

# EXTENDED RANGE NbO CAPACITORS THROUGH TECHNOLOGY AND MATERIALS ENHANCEMENTS

**S.Zedníček, I.Horáček, T.Zedníček, Z. Sita**

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

Phone: +420 465 358 126 Fax: +420 465 358 128

**Colin McCracken, William Millman**

AVX Limited, Long Road, Paignton,

Devon TQ4 7ER, United Kingdom

Phone: +44 1803697200 Fax: +44 1803697326

## ABSTRACT

A new family of capacitors based on Niobium Oxide has established itself in many applications. The initial series of these capacitors had some limitations in Capacitance per Voltage in a given case size compared with leading tantalum capacitors. Recent developments resulting from the technology enhancement of materials and processes, which increased anode Capacitance Voltage (CV) efficiency has enabled a new range of NbO product. The paper presents and discusses the performance and reliability of such capacitors and their lead-free solder and surge robustness features. This, together with the ability to use the parts at lower levels of voltage derating is a very vital alternative to ceramic and tantalum capacitors and thus brings benefits to designers of the current electronic equipments.

## INTRODUCTION

Niobium Oxide Capacitors have been successful in the market as an alternative to aluminum electrolytic, tantalum polymer and high CV ceramic technologies. The overall demand for these niobium oxide capacitors have grown every quarter since mass volume introduction in 2003.

The key features of the niobium oxide technology includes high resistance failure mode under operation conditions, higher ignition resistance, compliance with lead-free high temperature assembly, wide availability of materials and very good cost versus performance value. The key application areas today are personal computers and notebooks, the others include cellular phones, digital cameras, automotive and telecom.

There is a potential for further growth of NbO technology share by increasing of capacitors' CV

(capacitance times voltage factor) that will allow offerings of even higher capacitance in smaller packages.

## HIGHER CAPACITANCE THROUGH BETTER DIELECTRIC UTILIZATION

Solid electrolyte capacitors manufacturing from Niobium Oxide is in principles very similar to the Tantalum ones [4]. The dielectric is created on the base material (NbO or Tantalum) by electrolysis in a specific electrolyte using a forming voltage profile. The ratio of forming voltage to rated voltage of final capacitor is called Forming Ratio (FR) and its value depends on base material specifics and quality, on dielectric forming process and its control, dielectric robustness against further manufacturing steps and treatments etc. with respect to required reliability of the final capacitor. The forming ratio of current tantalum capacitors FR = 3.0 to 3.5 is typically, i.e. 4V capacitor is formed at 12 to 15 Volts, for instance. Historically they had been as high as 6.0

A typical FR of early Niobium Oxide capacitors is around 6.0. This obviously made original Niobium Oxide capacitors range limited in Capacitance per Voltage compared to standard Tantalum capacitors. Can the FR of Niobium Oxide be reduced to similar levels of Tantalum SMD's? To answer this question the dielectric quality needs to be improved significantly as well as some other specific solutions to capacitor design, materials and processes needed. Similarities of NbO processing to Tantalum lead naturally to the developments that allowed its reduction in FR on tantalum capacitors to be applied to Niobium Oxide. The further study of mechanisms in NbO capacitors as well as years experiences from life tests evaluations highlighted some other aspects – like anode and materials quality.

## NbO PRODUCTION PROCESS ENHANCEMENTS

### Anode quality

The main difference of NbO to Tantalum is referred to features of materials [4]. Firstly Niobium Oxide is typical CERAMIC material (hard, brittle) compared to METAL Tantalum characteristics (soft, malleable). This makes NbO anodes manufacturing extremely difficult. Second difference is in oxides: While Tantalum (conductive metal) has just one stable oxide ( $Ta_2O_5$  – dielectric features  $\epsilon_r=27$ ), the Niobium (conductive metal) creates not only stable NbO (conductive ceramic), but also other stable oxides from NbO<sub>2</sub> (high resistance semiconductor) to Nb<sub>2</sub>O<sub>5</sub> (dielectric  $\epsilon_r=41$ ). These sub-oxides exist on the NbO-Nb<sub>2</sub>O<sub>5</sub> boundary in NbO capacitor (although in limited scale) and influence the final capacitor features including life stability. That is why proper oxygen control in the system of NbO capacitor is important as well as elimination of induced stresses from powder and anode manufacturing. All of this can be overcome to some extent by higher forming ration, but these specifics of NbO-Nb<sub>2</sub>O<sub>5</sub> system must be very considered when moving towards lower FR.

