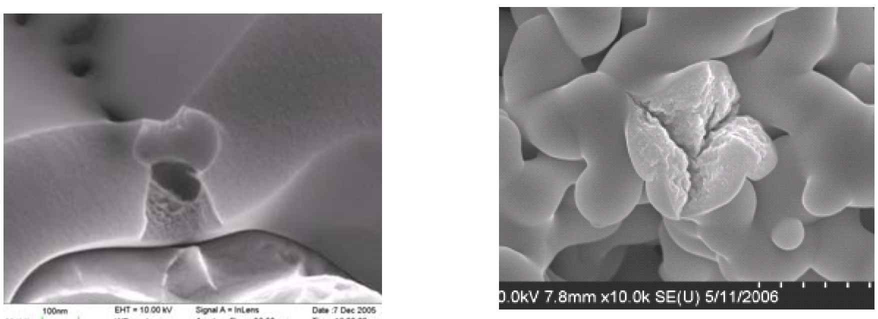


Fig. 6. Ta_2O_5 dielectrics formed on Ta surface enriched with carbon (left) and oxygen (right)

F1 technology includes de-carbonizing and de-oxidizing steps providing chemical purity to the anode surface.[4] F1 technology also provides strong anode-to-lead attachment since mechanical stress in this junction can also provoke crystallization. This allows forming of practically defect free dielectrics on the surface of Ta anodes manufactured with F1 technology (Fig. 7).

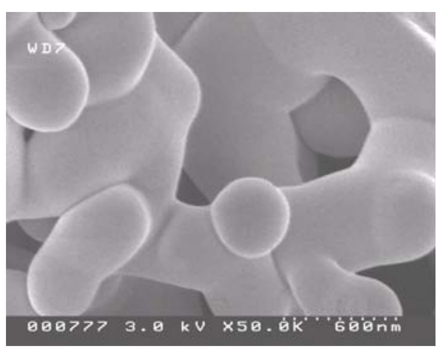


Fig. 7. SEM images of Ta_2O_5 dielectric formed on Ta anode manufactured with F1 technology.

Ta/MnO_2 capacitors with anodes manufactured with F1 technology demonstrate high DCL stability during accelerated Life test at 1.32 rated voltage and 85° C, while capacitors manufactured with conventional (control) technology degrade quickly at these accelerated conditions (Fig. 8).

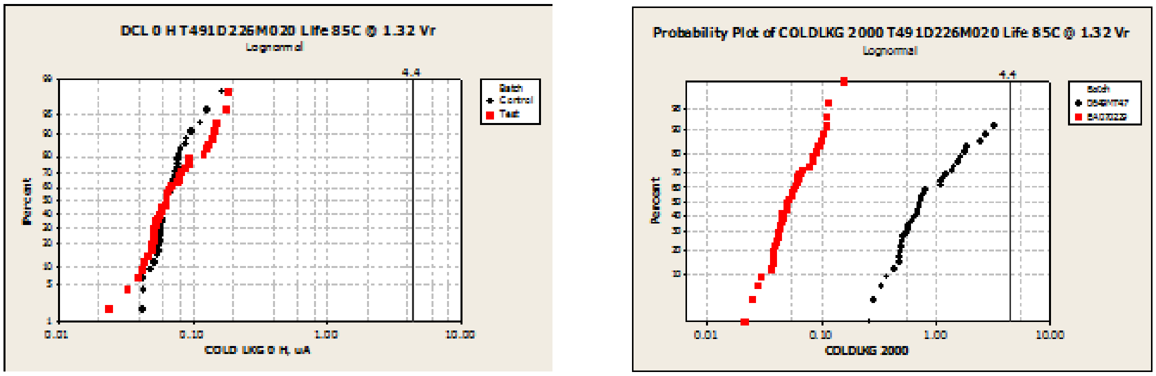
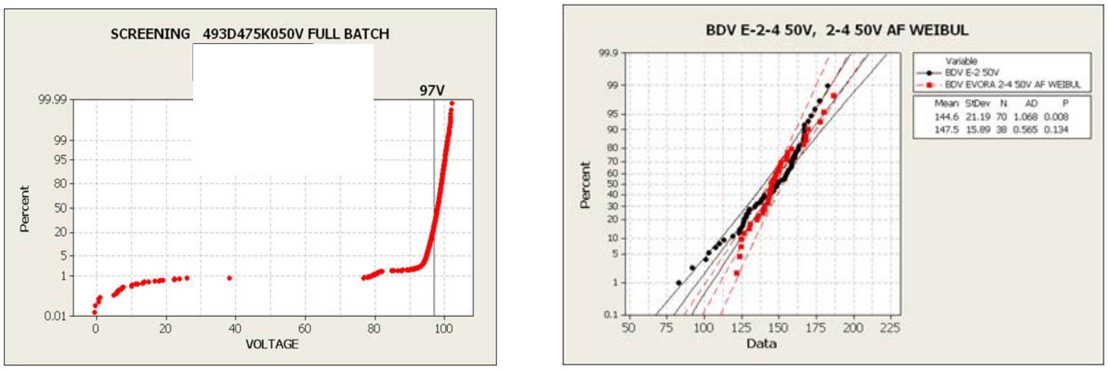


