Reliability and Critical Applications of Tantalum Capacitors

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Despite constant competition from aluminum and ceramic capacitors, tantalum (Ta) capacitors have been on the market for more than half a century. They still continue to grow, especially, relatively new types of Ta capacitors like Ta capacitors with conductive polymer cathode. The major parameters, which keep Ta capacitors on the market and make them attractive for use in electronic devices, are high volumetric efficiency (CV/cc), low Equivalent Series Resistance (ESR) and Equivalent Series Inductance (ESL), highly stable characteristics with respect to voltage and temperature, and high stability over long periods of time (i.e., high reliability).

High stability and reliability bring Ta capacitors into special applications, such as military, aerospace, and medical. At the same time, the key element of Ta capacitors, Ta_2O_5 dielectric, is inherently thermodynamically unstable. Stabilizing the dielectric and the Ta/Ta_2O_5 interface can be accomplished by kinetic means. Extension of high stability and reliability to higher temperatures and voltages requires a deep understanding of these thermodynamic and kinetic factors and the manufacturing technology to affect the practical realization of this science.

In this paper, we show how application of this knowledge can extend the working temperature of high reliability devices from 125°C to 200°C and the rated voltage to 125 V and above. We also explain how CV/cc and Energy/cc can continue to be increased at higher voltages.

A second topic of this paper is the extension of the rated voltage of Ta-polymer capacitors. Currently the low ESR of Ta-polymer capacitors can be realized only in lower voltage devices. Reliable devices with higher voltage ratings would continue to expand the market for this type of capacitor. Here the issue is not only stability of the dielectric and the Ta-dielectric interface, but also the fundamental properties of the dielectric-polymer interface. By understanding the properties of this interface, we show why a modification of chemistry of the polymer can lead to devices with significantly higher breakdown voltages.

Finally, we describe a new screening technique that is able to distinguish between weak unreliable parts and good reliable parts and also to select the "best of the best" parts for ultimate high reliability applications.

1. Review of Stability of the Ta_2O_5 Dielectric in Ta Capacitors

Ta_2O_5 and Ta form non-equilibrium pair of phases according to Ta-O equilibrium diagram. As a way of relaxing into a thermodynamically stable state, oxygen migration from the Ta_2O_5 dielectric into Ta anode takes place in vicinity of the Ta/Ta_2O_5 interface. This process results in accumulation of oxygen vacancies in Ta_2O_5 film, and, thereby, deterioration of the dielectric.[1]

The second reason that the Ta_2O_5 dielectric in Ta capacitors is thermodynamically unstable comes from its amorphous structure. Electron traps, associated with the amorphous structure, reduce mobility of electrons in strong electrical field and, thereby, prevent dielectric breakdown. On the other hand, amorphous dielectrics spontaneously trend to ordering and crystallization to reduce their internal energy. When crystalline inclusions grow in amorphous matrix of the film, they create mechanical stress due to difference in specific volume between amorphous and crystalline phases. Eventually this stress results in disruption of the dielectric, which is the major reason for the catastrophic failures of Ta capacitors.[2]

The obvious contradiction between Ta capacitors being on top of the list of reliable electronic components and Ta_2O_5 dielectric being thermodynamically unstable can be solved by kinetic means. Reducing the rate of oxygen migration, compensation of oxygen vacancies in the dielectric by oxygen coming from cathode, and suppression of the crystallization process are important goals in the design of reliable Ta capacitors.

As the Ta capacitors are heading toward higher CV Ta anode to increase their volumetric efficiency and to conductive polymer cathode to reduce their ESR, achieving these goals becomes more and more difficult. Critical applications, which require high operating temperatures and working voltages, are the most challenging with regards to stability and reliability of Ta capacitors. These challenges as well as physical obstacles and technological opportunities to meet the challenges, are the subjects of this paper.

