

Niobium Oxide Capacitors Brings High Performance to a Wide Range of Electronic Applications

W. Millman

AVX Limited, Tantalum Division, Paignton, Devon, TQ47ER, UK.

Phone: +44 1803 697294 Fax: +44 1803 697390 E-mail: william.millman@eur.avx.com

T. Zedníček

AVX Czech Republic s.r.o., Dvorakova 328, 563 01 Lanskrout, Czech Republic

Phone: +420 467 558111 Fax: +420 467 558128

Abstract

In the short period of time that Niobium Oxide capacitors have been available it has attracted a number of application design-wins where the technology has provided a perfect fit. First seen as a direct lower cost replacement for older tantalum capacitor designs it has in fact found a strong customer base within the latest designs of consumer and automotive products. This paper will explain where the performance and safety features of the niobium oxide technology have been recognised as the key parameter in the design of these latest electronic equipments and devices.

Introduction

It has been many decades since a totally new material has become established within the capacitor family of dielectrics. The main thrust for the development of niobium oxide capacitors was the fear of availability of tantalum in the late 1990's. This prompted a great deal of research into alternate materials that provided similar performance features. The most obvious was Niobium metal. Niobium is the sister element to tantalum sharing many of the key materials physical and chemical attributes and is in plentiful supply. It even had some prior history as a capacitor material with developments in the former Soviet Union, for both commercial and military applications. It suffered however from two major drawbacks. Firstly it shared a common supply chain in that the only sources at the time of capacitor grade niobium powder were also those that supplied tantalum. The other was that it was inferior in performance as regards to reliability, voltage range and limited upper operating temperature. Despite numerous product launches based upon niobium since then, none were found to provide a satisfactory solution. Another alternate material was niobium oxide.

Niobium Oxide is a most unusual material. Better described as a ceramic it has the bulk resistivity comparable to many common metals. Even more unusual is its ability to form a stable high quality dielectric film (Nb₂O₅) upon its surface by various techniques including electro-anodisation. Further it is possible to use many of the existing electrochemical processes and equipments utilised in the manufacture of tantalum capacitors. However the most valuable asset was in the finished capacitors performance and this paper will explore how this has been fully utilised within some of the most demanding of applications.

Reliability Considerations

Increasingly the choice of the most suitable capacitor technology goes well beyond simple circuit function or cost. Apart from the expected need for fit form and function designers must increasingly consider the impact of component failure. The impact of failure is also dramatised by the nature of the failure, more so even that the failure rate itself. A 'soft' failure causes little or no attention outside that of the

component supplier and the equipment maker. Any level of failure that creates a risk of burning, smoke or heating attracts a whole different level of attention. The recent world wide attention given to the risk of notebook and cell phone battery overheating is a testimony to this.

Reliability is increasingly seen as a key differentiator in the market for high value items such as automobiles and high end consumer electronics such as flat panel televisions. In both cases increasing numbers of discrete components are being applied to provide improved functionality and often in the case of automobiles increased safety. These complex electronic solutions have many hundreds of capacitors within them, even thousands in the case of flat panel televisions. Reliability and the consequences of a part failure are critical to the designer's choice of capacitor technology. Warranty costs are also a strong motivation for the designer to put the development of more reliable electronic parts at the top of their wish list.

Failure background

Firstly any capacitor technology has an established failure rate and is described by the supplier with a series of graphs that detail what the life determinators will be, such as operating temperature, voltage derating, circuit impedance and the like. Tantalum capacitors are well known for their very high reliability but equally are known for the failure mode being short-circuit or high dc leakage. The consequences of such a failure will largely depend upon the fault current available. However, it is not an exact science so the risk of over heating exists. The emergence of tantalum capacitors with an inherently conductive cathode system which replaced the manganese dioxide counter-electrode went some way to reduce the potential for ignition at failure. The manganese dioxide was an excellent aid to promote the self-healing of a damaged dielectric but in the event of a thermal run-a-way also provided oxygen to the fault site fuelling the risk of over-heating. Even in the case of the tantalum polymer the failure mode remained the same but the immediate consequences were mitigated. Aluminium capacitors on the other hand are not considered generally to have high reliability and its reliability is largely governed by the operating temperature. This is due to the counter electrode system being a liquid electrolyte and therefore subject to drying out. This technology has also been subject to recent well published issues when gas retardants failed to prevent the generation of H₂ gas during its operation with deleterious consequences. This was however an exceptional case and this technologies inherent failure mode is to lose capacitance, show increasing ESR and ultimately wear out as an open-circuit. MLCC technology has increasingly been adopted in capacitance values that would have been the traditional territory of solid and wet electrolytic capacitors. These higher capacitances have been achieved through combining thinner dielectric layers with more and thinner electrodes, often running into hundreds. These too can fail short-circuit and with such large metal loadings over heat under the right conditions. These failures are usually more associated with mechanical damage to the part causing fractures within the capacitor body structure. So it is clear there is no ideal capacitor solution to the potential of over heating.

