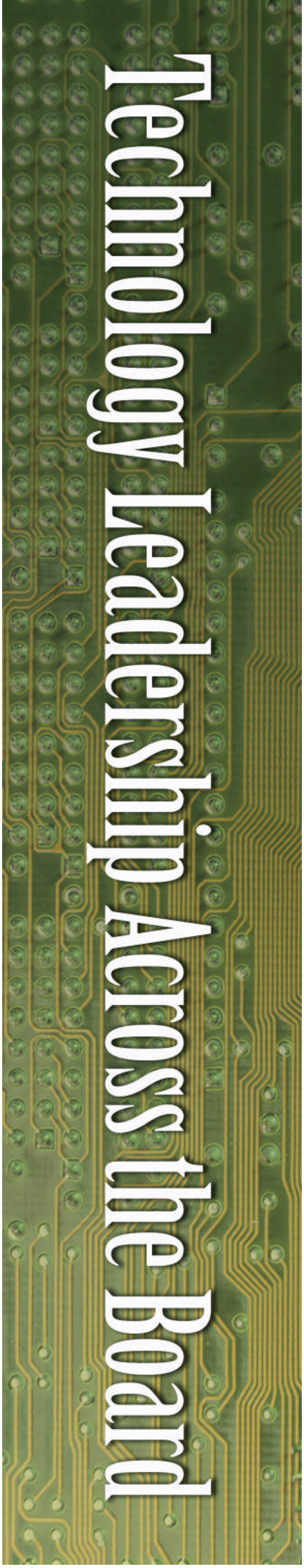


A KYOCERA GROUP COMPANY

A Study of Field Crystallization in Tantalum Capacitors and its effect on DCL and Reliability

T.Zednicek
AVX Czech Republic, s.r.o., Dvorakova 328, 563 01 Lanskroun, Czech Republic
Phone: +420 465 358 126 Fax: +420 465 358 128 Mail:
tomas.zednicek@eur.avx.com

J. Sikula
Czech Noise Research Laboratory, Brno University of Technology
Technicka 8, 603 00 Brno, Czech Republic

H.Leibovitz
AVX Tantalum Corporation, 401 Hill St.,Biddeford, ME 04005, USA
Phone: 207-282-5111Fx 207-283-1941
hleibovitz@avxtantalum.com

Abstract

Tantalum has been the preferred capacitor technology for use in long lifetime electronic devices thanks to the stability of its electric parameters and high reliability. Failure rate performance measurements over time show a decreasing number of failures resulting in practically no wear out - unlike some other capacitor technologies. As in basically any material at temperatures above absolute zero there are processes that can lead to deterioration of the capacitor, there are also self-healing processes that are more effective that result in an overall failure rate reduction. Despite this phenomenon there are some known degradation mechanisms - field crystallization of amorphous dielectric Ta_2O_5 and oxygen migration [14]. This paper summarizes the current status of knowledge concerning field crystallization, focusing on acceleration factors and the practical effects of field crystallization with respect to DCL and the reliability of tantalum capacitors.

INTRODUCTION

High stability and reliability are properties that make tantalum capacitors suitable for critical applications, such as military, aerospace, and medical. The Ta_2O_5 dielectric has been considered to be an amorphous material which is inherently thermodynamically sensitive [14]. An amorphous state tends to order and crystallize to reduce its internal energy [1] however the rate of crystallization depends greatly on temperature. In accordance to [17] there is no crystallization below 550deg.C. Field crystallization within a Ta_2O_5 dielectric film thicker than about 100nm (~25V capacitors) is known phenomenon that can be observed on the dielectric layer by SEM – seeFig.1. Once the Ta_2O_5 dielectric crystallizes conductivity and DCL (leakage current) increases. Conductivity of the crystallized structure is reported to be 1000 times more than the when the dielectric is in an amorphous state [9] nevertheless when field crystallization is “mild” the total amount of film connected to the crystalline form is proportionally so small that the overall DCL is not affected to a significant degree. Recent findings indicate that the Ta_2O_5 crystal phase is significantly less conductive than the amorphous phase due to the limited movement of electrons in crystals. The increase in DCL may still be caused by other mechanisms accelerated by the crystal growth as discussed in this paper. When crystalline inclusions grow in the amorphous matrix of the film, they can create another potential failure mechanism - mechanical stress due to the difference in specific volume between amorphous and crystalline phases. Eventually this stress can also result in a disruption of the dielectric resulting in a further increase in DCL. [13]

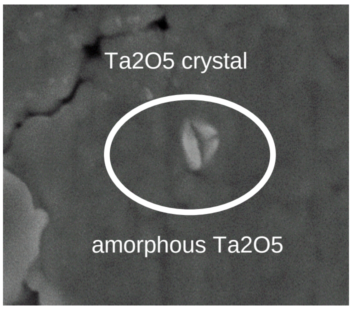
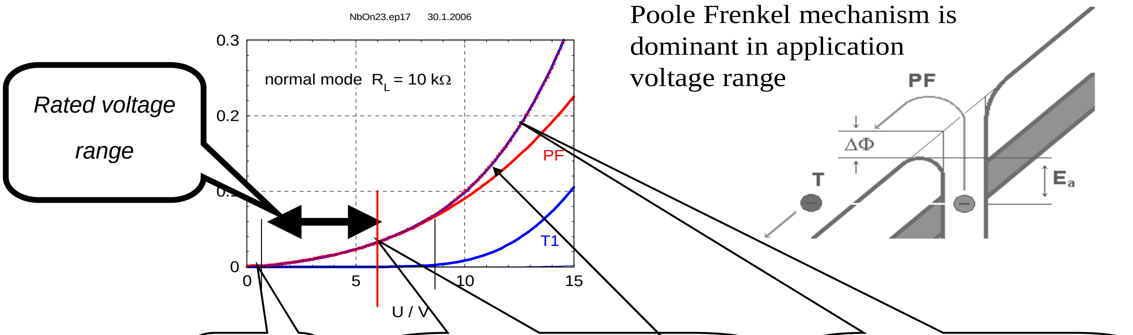