This was in the focus of anode quality development, which included both materials and techniques, and resulted in improved anodes.

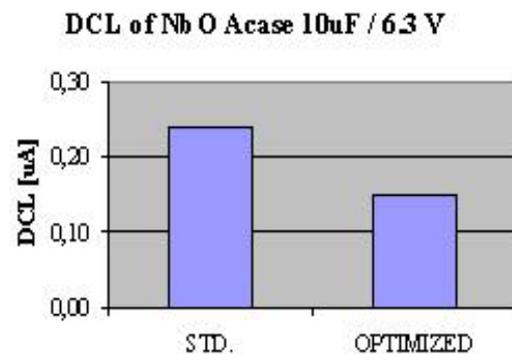
### Dielectric improvements – internal dielectric

The natural inspiration of NbO performance enhancements is coming from the latest continuous improvements carried in tantalum processing.

Dielectric quality is a critical parameter for every capacitor production. Tantalum and niobium pentoxides i.e. tantalum and niobium dielectric are being produced in situ on sintered anode body by electrochemical oxidization. This production step strongly influences the capacitor future behavior. During this process in homogeneities in the current field may lead to defects in dielectric. The defects are mostly observed as an oxygen vacancy in the oxide lattice. As with every oxide made in a wet medium the forming pentoxide is hydrated to some extent. Subsequent thermal annealing dries the oxide forming similar Oxygen vacancies. The Oxygen vacancies (sourced not only from this annealing process) and the some of the Oxygen diffusion were previously reported to be responsible for a dielectric breakdown.

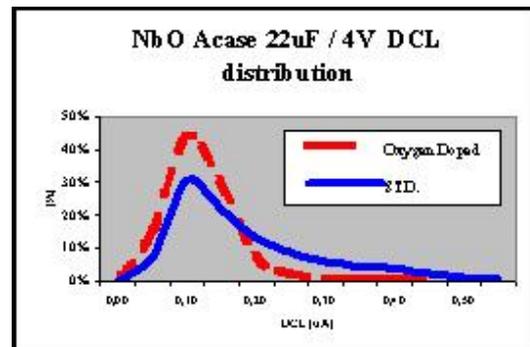
Another mechanism for the dielectric breakdown and increase of the leakage current might be impurity incorporation into the pentoxide structure or field crystallization due to the poor thermo management of the dissipated electrical energy. The chemical impurities reduction in materials and by better control to processing steps are bringing DCL down at least at the same scale as known from high end tantalums.

All the above was targeted in niobium oxide forming optimization. The gained benefits could be seen in fig.1.



**Figure 1:** An example of mean DCL improvement by forming condition optimization

Further DCL improvement was achieved by chemical oxygen doping of the dielectric i.e. elimination of oxygen vacancies again (see fig.2).



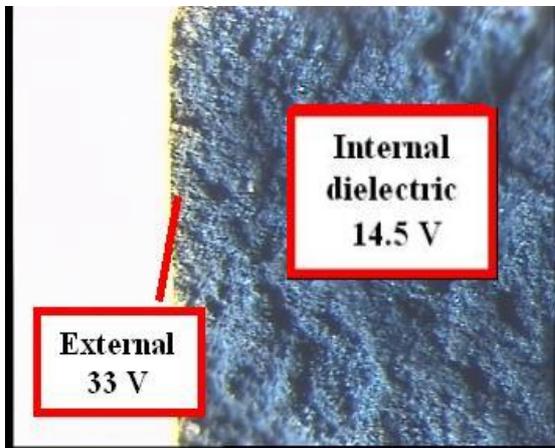
**Figure 2:** Change of the typical production batch DCL distribution by chemical dielectric doping. (DCL spec. limit is 1.76 uA)