Niobium oxide capacitors are examined in respect of their potential risk of ignition in various over-voltage and high current fault conditions and found to be very robust devices. The foundation of this performance is based upon three fundamental principles – low base material flammability, a high resistance failure mechanism and a higher breakdown voltage.

(1) Influence of the capacitor material on ignition potential

A closer examination of the behaviour of the various materials available to the makers of solid electrolytic capacitors revealed some interesting figures. When tantalum, niobium and niobium oxide powders were characterised for Minimum Ignition Energy (MIE) and burning rates a clear difference was observed. The niobium oxide being already an oxidised material required substantially more energy to ignite and once ignited burnt at a very low rate when compared with either of the metals, tantalum or niobium. See Fig 1. Note that the differences between the metals and the oxide are in the range of an order or more. References [1.] [2]

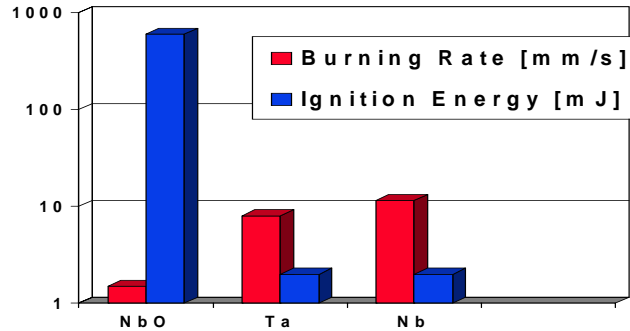


Figure 1: Flammability measurements

Influence of Dopants on Material Flammability

A study of the energy release from NbO after ignition was undertaken with a view of characterising the behaviour. Further we wished to examine the potential to modify its behaviour in such a way as to have a slower release of the conversion energy. Various NbO powders were submitted to TGA analysis and its thermal signature captured. See Figures 2 and 3. Note that the NbO burns once the temperature is in excess of about 415°C. This is a quite a vigorous reaction, heat is evolved (brown line, scale on RHS of plot) and there is a noticeable rise in temperature (pink line). A deliberately doped NbO material behaves very differently. The doped material did not become 'burnt' until the temperature was in excess of about 500°C, the reactions were less dramatic and appears to be 2-stage reaction. Note that the slower the release of energy the more likely that the heat will be safely dissipated by the capacitor body and have less potential for ignition. The peak temperature required in order to initiate the energy release is also significantly increased again reducing the potential for ignition.

Another marked difference was in the colour of the material after ignition. NbO burns leaving a white (Nb_2O_5) deposit; the doped materials produce a yellow material.

The overall weight gains were similar at about 22%, corresponding to about 14.5% oxygen in the original material that is an Nb:O ratio of 1:1.