Fig 1. SEM picture of Ta2O5 dielectric layer after crystallization

SUMMARY OF RECENT KNOWLEDGE AND REFERENCES ON FIELD CRYSTALLIZATION

Tantalum Capacitor DCL and Conductivity Mechanisms

The conduction mechanism of tantalum capacitors is considered to be bulk-limited. The dominant electric current transference mechanisms are Ohmic, Poole-Frenkel conduction, over barrier transport and tunneling. The value of the leakage current depends on the layer structure, their electron affinity and electrode’s work functions. Capacitor charging and discharging experiments demonstrate the existence of fast Q_1 and slow Q_2 localized energy states (or two channels) which make charging and discharging possible. It has been observed [10] that at low electric field strengths ($E < 100$ MV/m) the leakage current has a current Ohmic component with conductivity better than □= 10^{-12} □'cm^{-1}. The Ohmic component is observed in both normal and reverse modes, but conductivity is not the same in both modes. For the Poole-Frenkel component, the measured $□_{PF}$ coefficient corresponds to the insulating layer thickness only at a temperature of 300K. At higher temperatures the $□_{PF}$ coefficient does not decrease according to the theoretical prediction. This is probably due to tunneling when the electric field strength is greater than 100 MV/m. Figure 2. below shows the V-I curve for a 6.3V tantalum capacitor. Ohmic and Poole Frenkel conductivity are the main drivers up to the rated voltage. The tunneling mechanism increases conductivity of the capacitor from approximately 1.5 times the rated voltage. This is actually in agreement with the long-standing, experimentally-proven maximum acceleration factor permitted under Weibull testing - 1.528 xVr as stated in MIL STD 55365.



$$I = \boxed{G_o.\,U} + \boxed{G_P\,.U.\,\exp(b_P.\,U^{1/2})} + \boxed{I_{T0}.\exp(-U_o/U)}$$

Ohmic component — Poole Frenkel Component — Tunelling component

$I_o = G_o.\,U$

$G_P\,.U.\,\exp(b_P.\,U^{1/2})$

where

$b_P = (e^3/\pi\varepsilon_0\varepsilon_r d)^{1/2}/kT$

$I_{T0}.\exp(-U_0/U)$

where

$U_0 = (8\pi\sqrt{2m_{eff}}/3eh)\Phi_B^{1.5}t$

Fig. 2. V-I curve and conductivity mechanism of 6.3V tantalum capacitor

Ta_2O_5 crystal growth mechanism

The phase change of Ta_2O_5 from its amorphous state to a lower energy crystal stage can be initiated in two main areas:

1] **Surface defects** <u>during the manufacturing process</u> (due to impurities, abrasion, etc.)
2] Crystallization at nuclei <u>during the life test</u>, especially in the case of temperatures above 100degC and high electric field strength (above 100MV/m) in high voltage (U_R ~ > 25 V) capacitors.

1] Crystalline Ta_2O_5 growth due to impurities during manufacture

Avoiding crystallization of the Ta_2O_5 dielectric has been one of the great process challenges of tantalum capacitor technology since its beginning in early 1960s. Initial efforts targeted the minimization of contamination.

Since that time, phosphoric acid has remained the main forming electrolyte that suppresses growth of the crystalline phase. [6], [15]

Electro-chemical anodization (forming) is still considered as the best known practical and economical way to create a Ta_2O_5 dielectric on a tantalum anode. One of the disadvantages of this process is its sensitivity to surface impurities as the oxide grows on the surface and surface impurity has a significant impact on structure and quality of thin dielectrics. Surface impurities can cause direct growth of Ta_2O_5 crystals during the formation process and any "imperfection" in dielectric structure is a potential site for the growth of crystals – see Fig.3., and ref [6]

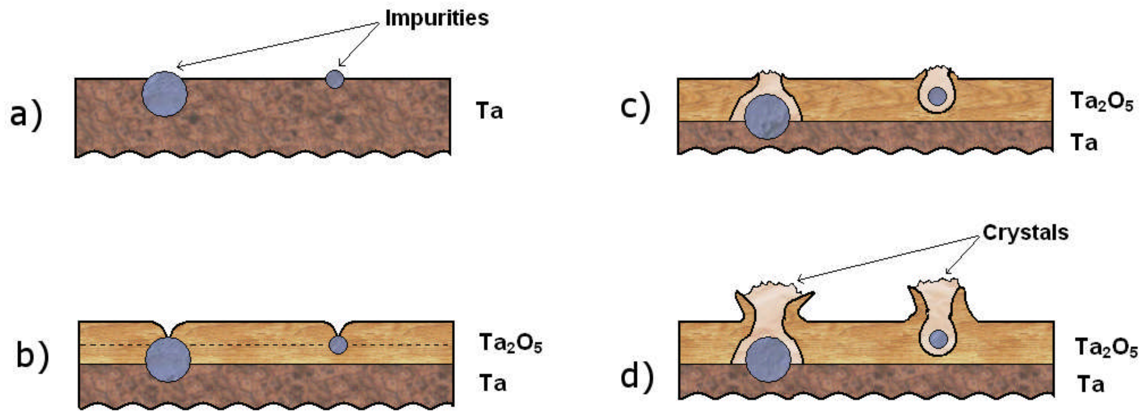


Fig.3. Schematic picture of Ta_2O_5 crystal growth on impurity sides a] before formation, b]after formation c] crystal growth during thermal treatment d] further growth of crystals during thermal treatment

Tantalum capacitor manufacturers and their tantalum powder vendors strive to continuously improve quality and to suppress impurities and minimize their effects. Long term manufacturing experience has also resulted in advanced test procedures to identify and control the levels of impurities. One of the most effective methods for the detection of impurities is thorough DCL measurement. Impurities can be detected either by measuring higher absolute DCL values at different temperatures, or by ratio of cold to hot DCL due to the differences in band gap (different conductivity mechanisms and their temperature dependence). In addition, 100% accelerated ageing is part of the manufacturing process to identify early life defects.

2] Crystalline Ta_2O_5 growth in life test

The presence of impurities - as discussed above - is not the only mechanism that can lead to growth of the crystals. Crystal growth can be also initiated at small areas of crystalline order in the dielectric (nucleation site, also called nuclei). [6]

The phase change of dielectric from amorphous to lower energy crystal state needs some initial energy.

The higher energy level needed for the re-ordering / crystallization process can be achieved by:

1] <u>thermal energy</u> – Temperatures in excess of 550deg.C are required to convert the amorphous oxide into crystalline oxide [16,17] Increase of DCL has been reported in life tests at temperatures above 100degC [2] on samples with observed intensive crystallization. .

2] <u>high electrical field</u> - high electrical field itself is NOT considered as an potential crystal growth risk factor under the normal application conditions experienced by tantalum capacitors. Nevertheless, if we consider the electric field in addition to the thermal energy, the combination of voltage and temperature creates a higher total energy and a higher crystal growth acceleration factor. In practical and long term experience no new failure mechanisms are created on CWR MIL tantalum capacitors tested in accelerated conditions at 85degC and voltages up to 1.528 x Vr per Weibull screening MIL-STD-55365.