2. High Operating Temperature

The maximum operating temperature in most types of Ta capacitors is 125° C. Under the hood automotive applications require maximum operating temperature 175° C. Oil exploration applications require further increase of operating temperature to 200° C and above. Though de-rating of working voltages is used at temperatures $T \geq 125^o$ C, increasing of operating temperature can be damaging to all elements of Ta capacitors and first of all to its amorphous dielectric film. This is because temperature increase accelerates exponentially both oxygen migration and crystallization processes in the Ta_2O_5 dielectric.

The first 200° C life test of Wet Ta capacitors manufactured with conventional technology resulted in rapid increase of d. c. leakage, dissipation factor, and capacitance. Failure analysis revealed change in color of the dielectric in anodes subjected to the 200° C life test (Fig. 1). This change in color is evidence of a reduction in thickness of the dielectric, which is consistent with the electrical test data.

Fig. 1. Virgin (left) and failed (right) anodes of the A-case 22 uF – 25 V Wet Ta capacitors subjected to 200° C life test.

Reducing thickness of the dielectric in Wet Ta capacitor during the 200° C life test can be caused by active oxygen migration through the dielectric-anode interface, accelerated by high operating temperature and d.c. voltage. Thin dielectric films in low voltage Ta capacitors are more susceptible to this form of degradation because area of oxygen depletion in these films occupies significant part of the total film thickness. A chemical reaction between sulfuric acid, used as the electrolyte in Wet Ta capacitor, and outer surface of the Ta_2O_5 film can also cause a reduction thickness of the dielectric during the 200° C life test.

To solve these problems, special technology was developed for high temperature Ta capacitors. This technology was focused on stabilizing of the Ta_2O_5 dielectric and its interfaces with the anode and electrolyte and included improvements in anode manufacturing process as well as the formation and heat treatment of the dielectric. The capacitors manufactured with this technology successfully passed the 200° C life test without any noticeable change of the electrical parameters.

As an example, Fig. 2 demonstrates the change in the d.c. leakage and capacitance in Wet Ta capacitors during the 200° C life test for conventional technology (control) and special high temperature technology (test).
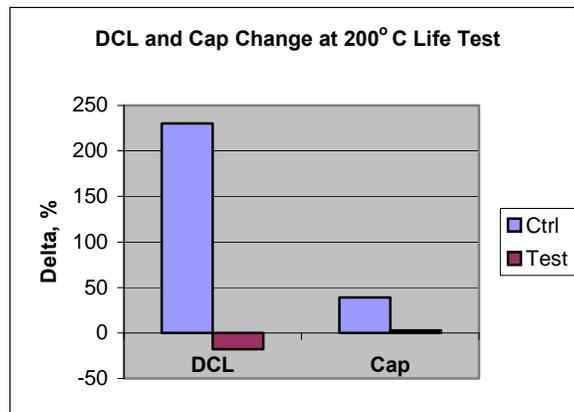

Fig. 2. Relative change of DCL and Cap during 200° C life test of A-case 22 uF – 25 V Wet Ta capacitors, made with conventional (control) and special (test) technology.

From Fig. 2 it is evident that conventional technology resulted in significant increase of the d.c. leakage and capacitance, while with the special technology these parameters remained stable.

3. High Working Voltage

Wet Ta capacitors have working voltages up to 150 V and typically require a formation voltage about 1.8 – 2.5 times higher than the working voltage. There are new medical applications of Wet Ta capacitors, where working voltage at body temperature exceeds 250 V. Solid Ta capacitors have working voltages up to 50 V, which typically requires formation voltages 2.8 – 3.5 times higher than working voltages. As thickness of the dielectric in Ta capacitors is directly proportional to the formation voltage, high voltage Ta capacitors have relatively thick dielectrics in the range of 0.3 – 0.7 microns.