Fig. 8. DCL distribution in D-case 22 uF – 20 V Ta/MnO_2 capacitors before (left) and after (right) accelerated life test (control vs. F1 technology)

With any advanced technology there is a probability that a small percentage of the finished capacitors may have hidden defects in their dielectrics, which were not detected during post manufacturing testing and can propagate and cause failures during the field application. Moreover, some harsh accelerated tests like Weibull grading test can induce hidden defects into the dielectric without being detected by existing techniques.

The most efficient way to detect hidden defects in the dielectric is breakdown voltage (BDV) test. Low BDV indicates defects in the dielectric, while high BDV close to the formation voltage indicates defect-free dielectric. Despite of its efficiency, BDV test can't be used for screening purpose since it's a destructive test. That's why simulated breakdown screening (SBDS) was developed that allows screening of the low BDV parts without any damage to the population of the capacitors.[5] This test is based on the analysis of the capacitance charge characteristics when voltage exceeding average BDV is applied to the tested capacitor with high series resistor limiting current in the circuit. To determine parameters of this screening, actual BDV is tested on a sample of the capacitors from each manufacturing batch.

Fig. 9 shows typical SBDS distribution in D-case Ta/MnO_2 capacitors 4.7 uF – 50 V manufactured with F1 technology (left) and actual BDV distribution on a sample of these capacitors before and after SBDS (right).



a b

Fig. 9. SBDS distribution (a) and BDV distributions before and after SBDS (b) in D-case Ta/MnO_2 capacitors 4.7 uF – 50 V manufactured with F1 technology

As one can see on Fig. 9a, there is about 1% tail on the SBDS distribution despite of the fact that the capacitors were manufactured with F1 technology and passed all the tests required by the Mil Spec. Actual BDV distribution after the SBDS (Fig. 9b) confirms that the parts with low BDV were removed, while no damage (no change in BDV) was done to the parts from normal population.

Ta/MnO_2 capacitors from the tail of the SBDS distribution and from the normal population were submitted to the accelerated life test (Fig. 10).

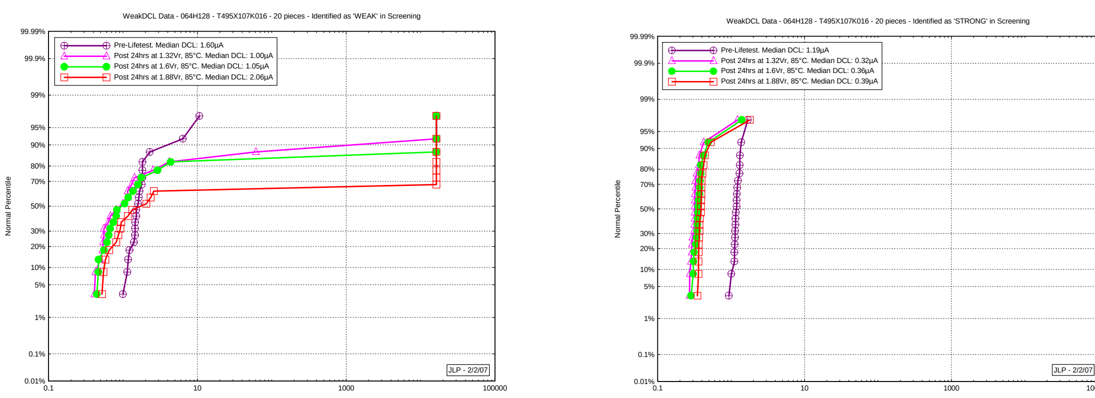


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Fig. 10. Accelerated life test of the Ta/MnO2 capacitors from the tail of the SBDS distribution (a) and from the normal population (b).