Limitations of DCL increase

Based on many years of experience and research we can see that the increase in DCL on samples with visually observed crystals (after DPA) is related to the following conditions:

1] **ambient temperatures above 100degC**, as per the earlier discussion, some activation energy is needed to initiate the process of DCL increase.

2] **tantalum capacitors with rated voltage above ~25V**. The presence of large crystals has been observed mainly in thicker dielectrics over approximately 100nm that are used with capacitors rated above 25V.

3] **crystals do not necessary lead to an increase of DCL**. Recent findings confirms that the crystal phase of Ta_2O_5 is even less conductive than the amorphous dielectric and it may not cause itself cause an increase of DCL. However the crystallization can be considered in conditions 1] and 2] as an accelerator of the other conductivity mechanism due to structure defects, mechanical issues etc.

Reliability considerations

It should be noted that tantalum capacitors are very reliable components, available specified to MIL standards up to Weibull C level (0.01%/1k hrs at 85°C, Vr, 90% confidence). This includes tantalum capacitors with rated voltages above 25V - levels where the growth of crystals can be observed. Tantalum capacitor technology has some unique features that positively impact the reliability and make tantalum capacitors the preferred choice for the most demanding missions:

- Tantalum metal has a very high melting point of ~2900degC, an important factor given that the temperatures experienced during vacuum sintering processes used for mechanical connection of powder particles and tantalum wire will reach between 1400-1700degC. Most general tantalum powder impurities (resulting from powder processes such as iron, nickel etc) will burn at such temperatures since their melting point is much lower. Hence <u>**sintering during manufacturing provides a very efficient cleaning function.**</u>
- Tantalum as an element belongs to the “noble metals” group – this means that it does not want to

react with other elements. Thus, in practice, tantalum **does not chemically react with impurities**. Instead, impurities create a structure defect (as shown in fig 3.) which can be considered as nuclei – potential site for "re-ordering" (crystallization) or vacancy as a charge trap (oxygen migration). Other capacitors technologies – such as aluminium devices with non-noble metal electrodes that react with impurities - will suffer many more instant failure sites, severely limitating reliability.

- Standard MnO_2 electrode systems feature a **self-healing mechanism** that provides an efficient process to self-heal defects in the dielectric. For more details see [7]
- **Continuous improvement** in tantalum powder and capacitor technologies have resulted in a significant reduction in the amount of impurities present. As can be demonstrated by tantalum manufacturers - today's tantalum capacitors are more reliable than ever before, and surge & life failures have dropped in proportion to the reduction in the amount of impurities present in tantalum powder – see Fig 4. and 5.

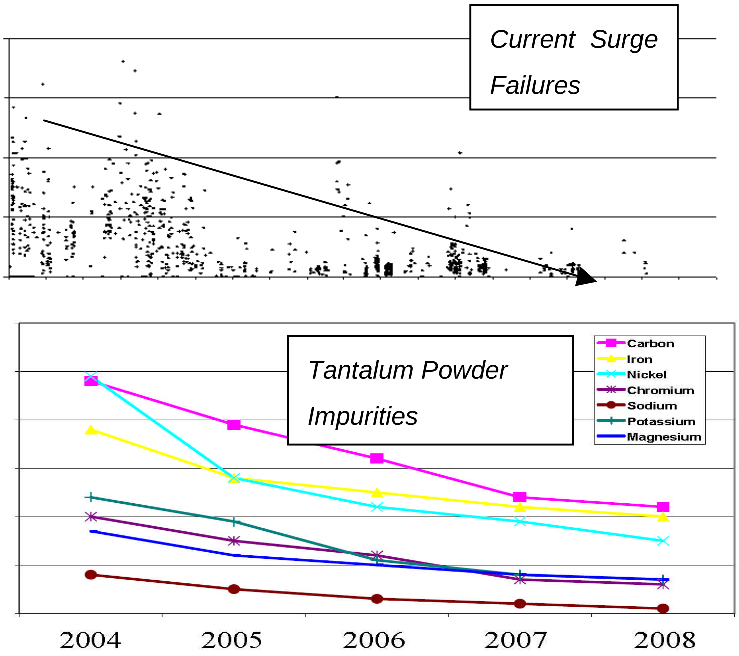


Fig.4. current surge failures trend (electrical surge testing at AVX) and tantalum powder impurities trend

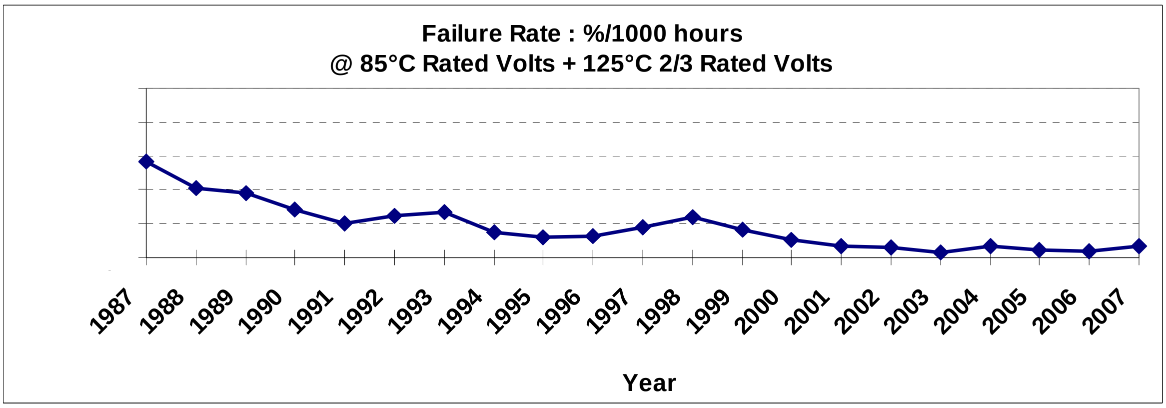


Fig.5. 85degC and 125degC life test failure trend, source: AVX

VERIFICATION – EVALUATION OF PRACTICAL EXAMPLE

Capacitors for analysis and evaluation

One extremely abnormally-behaving batch of D case tantalum capacitors 33µF 35V has been identified during 125degC life test 0.66xVr failing with high DCL. Another D33/35 “control” batch was randomly selected from the production for comparison. DCL behaviors of 24 samples from both batches at 125degC are shown in Figure 6. It must be said that the abnormal batch of D33/35 showed one of the worst results for DCL at 125°C ever seen in many years. This batch represents a unique challenge for analysis and study of field crystallization - the initially-suspected root cause for the poor performance.