The major problem with reliability of the high voltage Ta capacitors is that amorphous dielectric in these capacitors is highly susceptible to the crystallization. This phenomenon has pure thermodynamic nature. An interface between two different crystalline phases requires misfit dislocations to adjust crystalline lattices of these phases. When one of the phases is amorphous, like in the case of amorphous Ta_2O_5 film on crystalline Ta, misfit dislocations are not needed. Since misfit dislocations introduce additional energy to the system, the amorphous film on crystalline substrate allows lower internal energy than a similar crystalline film would be. On the other hand, the disordering of atoms in amorphous film brings additional energy to the system. The balance in internal energy and, therefore, the balance between the tendency to remain amorphous or to crystallize depend on the ratio between the film surface and volume. This ratio becomes smaller with increasing thickness of the dielectric, which shifts the balance toward the crystallization.

The first 125 V life test of Wet Ta capacitors manufactured with conventional technology resulted in a few catastrophic failures due to rapid DCL increase. Failure analysis showed change in the color of the dielectric from green in virgin parts to gray in failed parts (Fig. 3).
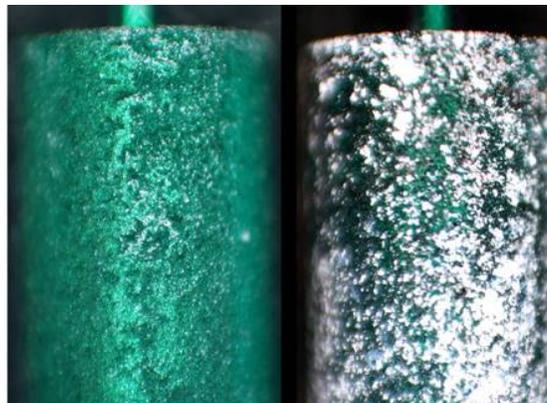

Fig. 3. Virgin (left) and failed (right) **a**nodes of A-case 3.6 uF – 125 V Wet Ta capacitors subjected to 125 V life test.

SEM analysis confirmed that gray color of the dielectric comes from the numerous crystallization sites (Fig. 4). Growing crystals in amorphous matrix of the dielectric disrupted the dielectric film, causing the DCL increase.
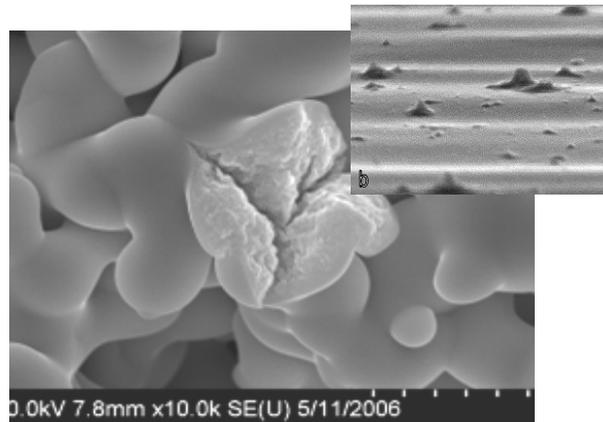
Fig. 4. SEM image of the gray area on failed anode shown on the Fig. 3 right

From these results, improvement of the technology of the high voltage Ta capacitors was focused on suppressing crystallization of the amorphous dielectric. The crystallization starts from small nucleases of the crystalline Ta_2O_5 phase, which form on the surface of Ta anode inside the Ta_2O_5 film during anodizing (insert in the Fig. 4).[2] Size and density of these crystalline nucleases are directly proportional to the concentration of impurities in Ta anode, such as iron, carbon, and oxygen. Mechanical damage of the anode surface can also initiate the crystallization process.

Improvements to the anode manufacturing technology were made to minimize contamination and damage of the Ta anodes during their pressing and sintering. Special attention was paid to reducing of carbon content in anodes, coming from organic binder, and oxygen content in anodes, coming from natural surface oxide. Thickness of the natural surface oxide was minimized due to controlled passivation of Ta anodes after their sintering.[3] High purity surface of sintered Ta anodes resulted in reduced density and size of the initial crystals in amorphous matrix of the Ta_2O_5 film. Additional possibilities came from the heat treatment of the formed anodes, which allowed breakage of the initial crystals from the anode surface and, thereby, interruption of their further growth.[2]

This high voltage technology suppresses crystallization of the amorphous Ta_2O_5 dielectric and, thereby, allows manufacturing of high voltage Wet and Solid Ta capacitors. It was also used for manufacturing of described below high energy efficient Ta capacitors.