According to Fig. 10, there were 7 catastrophic failures (29%) in the tail, while no failures or DCL increase in the normal population. This confirms that the tail of the SBDS distribution represents unreliable parts with hidden defects in the dielectric, while normal population of the capacitors is not affected by the SBDS process.

The generally accepted criterion for the long term reliability is **BDV ≥ 2Va.** According to Fig. 9b, minimum BDV = 85 V before SBDS, which requires approximately 20% de-rating to satisfy the criterion for the long term reliability. After the SBDS minimum BDV = 125 V, (**BDV > 2Vr**), which means that these 50 V capacitors don't need any de-rating and can be used at rated voltage at $T \leq 85^o$ C.

Moreover, Ta/MnO_2 capacitors with F1 and SBDS are highly reliable even with acceleration vs. rated voltage. As an example, Fig. 11 shows room temperature and hot DCL distributions when 50 V Ta/MnO_2 capacitors with F1 and SBDS were submitted to the 2000 h Life test as 63 V capacitors.

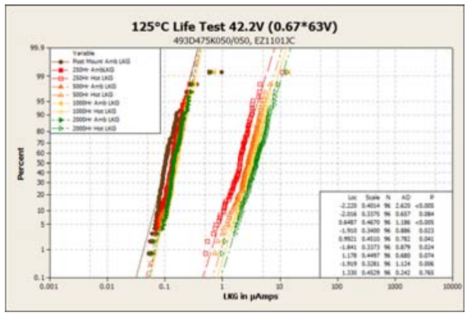

Fig. 11. Room temperature and hot DCL in 50 V Ta/MnO2 capacitors with F1 and SBDS tested as 63 V capacitors.

According to Fig. 11, both room temperature and 125^o C DCL in these capacitors remain stable during 2000 hours testing with 25% acceleration (not 50% de-rating).

Short Term Reliability

Thermal shock during board mounting can cause damage to some capacitors and early (power on) failures. J. Prymak and J. Marshall developed surge step tress test (SSST) to evaluate short-term failure rate at given application voltage.[6] In this test several short pulses are applied to the capacitor with gradually increased amplitude until the capacitor fails (fuse blows). Current in the circuit is limited only by very low internal resistance of the power supply. Generally accepted criterion for the short term reliability, is **FR @ Va ≤ 100 ppm,** where **FR** is failure at application voltage **Va.**

Fig. 12 shows SSST results for two batches of Ta/MnO_2 capacitors 4.7 uF – 50 V. To achieve FR = 100 ppm on the batch shown on the left distribution, application voltage should be below 25 V, which means more than 50% de-rating vs. rated voltage 50 V. At the same time the batch shown on the right distribution doesn't require any de-rating since FR at rated voltage is below 100 ppm. Both batches were manufactured with F1 technology and SBDS

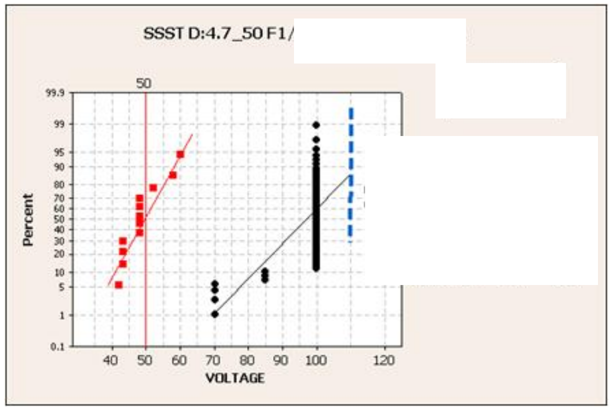

Fig. 12. SSST results for two batches Ta/MnO_2 capacitors 4.7 uF – 50 V manufactured with F1 technology and SBDS.