### Dielectric improvements – anode surface

In the final capacitor construction, the anode outer surface is the most electrically stressed area and especially the sharp edges are heavily exposed. Therefore if an electrical break down appears, then it is frequently at the outer surface. By the same way

the outer apparent anode surface is the most mechanically stressed area inside the capacitor. These mechanical stresses are not coming from the encapsulation only. They may appear mainly as a thermo-mechanical stress such as IR reflow or with every heating cycle of the capacitor.

There is a unique technique for protection of the outer surface so-called “shell form” used in some tantalum devices, which means that the dielectric thickness is significantly increased selectively at the outer surface only. Although this technique had to be significantly modified for NbO capacitors the resulting appearance looks very similar to the one on tantalum capacitors [1] (fig.3).

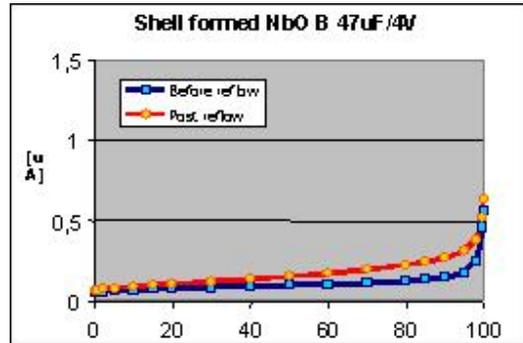
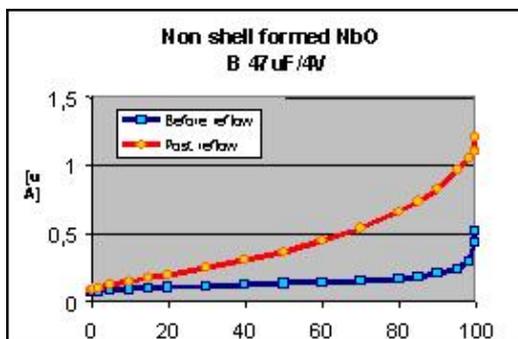


**Figure 3:** Example of NbO capacitor shell formation. Micro picture of anode cross-section.

Niobium oxide capacitors robustness to 3x lead free reflow was improved by such shell formation (fig.4).

The specification of leadfree profile is

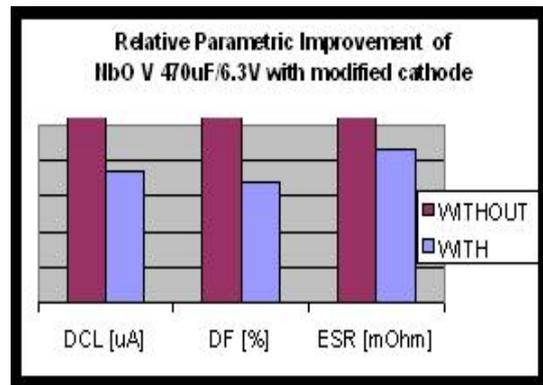
- peak temp. max 255+/- 5°C
- time at 260°C 10 sec
- time at >230C: 60s
- max heat up gradient: 2.5°C /s



**Figure 4:** DCL distribution- 3x lead free reflow stability (DCL limit is 3.76 uA)

### Internal manganizing

Internal dielectric coverage by manganese dioxide plays an important role not only for the capacitor future capacitance. It influences DCL and its stability [2] Side bonuses from the coverage improvement are more favorable DF and ESR. Benefits in NbO capacitors gained with modified internal manganising are shown in chart. (Fig.5)



**Figure 5:** Example of NbO capacitor parametric improvement through internal manganising modifications.

### Assembly encapsulation and screening

Similar to tantalums, the thermo-mechanical stresses coming from thermal shocks have impact to final performance and stability of the capacitor.