4. High Energy Efficiency

Application of Ta capacitors in medical devises, like cardio defibrillators, makes stored energy (E) a critical parameter of the capacitor. As $E = CV^2/2$, increasing of operating voltage provides parabolic increase in the stored energy. At the same time, increasing of operating voltage, and, thereby, formation voltage results in charge $Q = CV$ decreasing in Ta capacitors.[4] Superposition of these two trends results in energy reaching its maximum and then rolling down with increasing of formation voltage. As an example, Fig. 5 shows this effect for Ta anodes sintered with 50k CV/g Ta powder.
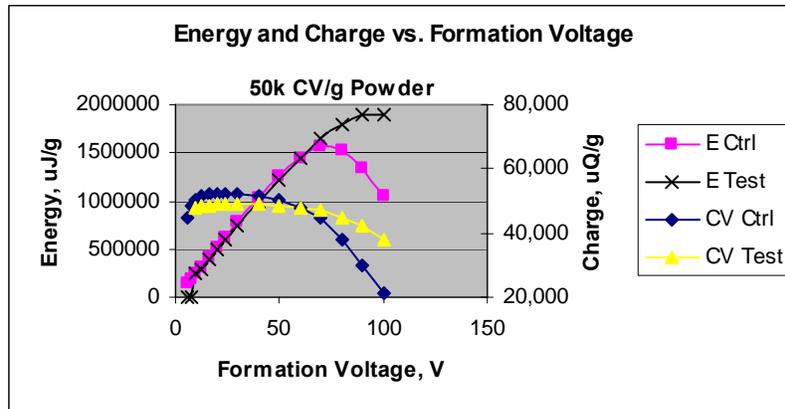
Fig. 5 Specific charge and energy of Ta anodes sintered with 50k CV/g Ta powder with conventional sintering (control) and Y-sintering (test)

The reason CV decreases with formation voltage is uneven structure of sintered anodes. This includes thin necks between sintered particles versus the particles themselves as well as wide range of the pore sizes in sintered anode. During formation, the dielectric Ta_2O_5 film grows inside and outside of the initial anode surface, eating metal through the thin necks and clogging fine pores. This results in reducing of the active surface area of Ta anodes which causes CV decreasing with increasing formation voltage.

Forming of Ta anodes at the range of voltages where CV is rolling down, can adversely affect reliability of Ta capacitors. This is due to increase of current density in partially eaten "necks" and very small pores, which causes local temperature increase and thereby stimulates local crystallization of the amorphous matrix of the Ta_2O_5 film.

The obvious way to increase charge and energy efficiency of Ta capacitors is making anode structure more uniform, which includes thick necks between sintered particles and large open pores. In conventional sintering these two structural elements, necks and pores, are in contradiction to each other. Higher press density and sintering temperature result in thicker necks, but smaller pores due to shrinkage of the anode. Conversely, lower press density and sintering temperature results in larger pores, but thinner necks between the sintered particles.

This contradiction can be solved by combination of sintering with the deoxidizing (so-called Y-sintering), when surface diffusion at lower temperatures provides the necks growth simultaneously with increasing of the pore size.[5] According to the Fig. 5, the test anodes with this morphology demonstrate more stable CV and, thereby, higher stored energy in comparison to control anodes with conventional sintering. Further improvements to this technology in terms of uniformity of Ta anodes can be expected, including of Ta flakes and filaments.