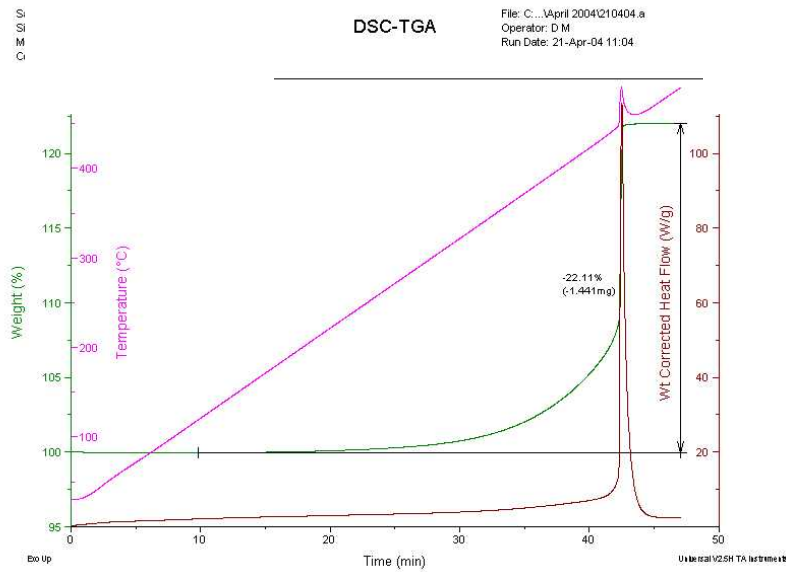


Figure 2: NbO non-doped TGA analysis

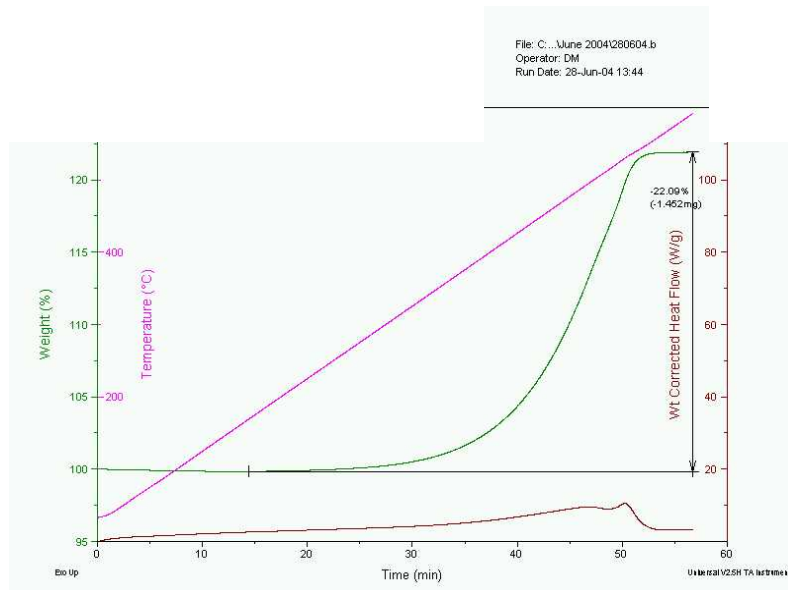


Figure 3: Doped NbO TGA analysis

The next step was to measure the time taken for the conversion process from NbO to Nb₂O₅ in a powder ‘fire train’ test for comparison purposes. This is a standard flammability test where a powder is laid out in an inverted V shape pile of pre-determined dimensions and from which one end is ignited. The time taken for the all of the material to burn (convert) i.e. travel down the entire line of powder is measured in

minutes and seconds. The doped material took approximately eight (8) times longer to complete its conversion process illustrating that the energy release curves shown by the TGA analysis did demonstrate itself as a much slower energy release system.

The potential benefits to the capacitor are being studied and it is hoped that the slower release of energy and the higher temperature required to initiate the conversion process will further reduce the potential for over-heated components and ignition of failed components

(2) High Resistance Failure Mechanism

The next step was to measure the electrical resistance of a shorted capacitor deliberately created by application of an over-voltage condition. A current limit was applied to prevent Joule heating with the various capacitor technologies under test. See Figure 4.