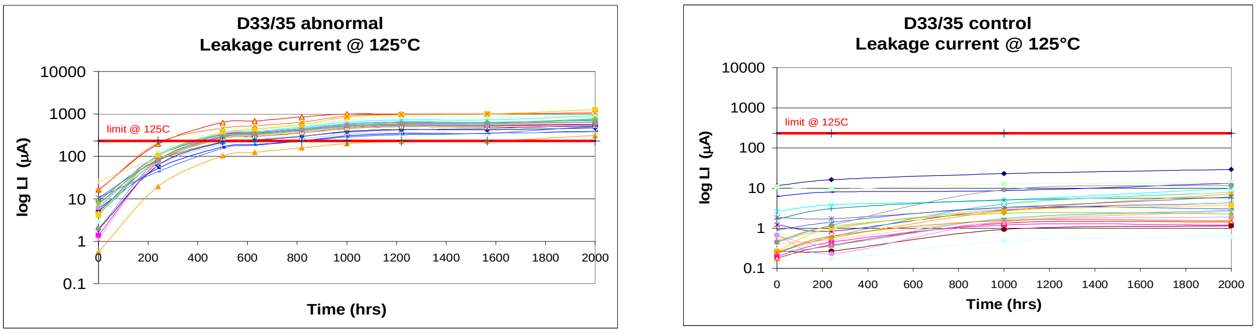
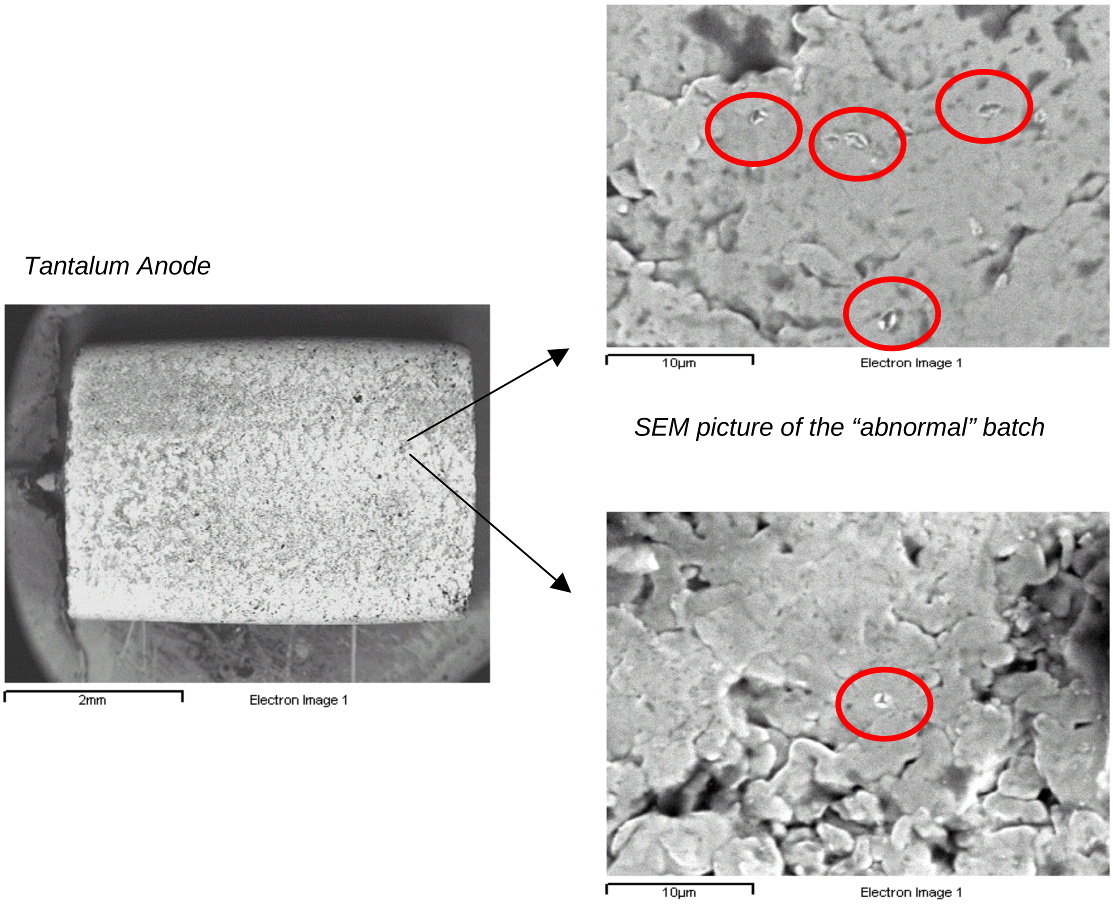


Fig.6. comparison of D case 33µF 35V DCL@125°C of abnormal and control batch

A fast increase of DCL@125degC within the first 500 hours was observed in the behavior of the abnormal batch. After this time a small increase in DCL and signs of DCL saturation above the specification limit occurred. The positive statement is that despite the high DCL and saturation trend, up to the date of writing this paper, no parts have experienced hard short circuits.

DPA analysis

Two samples from both batches have been subjected to etching and DPA analysis. SEM pictures from both batches are shown in Fig.7.


Tantalum Anode

SEM picture of the “abnormal” batch

SEM picture of the “control” batch

Fig.7. SEM analysis of a tantalum anode pellet from abnormal and control D33µ 35V batches

Field crystallization was found on the dielectric surfaces of both batches. However the level and density of field crystallization on the “abnormal” batch was significantly higher. It was more difficult to find the crystals in the “control” batch.

Study of manufacturing history

The next logical step was to compare the manufacturing data of both batches, especially at operations where DCL values are measured and analyzed. The first process where voltage is applied in cold and hot conditions to the capacitors is Pulse Age. Pulse Age together with Ageing is considered to be the first indicator of the DCL batch quality. Capacitors are then subjected to hard surge current screening and measurement of DCL and Short Circuits. Fig.8. shows the performance of the “abnormal” batch during these manufacturing processes in comparison to the other batches of D case 33µF 35V.