5. High Voltage Polymer Capacitors

The most radical changes to Ta capacitors during long time of their mass manufacturing were associated with reduction of the equivalent series resistance (ESR). They included replacement of

original liquid electrolyte cathode with more conductive solid MnO_2 cathode and later with even more conductive polymer cathode (Fig. 6).
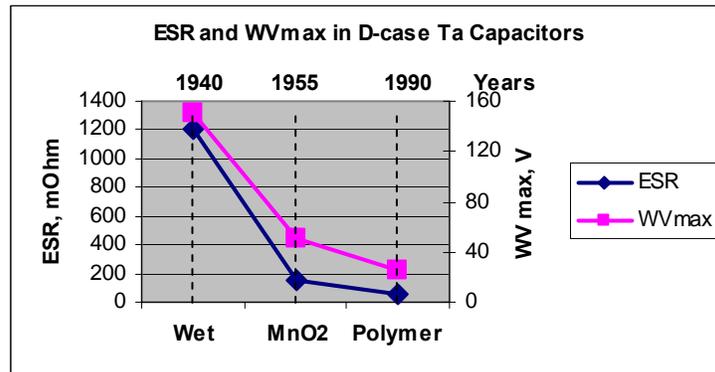

Fig. 6 Evolution of Ta capacitors in terms of ESR and working voltages

Fig. 6 also shows that the ESR reduction in Ta capacitors was accompanied by reduction of working voltage, especially, in polymer capacitors. At the same time, high voltage polymer Ta capacitors can be highly attractive for the end-electronics because they combine low ESR with safety features. When failed in low impedance circuits, polymer Ta capacitors are more resistant to igniting and burning than Ta capacitors with MnO_2 cathode, and this difference becomes more pronounced at higher working voltages.

Fig. 7a demonstrates I(V) characteristics of Ta capacitors with the same anode and dielectric film, but different cathodes. As one can see, in Wet Ta capacitors d.c. voltage can be increased almost to the formation voltage without significant current increase. At the same time, in solid Ta capacitors with MnO_2 and polymer cathodes current starts to increase much earlier, and their BDV readings are much lower than the formation voltage. This is the major reason for lower working voltages in MnO_2 and polymer capacitors in comparison to Wet capacitors.
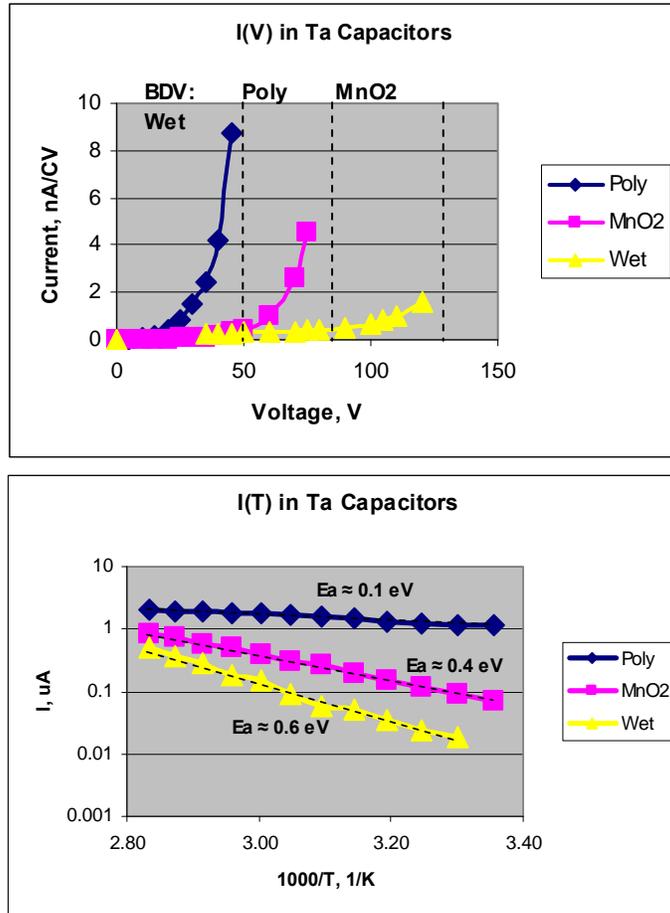
Fig. 7. I(V) (a) and I(T) (b) characteristics of formed to 125 V Ta capacitors with liquid electrolyte, MnO$_2$, and polymer cathodes

From current-temperature I(T) characteristics of Ta capacitors with liquid electrolyte, MnO$_2$, and polymer cathodes (Fig. 7b), activation energy of the current flow in these capacitors was also decreasing from about 0.6 eV in Wet Ta capacitors to about 0.4 eV in MnO$_2$ Ta capacitors and to only 0.1 eV in polymer Ta capacitors.