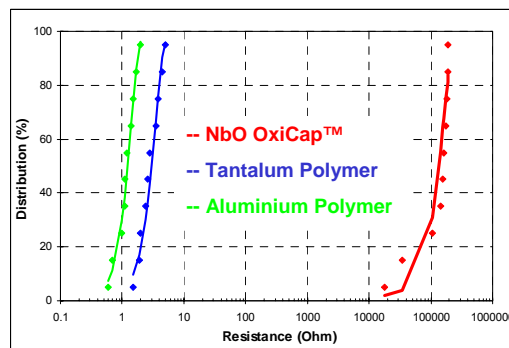


Figure 4: DC resistance after over-voltage breakdown

Figure 4 shows that while the polymer technologies have shorted to a narrow range of single digit ohms the niobium oxide dc resistance was in the order of tens to hundreds of ohms. A failed capacitor is effectively a resistor and if large currents are available and low resistances exists, the potential for over heating exists and in some cases ignition. The mechanism that creates this high resistance failure mode for niobium oxide capacitors has been well described in other technical papers [3] [4] [5] and involves the generation of a resistive phase of NbO₂ at the point of failure in the dielectric due to localised heating and is well described as a ‘self-arresting’ mechanism. See Figure 5

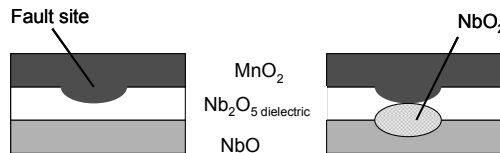


Figure 5: Self Arresting Mechanism - Formation of NbO₂

Long Term Stability of NbO2

The major benefit niobium oxide brings to the failure mode is the natural limitation to the fault current as a result of the high resistance breakdown path. This however has to be examined as to how stable this phase is and what could prompt the reduction of its resistance that could re-introduce a risk of ignition. To examine the behaviour of NbO2 it was decided take failed capacitors over a range of levels of resistance created by over-voltage breakdown and submit them to various life testing both with and without the presence of humidity.

The test graphs below Fig 6 and Fig 7 show the post BDV (breakdown voltage) resistances measured as Insulation Resistance (IR) in ohms and plotted as a series with the lowest initial value on the left hand side and the highest on the right hand side, allowing any change in resistance related to its initial value to be seen more clearly.

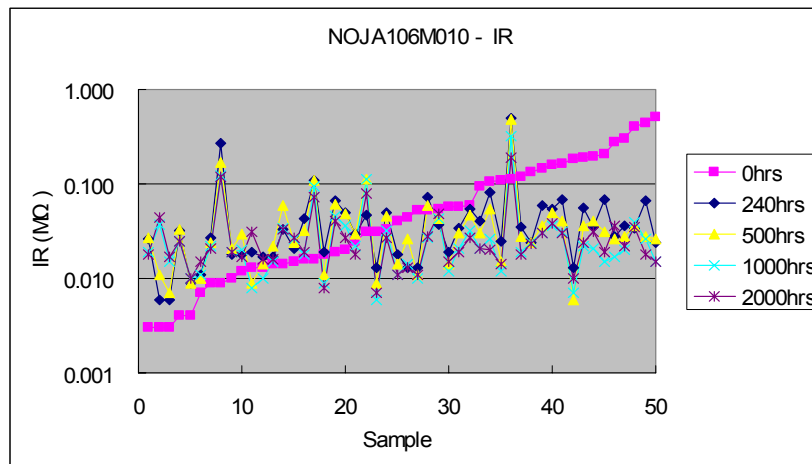


Figure 6: IR Change on 85%RH/85C Vr 2000hrs test n=50

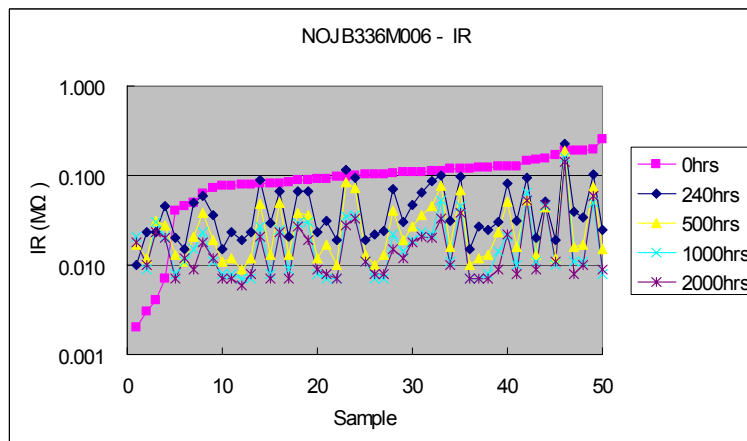


Figure 7: IR Change on 85%RH/85 Vr 2000hrs test n=50

The test graphs above show that in the long term tests on two different codes the insulation resistance actually coalesces around a central band of between approximately 10kohms and 100kohms. This provides assurance that a failed components condition is unlikely to radically change over time. It also is suggestive of the moisture in the component providing multiple parallel paths which would be very unlikely to support high current flows in any case.