The experiences from some special Tantalum products encapsulations were well adopted into new NbO capacitors, resulting in lower stress resin system.

It also has been found that the stability of DCL can be further more improved by fine tune of assembly

of NbO parts operations, such as pre-treatments and optimized ageing conditions.

## NEW NbO CAPACITORS PERFORMANCE

### Breakdown Voltage characteristics

The process enhancements and improved anode quality through materials and method were used in making NbO capacitors with internal forming ratio about 40% reduced.

The performance of such devices shows similar characteristics, good life stability and non-burning features up to rated volts as typical for current Niobium Oxide capacitors. For example see the P case (0805 footprint equivalent) 10uF/4V.

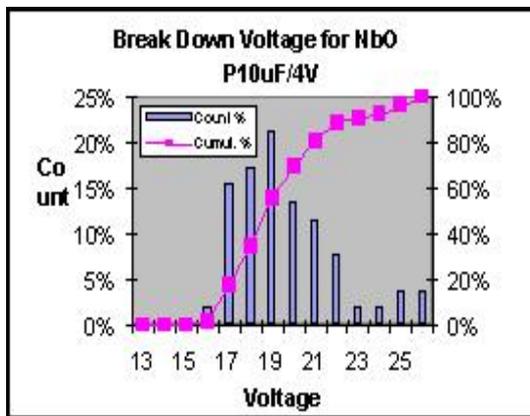


Figure 6: A typical break down voltage distribution for NbO capacitor 0805 P 10uF/4V

Apparently, although the internal forming voltage in this case is about 14 Volts, the break down takes place at most about 18 to 19 volts (Fig.6).

The breakdown voltage distribution chart used for original technology comparison [4] can now be updated by reduced FR NbO measurements (see fig.7). The new NbO BDV characteristics are remaining high thanks to good dielectric and system quality and due to high resistance mode in the system (which does not exist in tantalum systems).

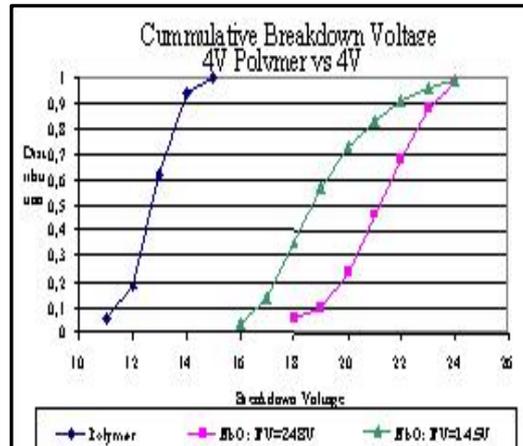


Figure 7: Cumulative chart of typical break down voltage distribution:

4 Volt Polymer - formed at about 14V typically, standard 4V NbO capacitor - formed at 24.8Volts and new 4V rated NbO formed at 14.5Volts

### High resistance mode in breakdown of NbO part

The high resistance failure mode is one of the key safety features of NbO capacitors. There is an unique additional self-healing system where in case of the dielectric breakdown the NbO<sub>2</sub> semi-conducting phase is grown in the breakdown area. This principle naturally limits the local breakdown current below critical level even with significant voltage overload. [3] Fig.8 shows V-A characteristic of P10uF 4V capacitor after breakdown of the main dielectric. The capacitor keeps "safe" if the applied voltage is below 15-16V in the example above e.g. well above specified 4V rated voltage.