One more distinction between MnO$_2$ and polymer Ta capacitors was detected by analysis of thermally stimulated depolarization current (TSDC) in these capacitors, performed at the Center for Dielectric Study at the Penn State University (Fig. 8). According to the Fig. 8, polymer Ta capacitors trap significant amount of the electrical charge, which can be released by high ramp heating, while MnO$_2$ Ta capacitors don't demonstrate this property.
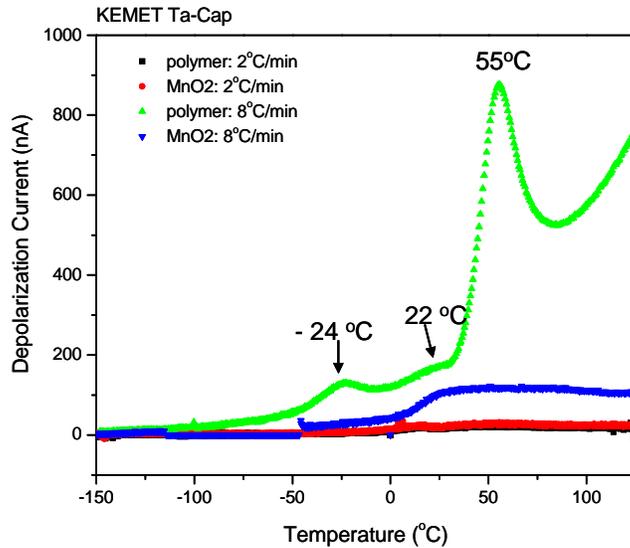
Fig. 8. Thermally stimulated depolarization current (TSDC) of D-case Ta capacitors 15 uF – 25 V with either polymer or MnO_2 cathode (Center of Dielectric Study at the PSU)

Combination of the I(V), I(T), and TSDC data allows following assumption about the electrical properties of the high voltage polymer Ta capacitors. Similarly to Schottky emission in metal-semiconductor contact, current flow in these capacitors is limited by a barrier on the dielectric-polymer interface.[6] If the conductive polymer is produced chemically on the dielectric surface by reaction of monomer and oxidant (in-situ polymerization), then the monomer and/or oxidant interact with the dielectric surface, creating traps for the current carriers. When voltage is applied, electrical charge is accumulated on these traps, reducing the barrier and, thereby, increasing current flow. As a result, in-situ manufactured polymer Ta capacitors even with thick "high voltage" dielectric have limited working voltages.

This model explains differences between polymer Ta capacitors with in-situ polymerization and pre-polymerized dispersion (Fig. 9), which were also reported in [7] .
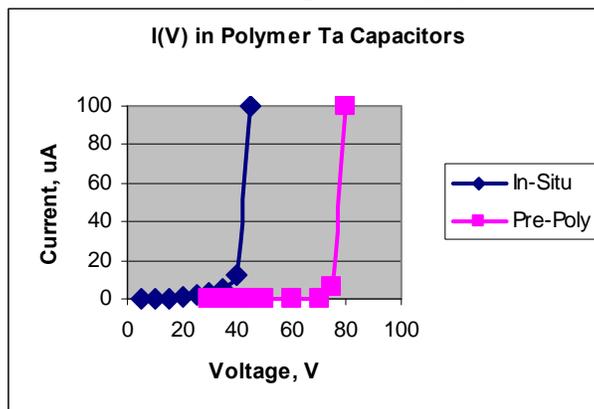

Fig. 9. I(V) Characteristics of D-case polymer Ta capacitors 15 uF – 25 V with either In-Situ polymerization or Pre-polymerized cathode

Deposition of the pre-polymerized dispersion on the dielectric surface does not create electrical traps at the dielectric-polymer interface, and, thereby, keeps the barrier high and the current low at much higher voltages than those with in-situ polymerization. This model requires additional analysis and verification; however, a physical possibility to make high voltage polymer Ta capacitors has been demonstrated.