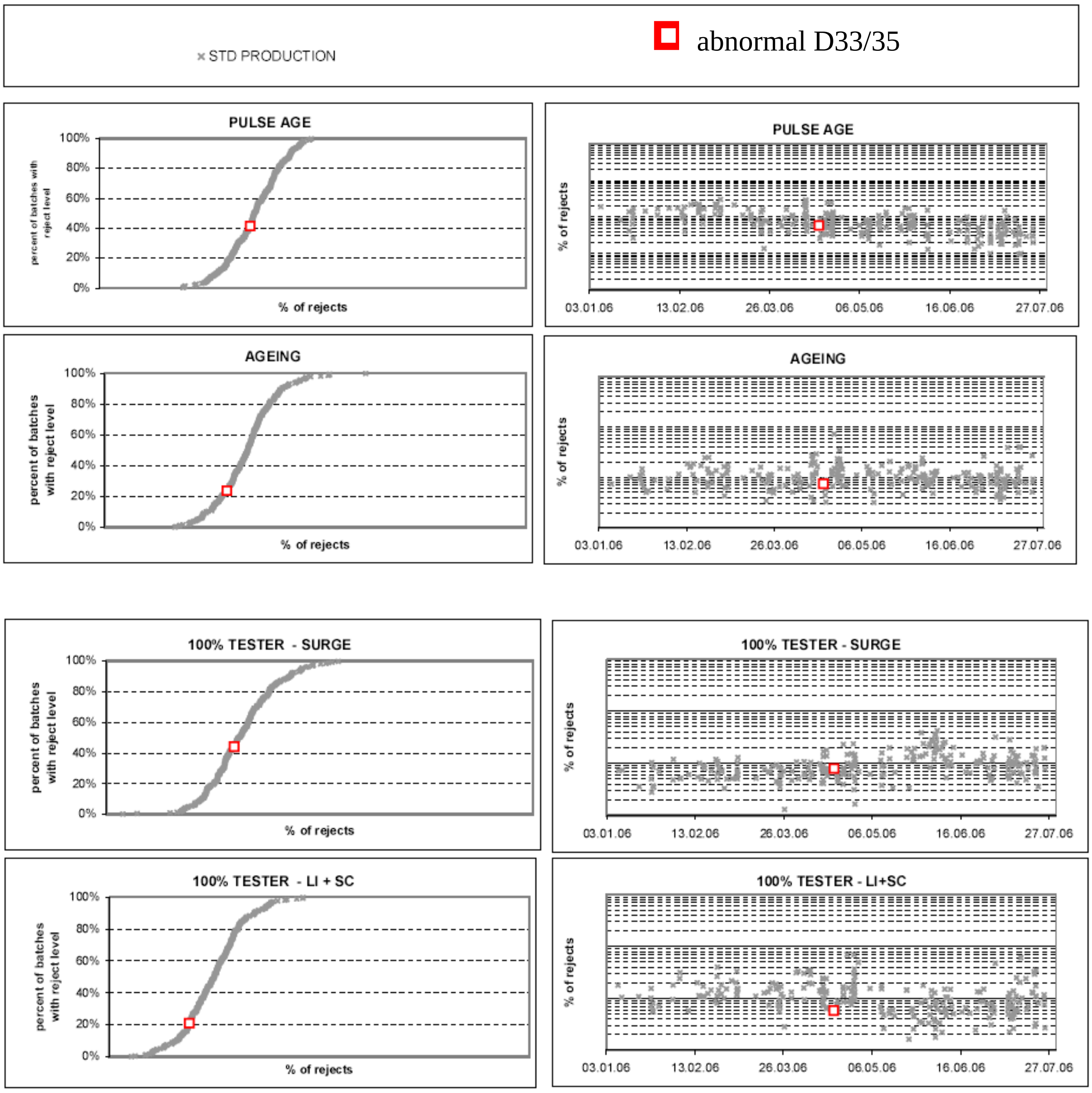


Fig.8. manufacturing history of the "abnormal" batch (LI = DCL, SC = Short Circuit)

As visible in figure 8. the abnormally-high DCL batch that failed life testing at 125degC did not show any indication of abnormal behavior during the manufacturing process. On the contrary, considering DCL and SC absolute values it was among the better production batches.

Figure 9 shows the DCL performance of the "control" batch in the manufacturing process.

The manufacturing history shows inferior DCL and SC performance for the "control" batch compared to the "abnormal" batch.