A similar set of tests were also conducted with failed parts submitted to 1000 hours of room temperature application with full rated voltage applied. See Figures 8 and 9 below.

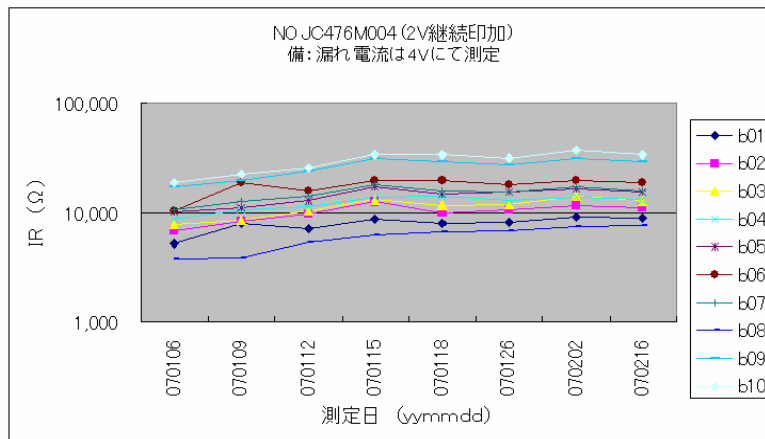
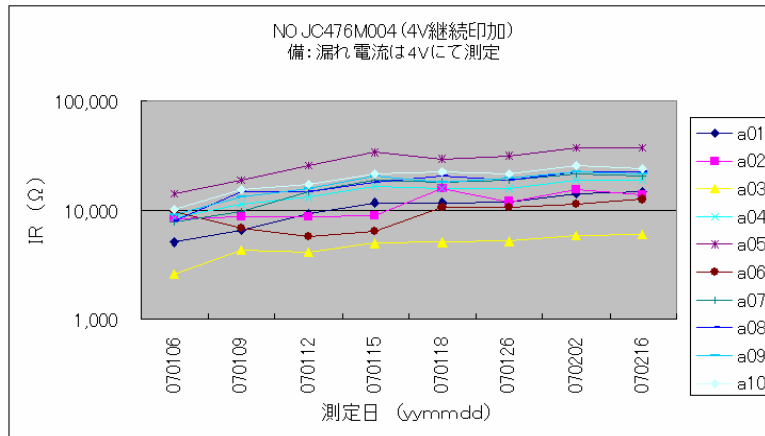


Figure 6 & 7: IR Change on 25c Vr 1000hrs test n=10

The results were a contrast to that previously conducted in a humidity environment. In this case the insulation resistance actually increases with time and changes from approximately an average post breakdown resistance of 10kohms to 20kohms post test.

(3) Breakdown Voltage Investigation

A set of comparison tests were conducted to determine the relative levels of breakdown voltages for various capacitor technologies. See Figures 8 below.

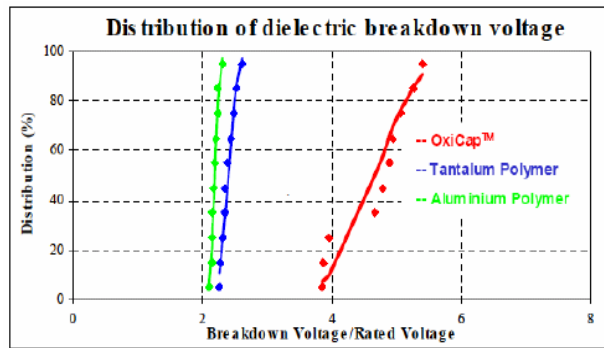


Figure 8: BDV comparison in current limit mode

The level of voltage needed to create a breakdown in niobium oxide capacitors of the same voltage rating was clearly substantially higher than in the other technologies. The breakdown voltage levels for a given case size and capacitance value on three different voltage rating of 4, 6.3 and 10v of niobium oxide capacitors is shown in Figure 9 below.