6. New Screening Technique

Usage of the highest purity raw materials, advanced technology, and most sophisticated machinery can not guarantee that all of the finished capacitors have ideal, flawless dielectric. Some of the finished capacitors may have defects in their dielectric due to occasional contamination or damage coming from machinery malfunction or the human factor.

Hidden defects in the dielectric, which are not healed by the end-of-line ageing and detected by final electrical testing, can progressively worsen during field application and cause failure of a capacitor. That's why accelerated ageing, surge test, re-flow test, etc. are incorporated in the manufacturing of Ta capacitors to display hidden defects in the dielectric and to screen out non-reliable parts. The problem with these techniques is that they cannot guarantee exclusion of all the non-reliable parts and, when intensified, can deteriorate performance and reliability of the general population of the capacitors as a result of the testing.

That's why special screening technique was developed which allows screening of non-reliable capacitors with hidden defects in the dielectric without any damage to the general population of the capacitors. This technique also allows screening of the most reliable "space quality" capacitors for special applications which don't tolerate even smallest probability of a failure.

The screening is based on simulation of breakdown voltage (BDV) test without actual damaging parts. BDV test is an ultimate test of dielectric in the capacitors. Low BDV indicates defects in dielectric and, thereby, high probability of failure in the field. High BDV indicates flawless dielectric and, thereby, reliable field performance. As an example, Fig. 10 shows distribution of screening voltage within a lot of X-case solid Ta capacitors 100 uF – 16V. Screening voltage correlates with actual BDV in individual capacitors.
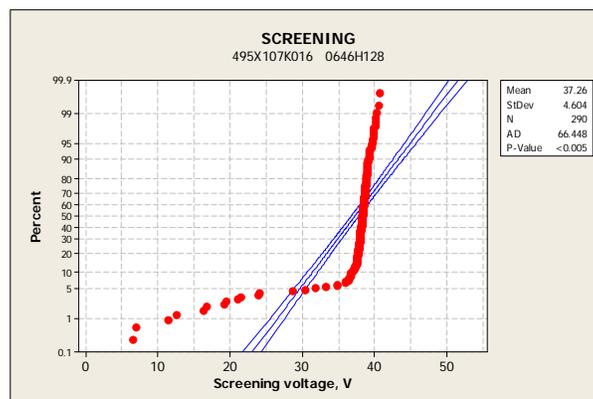

Fig. 10 Distribution of screening voltages in X-case Ta capacitors 100 uF – 16V

As one can see, about 95% of the distribution lies in the narrow range of voltages (general population), while 5% of the distribution spreads out towards low voltages ("tail"). DCL readings in all the parts were much lower than DCL limit for this rating (Fig. 11). According to the Fig. 11, DCL readings were not practically changed during the screening, which confirms its non-destructive nature.
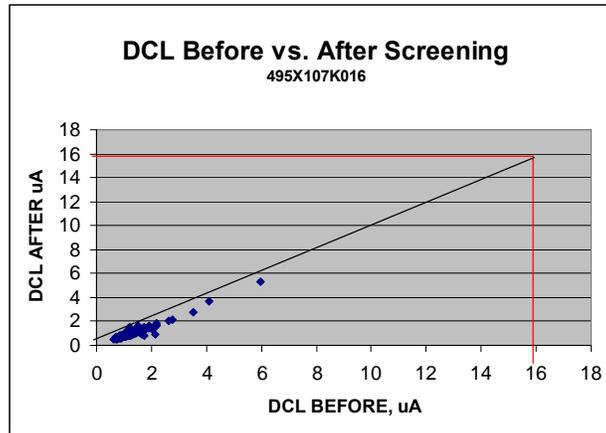

Fig. 11. DC leakage in X-case Ta capacitors 100 uF – 16 V before and after screening.