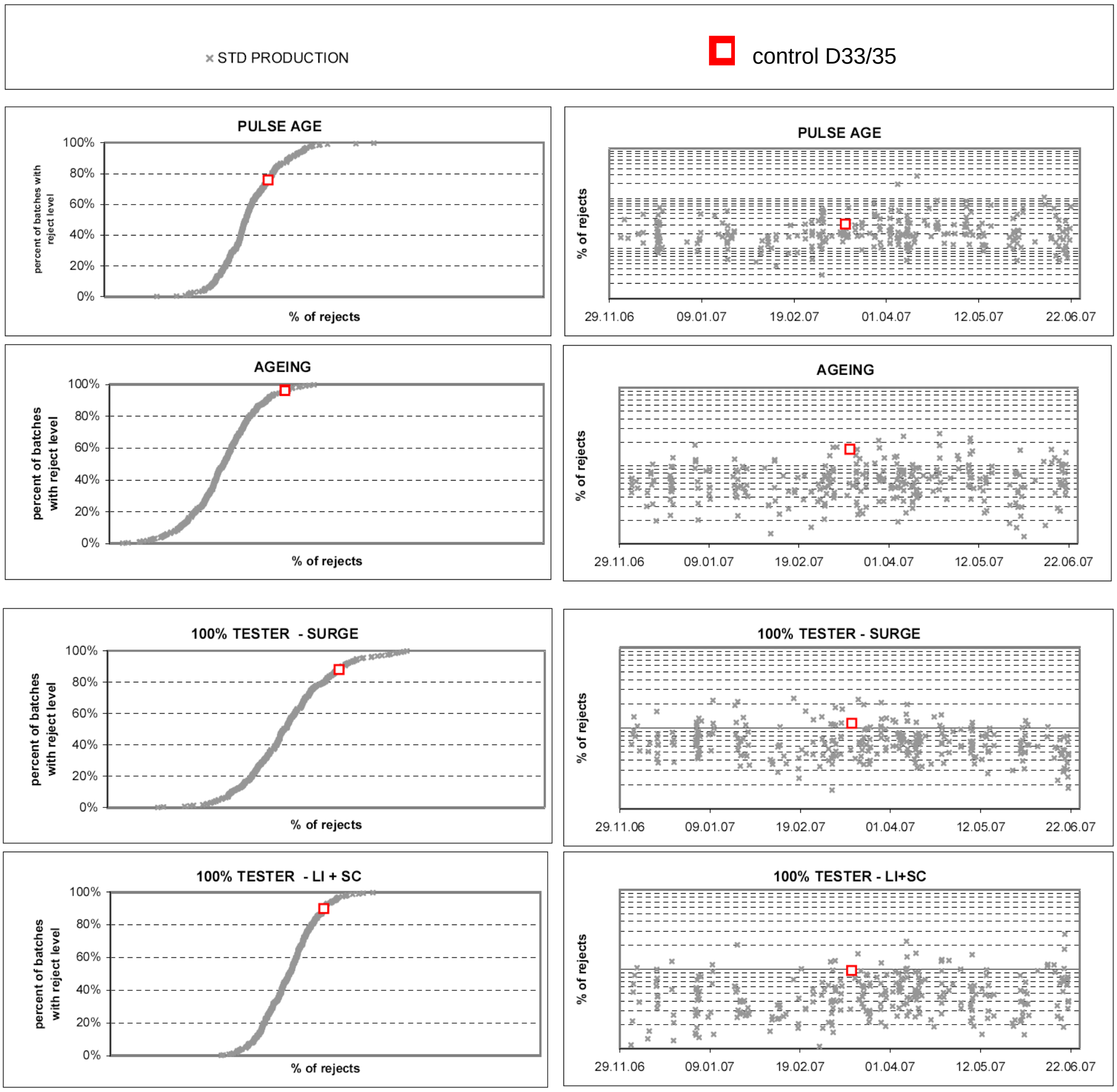


Fig.9. manufacturing history of the "control" batch

It is evident based on the information in figures 8 and 9 that **the abnormal batch could not be identified during manufacture using standard techniques.**

Weibull testing

Both the abnormally-behaving batch and the control batch were subjected to Weibull testing at 85degC and 1.5xVr voltage acceleration Fig10.

Batch	Beta	Failure Rate	Rated Voltage	BI Voltage	Stress Factor	Acceleration Factor	Start Qty	Test Qty	Failures Time 0	Time 1	Failures Time 1	Time 2	Failures Time 2
control	0.24	0.0057	35	52.5	1.5	11923.2626	957	780	177	2.25	243	68.25	317
abnormal	0.17	0.0043	35	52.5	1.5	11923.2626	951	795	156	2.25	233	58.25	285

Fig.10. Weibull statistical results for abnormal and control batches

Weibull tests showed slightly better results for the abnormal batch in when considering Failure Rate and Beta parameters. It should be noted that the D case 33µF 35V is outside the MIL CV matrix and thus the results and correction / acceleration factors can not be guaranteed. Nevertheless, the results show that the **abnormal batch behaved "normally" at 85degC, and therefore this batch can be considered to be at least as <u>reliable</u> as the other batches at this temperature, even with acceleration as high as 1.5xVr.** These findings validate the referenced statement in first section of the paper that:

1] the crystal growth occurs at temperatures higher than 100degC; and

2] voltage vs temperature acceleration 85degC and 1.5xVr does not generate a new failure mechanism, ie it does not exceed the critical activation energy even in the case of abnormal batch**.** In accordance to our Weibull results we can state that the **parts failing with high DCL at 125degC are still capable of reliable operation at least up to 85degC.**

Comparison with lower voltage parts

The next issue to be addressed was to confirm that the field crystallization occurs in layers thicker than about 100nm – which would mean that capacitors rated for use below 25V should not experience crystallization. Is it possible to identify 16V capacitors with high DCL at 125degC life test issues? Two batches of D case 150µF 16V products with DCL values approaching the specification limit after 2000 hours at 125degC have been found. See Fig. 11.

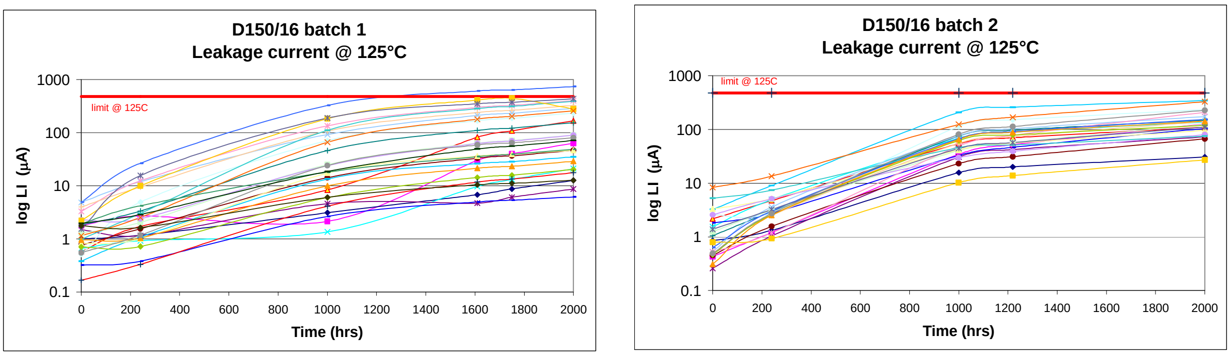


Fig.11. DCL increase in 125degC life test on two "edge" D150/16 batches

The parts with highest DCL values from both batches have been selected for DPA and surface analysis – see Fig.11.

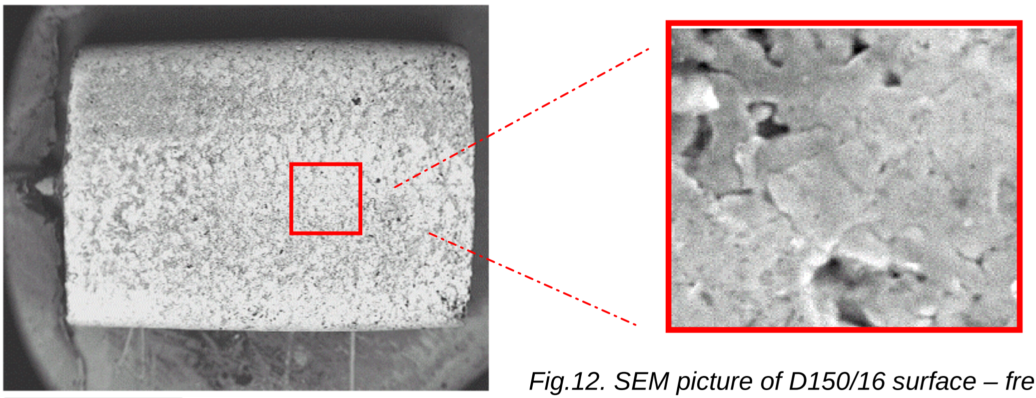


Fig.12. SEM picture of D150/16 surface – free of crystal phase

There have been no signs of field crystallization found during the DPA of D150/16 batches with abnormally-high DCL behavior. Based on this we can conclude that: **there is no indication that the D case 150µF 16V high DCL@125degC parts would tend to show field crystallization failure mode.** In the case of “abnormal” D 150/16 batches we can still observe an increase in leakage current with a trend towards saturation after 1000hours – as we can see, this is similar trend to the case of the abnormal D33/35 batch just at a lower DCL ratio compared to the specification limit.