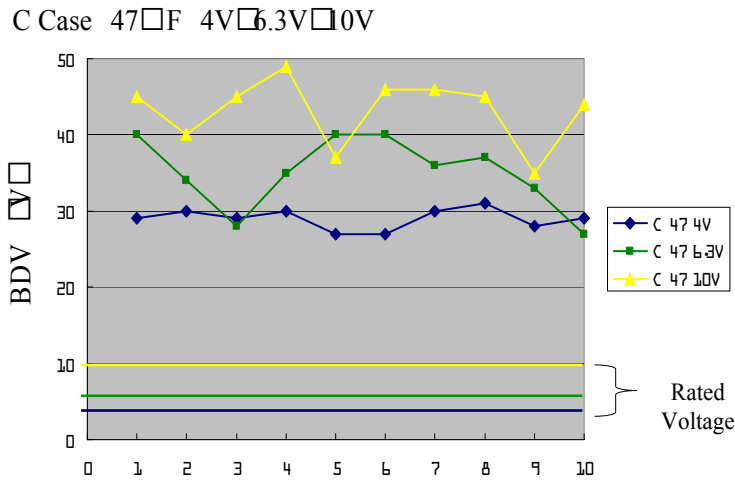


Figure 9: BDV comparison of different rated NbO capacitors

The level of voltage needed to be applied in order to generate a breakdown is clearly related to the rated voltage of the capacitor and it is also substantially above the rated voltage of the capacitor. These results were conducted with a current limit in place to

prevent subsequent Joule heating. Another series of tests were conducted on a large 6v rated niobium oxide capacitor this time with and without deliberate current limitation in order to understand the relative impact of current availability on BDV.

Table 1

Sample No.	B.D.V. [V]
	NOJD227M006
1	25.80
2	26.40
3	27.10
4	27.20
5	27.30
6	28.00
7	28.10
8	28.30
9	28.60
10	28.90
11	29.40
12	29.70
13	30.10
14	30.20
15	30.20
16	30.40
17	31.10
18	31.60
19	31.80
20	31.80
21	32.50
22	32.80
23	33.70
24	34.60
25	35.70
median	30.30
stdev	2.19

Table 2

Sample No.	B.D.V. [V]
	NOJD227M006RWJ
1	11.18
2	12.96
3	10.82
4	12.84
5	10.25
6	13.15
7	12.89
8	12.28
9	11.88
10	14.01
median	12.56
stdev	1.18

Table 1 and 2: BDV in current limit and unlimited mode

Again in the current limited case we saw the BDV of a 6v rated niobium oxide part have a very high margin of safety with typically over 30v required. When parts from the same population were tested with no deliberate limitation of current we saw the BDV reduced but still maintain a very high level of margin i.e. twice the rated voltage of the capacitor.

Why should this be of importance to designers? Many customers are already satisfied with the reliability and safety of a niobium oxide capacitors but an examination was required of the subsequent behaviour if the input voltage of a regulator was to appear across the capacitor on its output stage should the regulator fail. The application conditions at the output stage of most voltage regulators are relatively benign, with limited potential for over-voltage or current surge. In such cases limited voltage derating is applied by the designer. But should the regulator fail, for what ever reason, then the input voltage and current availability changes dramatically. A voltage well in excess of the rated voltage of the capacitor would appear across it and should it breakdown then a large fault current would be available.

Here again we see the relative advantage in the use of niobium oxide capacitors in such applications in its ability to withstand levels of voltage above its rated condition. And

even if it were to fail the subsequent thermal damage would be limited due to the self-arresting mechanism and the low flammability of the base capacitor materials.

Burning Investigation

Given the potential for voltage regulators to fail, causing the much higher input voltage to appear across the output capacitor, also with a large availability of fault current, it is necessary to examine the behaviour of various capacitor technologies. The same group of capacitors (Fig 8) that had been deliberately short-circuited by application of a current limited over-voltage condition were chosen for this test. The voltage was slowly raised and the current monitored. See Figure 10.