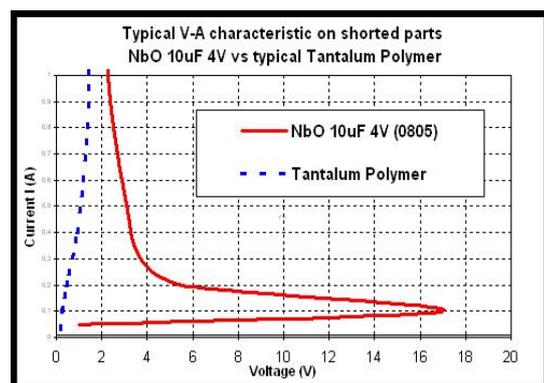
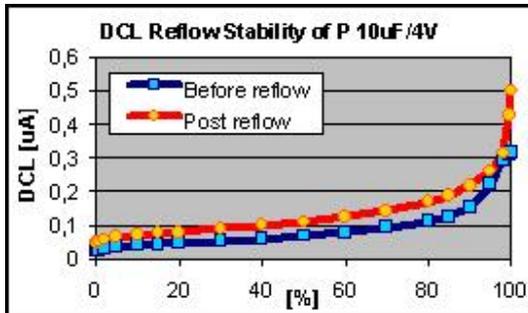


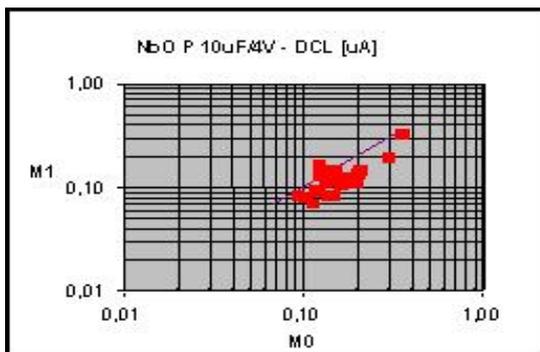
Figure 8: A typical high resistance behavior after breakdown of NbO capacitor 0805 P 10uF/4V compared to Tantalum Polymer

### Leadfree robustness and stability

The parts were treated to 3x lead-free reflow with very good stability (260C peak temperature) (fig.9)



**Figure 9:** A typical DCL reflow behavior of NbO capacitor 0805 P 10uF/4V (DCL spec limit 0.8 uA) And finally, there is good stability on 125 °C, 2/3 of Ur life testing (fig.10) – accelerated life conditions.



**Figure 10:** Life test (125°C, 0.66 rated voltage, 1000 hours) result of NbO capacitor 0805 P 10uF/4V

### CONCLUSION

As pointed out in [4], similarities of NbO processing to tantalum production enable very fast and significant improvements in new family of capacitors based on stable NbO material, if the materials specifics are seriously considered.

The newly adjusted materials and processes from anode to assembly resulted in introduction of new range of high CV capacitors by reduction of forming voltage without any “harmful side” effect to features of the finished parts.

The forming ratio on NbO capacitors has been reduced now close to a level seen on conventional tantalum capacitors and thus NbO capacitors have a new potential for space limited applications where

high CV capacitors are needed such as cellular phones, digital cameras or handheld devices.

The remaining 80% rating rules of NbO capacitors mean for instance use of 4V rated devices for 3.3V applications. In this example the newly introduced capacitance range shows such Capacitance available like 10µF in 0805 (P case), 33 µF in 1206 (A case), 68 µF in 1210 (B case), or 220µF EIA6032 C case and low profile EIA7343-20 (Y case) etc.

### REFERENCES

- [1] Horacek, I at col., AVX „Lowest ESR at High Voltage - Multianode Tantalum Capacitors“, CARTS EUROPE 2004, CTI, Nice, October 2004
- [2] Gill, J, AVX, “Surge in Solid Tantalum Capacitors”, AVX Technical Information Paper, www.avxcorp.com
- [3] Sikula, J, at col., CNRL Brno University of Technology, “Conductivity Mechanisms And Breakdown Characteristics Of Niobium Oxide Capacitors“, CARTS EUROPE 2003, CTI, Stuttgart, October 2003
- [4] S.Zednicek, Z.Sita at col.,AVX ”Low ESR and Low Profile Technology on Niobium Oxide” CARTS USA 2004, CTI, San Antonio, April 2004