Cross-sections of the Ta/MnO_2 capacitors from these two batches are shown in Fig. 13. On these cross sections light rectangular is Ta anode with oxide dielectric, dark layer on anode surface is external MnO_2 with thin carbon coating, following by silver coating, silver adhesive, and lead-frame.

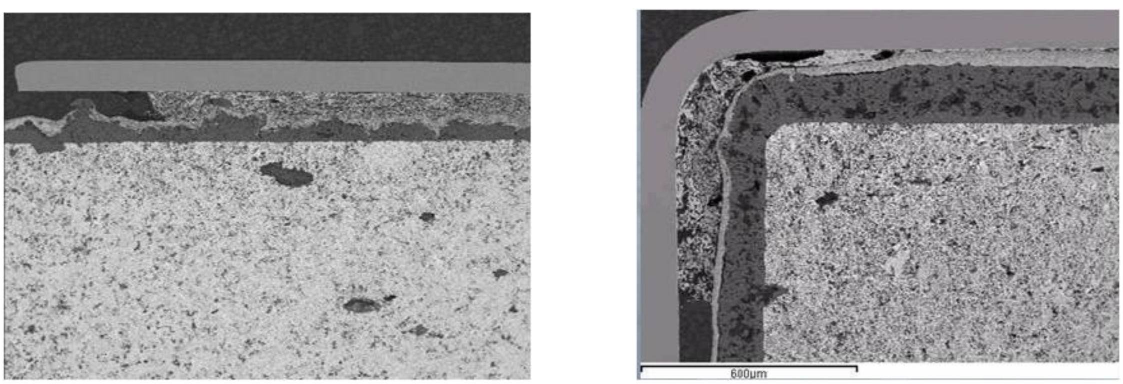

Fig. 13. Cross sections of the Ta/MnO_2 capacitors 4.7 uF – 50 V from the two batches shown on Fig. 12.

From Fig. 13, the difference between these two batches becomes obvious. On the left one can see irregular thickness of the external MnO_2 coating where silver penetrates close to the dielectric on anode surface. On the right, external MnO_2 layer is uniformly thick, without silver penetration toward the dielectric surface. Irregular thickness of the external MnO_2 coating is caused by misprocess and can be avoided by careful process control.

Additional reasons for high failure rate at the SSST are poor contact between silver adhesive and lead frame caused by anode misplacement and not sufficient cure at assembly as well as exposure of the finished capacitors to humidity prior to the board mounting. These issues also can be avoided by careful control of the assembly process and keeping finished capacitors dry prior to the board mounting. With these measures Ta/MnO_2 capacitors manufactured with F1 technology and SBDS meet both long term and short term reliability criteria without de-rating.

Conclusion

Presented in this paper results demonstrate that there are no "inherent problems" with Ta/MnO_2 capacitors coming from their basic structure and that their performance and reliability depend only on the art of the manufacturing process and screening techniques. With F1 technology and 100% simulated breakdown screening (SBDS) these capacitors meet criteria for long term reliability without de-rating.

To meet short term reliability criteria without de-rating, additional attention should be paid to the anode top coating and assembly process as well as keeping the capacitors dry before the board mounting. SSST on a representative sample of each bath verify short term reliability. From the yield consideration, 20% de-rating can be recommended to avoid scraping batches with FR at rated voltage slightly higher than 100 ppm.

Using Ta/MnO_2 capacitors with low (no) de-rating allows radical increase in the volumetric CV/cc and weight CV/g efficiency of these capacitors (smaller size and lighter weight), which are the major selling points of Ta capacitors. At the same time, smaller anodes results in higher equivalent series resistance (ESR), which is directly proportional to the external surface area of the anode. Multi anode technology as well as more conductive external layers on anode surface can mitigate this problem when low ESR is requested. Low (no) de-rating will also ensure sufficient supply of the Ta powder due to reduction in the anode weight for given rating of the Ta/MnO_2 capacitors.

Acknowledgments:

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