Discussion

The observation on practical results and evaluation of D33/35 and D150/16 batches leads us to the following findings:

1] field crystallization can not be the only driving process responsible for DCL increase during 125degC life test;

2] in the case of higher voltage parts, field crystallization can also cause some increase in absolute DCL at 125degC values. This may also be in agreement to conclusions of Pozdeev-Freeman [14] about two failure mechanisms interacting – field crystallization and oxygen migration.

V-I curves measured for abnormal batch samples with a clear identification of field crystallization (Fig 13.) has shown some random current fluctuations - effects caused by a fluctuation of surface potential and electron mobility. The samples were also subjected to DCL vs temperature measurement. See Fig.14.

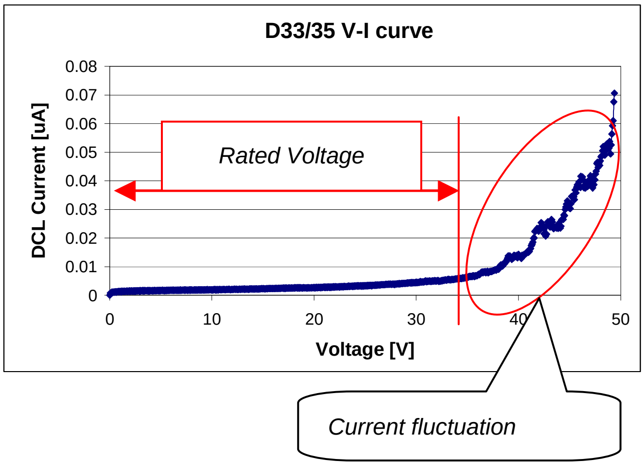


Fig.13.V-I characteristic of abnormal D33/35 samples

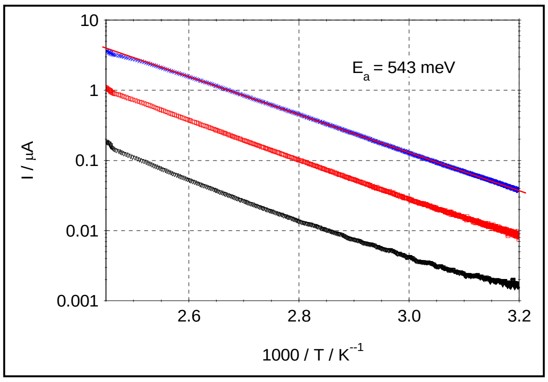


Fig.14 DCL with temperature dependence of three different samples – minimum, mean and maximum of abnormal D33/35 – samples 1/T vs Log I chart.

The DCL behavior of D33/35 units with crystallization has been confirmed to be due to the Poole-Frenkel mechanism –the same type of mechanism as measured in the case of capacitors without field crystallization. In this instance it is simply an abnormal batch so it reaches higher DCL absolute values.

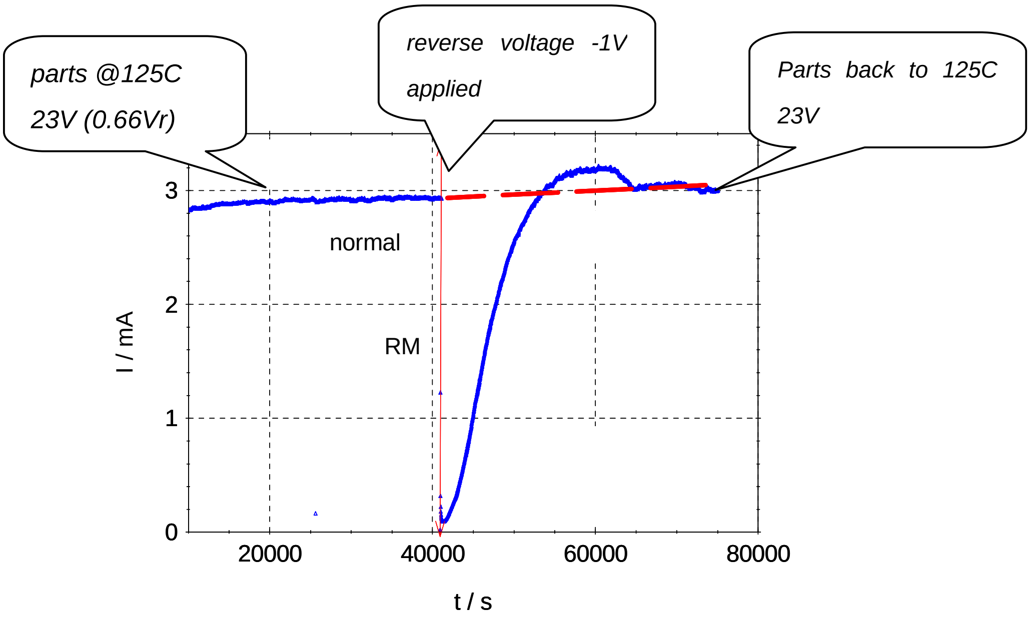
This observation suggests that since we cannot attribute the increased DCL behavior to crystallization, we need to consider the conductive mechanism of the crystal phase, which can result in more of the structural defects being induced nearby the crystals. This may increase the current due to the Poole-Frenkel mechanism through the dielectric.

The visually observed crystals may not cause a direct increase in DCL due to their conductivity, as generally crystal (bulk) / surface / edge conductivity are not expected to be of the Poole-Frenkel type as measured in the case of Fig.14

Sikula [10] also measured VA characteristics for thick insulating layer (d >100 nm e.g. >25V tantalum capacitors) and observed that at low electric fields of E < 100 MV/m leakage current has a current Ohmic component with conductivity better than $\sigma = 10^{-12}\ \Omega^{-1}\text{cm}^{-1}$.

One additional observation was found as a result of the discussion – 10 samples of the abnormal D33/35 parts with high DCL @ 125degC were put at reverse voltage -1V during the 125degC life test and then returned to the original voltage. The DCL dropped after the reverse voltage and then within six hours it slowly approached back to its original values. See Fig.15.