Twenty capacitors from the tail and from the general population were submitted to highly accelerated test at elevated temperature and voltage. About 30% of the capacitors from the tail failed catastrophically and burned during the test (Fig 12 left), while no failures occurred in general population (Fig. 12 right)
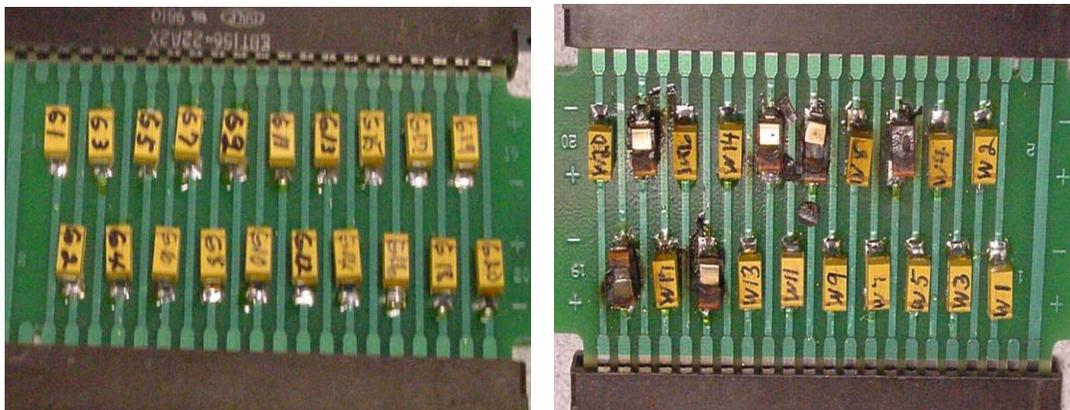

Fig. 12. Circuit boards with tested parts from the tail (left) and general population (right).

One more example on Fig. 13 demonstrates results of accelerated life test of Ta capacitors, non-screened and screened prior to the test.
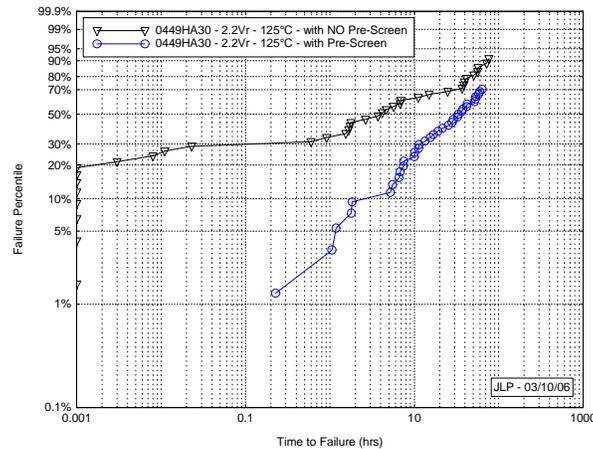

Fig. 13.Accelerated life test of C-case Ta capacitors 10 uF – 16 V with and without screening prior to the test

As one can see from the Fig. 13, significant number of the non-screened capacitors failed at "power on" and very early stage of this highly accelerated test. In contrast to that, screened capacitors did not show any early failures and their time-to-failure distribution was uniform.

Conclusion

Making Ta capacitors for critical applications such as high temperature and high voltage ones is a real challenge. It comes from the fact that the key element of the Ta capacitor, Ta_2O_5 dielectric, is thermodynamically unstable, and this instability becomes more pronounced with increasing of operating temperature, working voltage, and electrical field in the dielectric. However, from physical standpoint there is no "brick wall" for making Ta capacitors which can be stable and reliable in these critical applications. Moreover, they can be more charge and energy efficient. As this paper shows, with good understanding of physical processes, taking place in Ta capacitors during their manufacturing and in the field, and an adequate technology, focusing on stabilizing of the Ta_2O_5 dielectric and its interfaces with anode and cathode, this goal is achievable.

Acknowledgments

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