The V-I curve for the various technologies reveal a marked difference in behaviour

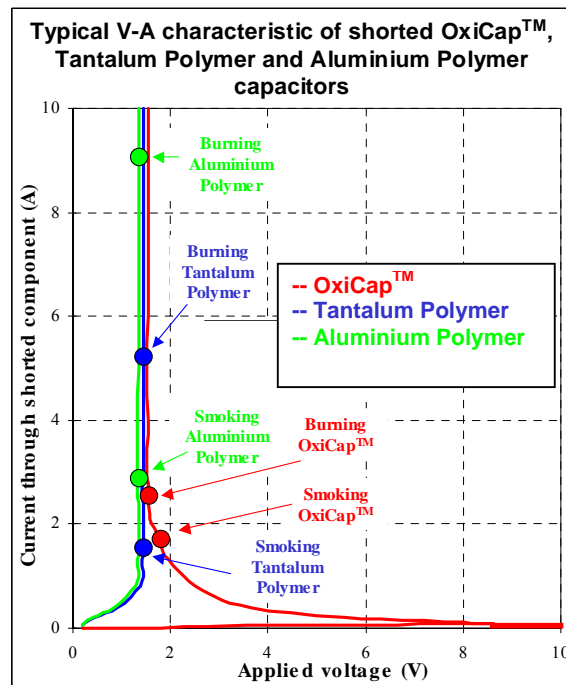


Figure 10: V-I Curve for different capacitor technologies

In the case of the two polymer technologies the early part of the V-I curve is best represented as being a resistor-like behaviour. Not only resistor-like but also that of a low value resistor as presented in Fig 4. with an ohmic value of approximately 1 to 2 ohms. Given this value it is quite easy even at low voltages to have a high level of power being generated. Indeed, at less than 2v applied the two polymer technologies begin to emit smoke as the Joule heating exceeds the capacitors bodies ability to safely dissipate the heat. Increasing the available current allows the heating to progress further.

In the case of the niobium oxide part no appreciable level of current is drawn even as the voltage applied is in excess of the capacitor rated voltage. This is also in line with the failure being characterised as a high-resistance type. Only when the applied voltage well exceeds the rated capacitor voltage does a current begin to flow and as in the case of the

other two technologies once it exceeds the ability of the part to safely dissipate the heat does the part begin to smoke.

Summary

The behaviour of various solid electrolytic capacitors was examined under extreme voltage conditions to evaluate their behaviour and potential to over-heat and possibly ignite. Three areas were focussed upon to better understand the opportunity to reduce the potential for ignition - base material flammability, the dc resistance value of the shorted-circuited device and the level of voltage above its rated voltage necessary to cause a breakdown.

The first benefit derived from the use of niobium oxide as a base material for a solid electrolytic capacitor is in the higher level of energy required to ignite the material and secondly the much reduced burning rate when compared with conventional metal choices. Further by applying various dopants to the compound it is possible to modify the manner in which the energy is released once under combustion as well as the energy level required to initiate it.

The largest single benefit in the use of niobium oxide is its ability to develop a high resistance failure mode in the event of electrical failure. This 'self-arresting' mechanism self limits the available fault current that can occur. The nature of this high resistance NbO₂ phase developed at the failure site was also assessed by long term life testing in both dry and humid environments and found to be stable.

In current limited voltage breakdown testing niobium oxide based capacitors exhibited a higher voltage threshold before breakdown would occur than its metal based technologies. Even in BDV tests with high current availability the threshold voltage for breakdown to occur although lower were still much higher than that of the capacitors rated voltage.

Due to the nature of the lower dc resistance levels exhibited by failed metal-polymer capacitors it is possible for smoking and eventual burning of parts to occur at relatively low voltages if sufficient current is available. In the case of niobium capacitors this only occurs at voltages in excess of the capacitors rated voltage.

Designers particularly in automotive and consumer applications are increasingly focussed not just upon the expected level of component failure but the consequences of such a failure. Even in the case where a failure in another part of the circuit leads to an application of out-of-specification conditions the performance of the capacitor has to be examined. Under these circumstances more designers are choosing to adopt niobium oxide technology as generally the safer option. This is also the case in comparison to Aluminium electrolytic capacitors but for other performance features not covered in this paper [7].

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