The fact that DCL of the abnormal batch returned to the “normal” DCL level after the reverse voltage and then it slowly returned back suggest that **the process responsible for the high DCL is REVERSIBLE and thus it may not be caused by increased conductivity of the crystal phase**. Such behavior can be described more likely by diffusion or charge movement mechanisms.



parts @125C 23V (0.66Vr)

reverse voltage -1V applied

Parts back to 125C 23V

Fig.15. DCL with time on the abnormal D33/35 batch a] 125C,Vc b] reverse voltage c] back to 125C, Vc

Effect of surge currents

While writing this paper one more question was raised: “Can a hard surge current have an effect on reliability and DCL results of the abnormal batch, eventually causing short circuits during life testing ?”

Such testing and analysis is out of the main scope of this paper, and there were not enough samples left from the abnormal batch of D33/35 products to complete any meaningful surge testing. However, long term experience with tantalum capacitor technology shows that there is no relationship between the surge current failures and life failures as the physical basics of the failures are different. Surge current failures versus Weibull screening have been rigorously tested by Teverovsky, NASA [12] who concluded in his paper:

- life test at 125degC and V=1.5Vr up to 250 hours resulted in statistically significant failures, but no differences between hard surge and non-surged groups were observed
- hard surge testing was not a significant factor in life testing. The life test did not degrade surge current breakdown voltages. For this reason, B and C surge testing (before and after Weibul test) in accordance with MIL-PRF-55365 can be considered as equivalent
- at relatively low voltages (applications with derating) solid tantalum capacitors can withstand a practically unlimited number of high current cycles with amplitudes exceeding hundred amperes. This suggests that there is a certain threshold voltage below witch surge current failures do not occur.

Summary

1] One abnormally behaving batch D33uF 35V has been identified with significantly higher level of crystallization compare to the control batch. This batch behaved identically during the manufacturing process to the other batches in statistically reasonable production sample. The batch showed high DCL increase at 125degC life test whereas at 85degC with 1.5xVr acceleration it did not show any signs of deterioration compare to the control batch.

2] DCL measurement and testing during the manufacturing process can not be considered as an universal indicator of crystallization sites or a measure of potential crystallization during high temperature operation life as demonstrated in our experimental case. These findings emphasize the need for complete product characterization and load testing for mission-critical applications such as aerospace, military and medical.

3] Field crystallization may not be the only nor the main driving process responsible for DCL increase during 125degC life testing. Other mechanisms, such as Oxygen or other ions migration, may present.

4] The exact conductivity mechanism related to the crystal Ta_2O_5 phase is not yet fully understood. However the latest findings suggest that the crystals themselves are good insulators with very limited conductivity: also surface/edge conduction may not present. However the crystallization can be considered as an accelerator of the other conductivity mechanism in temperatures above 100degC and dielectric thickness over 100nm due to the structure defects, mechanical issues etc.

5] The high DCL capacitors at 125degC life testing with visually observed Ta_2O_5 crystals shows the Poole-Frenkel conductivity mechanism.

These studies and conclusions are based on limited statistical data and one exceptional batch. Further investigation is necessary to confirm the conclusions on a larger sample to provide validity to these findings.

Conclusion

Based on the presented observation and analysis we can conclude that despite the fact that field crystallization is usually cited as the tantalum capacitor failure mode, it may have only a limited impact on the practical usage of tantalum capacitors by end users.

Field crystallization may become a factor under these main conditions:

- high voltage capacitors above ~ 25V
- testing temperatures above 100degC

Capacitors with potential crystallization sites may not show any deterioration of reliability at operating temperatures below 85degC. This has been verified on samples with high crystallization sites using Weibull testing at 85degC with a 1.5xVr acceleration factor. Even in the case of the batch of D case 33μF 35V capacitors with the highest DCL failure rates at 125degC life ever seen in our history, DCL did not increased to achieve catastrophic values or result in short circuits, and it saturated during the life test. If standard 50% derating procedures for tantalum capacitors operating at 125degC had been applied, this batch may not have been considered as problematic for end users as the DCL values would have been significantly lower.

References

[1] Reliability and Critical Applications of Tantalum Capacitors Yuri Freeman, at col. KEMET Electronics Corporation. CARTS Europe 2007

[2] Failure mechanism of solid tantalum capacitors, Goudswaardand f. J. J. Driesens
N. V. Philips, Eindhoven, Netherlands. Electrocomponent Science and Technology 1976, Vol. 3, pp. 171-179

[3] Sikula, J et.al, Niobium Oxide and Tantalum Capacitors: Leakage Current and M-I-S Model Parameters, CARTS USA, Albuquerque 2007

[4] Sikula, J et.al, Charge Carrier Transport in NbO and Ta Capacitors in Temperature Range 100 to 300 K,

CARTS Europe, Bad Homburg 2006

[5] Sikula, J et al., Tantalum Capacitor as a MIS Structure; CARTS USA 2000, 102-106

[6] Jackson, N.F. Field crystallization of anodic films on tantalum, Allen Clark Research Centre, Towcester, Northants., UK, Journal of Applied Electrochemistr,Volume 3, Number 2 / May 1973 ISN 0021-891X (Print) 1572-8838 (Online)

[7] Zednicek T., Voltage Derating of tantalum capacitors, AVX technical paper, www.avx.com

[8] Pozdeev-Freeman, Y. New aspects of Crystallization in Amorphous Ta2O5 Films, CARTS USA 2000, Huntington Beach California, Pg 140-145

[9] Ezhilvalavan and Tseng., Conduction mechanisms in amorphous and crystalline Ta2O5 thin films, Journal of Applied Physics Vol 83, Number 9 May 1998

[10] Sikula, J et al., Niobium Oxide and Tantalum Capacitors Leakage Current, Restoring Voltage and Reliability; CARTS USA 2008

[11] Gmelins Handbook

[12] Teverovsky, A. Effect of Surge Current Testing on Reliability of Solid Tantalum Capacitors, CARTS USA 2008

[13] Samsonov, G.V., Handbook of Physico-Chemical Properties of Oxides, Moscow, Metallurgia. 1978

[14] Pozdeev-Freeman,Y., Tripp,T., Major Degradation Mechanisms in Tantalum and Niobium Based Capacitors, CTI, 2008

[15] Vermilyea, D.A., J Electrochem. Soc. 104 (1957) 542

[16] Young,L., Anodic Oxide Films, Academic Press (1961), p.116

[17; Pawel RE and Campbell J.J.,Journal of Chemical Society, Nov.1966,p.1204