

# T I C

## TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

### PRESIDENT'S LETTER

Dear Friends,

From October 11th to 13th 1998 the T.I.C. will meet in Prague, Czech Republic, where we will hold the Thirty-ninth General Assembly on October 12th. The Assembly and technical sessions will be held at the Inter-Continental Hotel where rooms have been booked for delegates to stay.

The registration desk will be open on Sunday October 11th and participants and those accompanying them will be welcome at a reception that evening at the hotel. The General Assembly will be the first event on Monday morning, and the remainder of the day will be occupied with a full and wide ranging technical session. A gala dinner will be served in the evening in the splendid surroundings of the Mayor's Parlour, a short coach ride from the hotel, located on an island in the river, beneath Prague Castle.

On Tuesday October 13th, a plant tour of the AVX Tantalum Capacitor facility is planned, with the invited delegates travelling by bus to Lanskroun in the morning and returning to Prague in the late afternoon at the close of the meeting.

Sightseeing programmes will be arranged for those accompanying delegates to Prague.

Early registration is highly recommended for those wishing to attend the conference: invitations will be sent to the nominated delegates of member companies, others interested should contact the Secretary General, T.I.C., 40 rue Washington, 1050 Brussels, Belgium, telephone +32.2.649.51.58, fax +32.2.649.64.47, e-mail: tantniob@agoronet.be.

It only remains for me to wish you a pleasant summer and I look forward to seeing you all in Prague.

Bill Millman

### SUMMARY

President's letter .....	1
Comparison of tantalum and niobium solid electrolytic capacitors .....	2
New structure of surface mount type tantalum electrolytic capacitor .....	5
Member company news .....	8

### MEETING IN PRAGUE

#### TECHNICAL PROGRAMME

The papers to be presented in the technical programme from 10a.m. on Monday October 12th will focus on the tantalum and niobium industry in Europe, while also covering the world situation.

Dr Heisterkamp of Niobium Products, the CBMM company in Germany, will review the outlook for niobium in Europe, and Dr Korinek, Technical Adviser of the T.I.C., will summarise developments in the tantalum industry in Europe and other parts of the world. Presentations on capacitors will include a joint paper by AVX and Professor Sikula of the Technical University of Brno on noise analysis and a contribution on the purchasing of capacitors by the Philips group. Mr G. Louch, a world-wide Marketing Manager of AVX, will talk about markets and trends for tantalum capacitors. Papers on the selection of capacitors for computers and on aspects of tantalum and niobium use in Japan and the USA are also planned, in a total of at least eight presentations.

The general programme is outlined in the President's Letter.



Prague: the Castle and the river Vltava, from the Charles Bridge

### EXECUTIVE COMMITTEE

At the meeting in Brussels in April, the Executive Committee reviewed the financial situation of the T.I.C. and were pleased to report that the annual membership fee will once again remain unchanged, for the year ending June 30th 1999.

Collection of statistics is an important activity for the association, and the Committee members are always looking for ways to improve the scope and accuracy of the data. Reporting by capacitor manufacturers on their receipts of tantalum powder and wire has been established since July 1997 and so far reporting response has been 100%. Now the reporting on raw materials is to be extended to the receipts of traders, which should bring the figures for primary production more nearly into line with the data for processing.

#### General Assembly 1999

The Fortieth General Assembly will be held from October 24th to 26th 1999 in Perth, Western Australia.



# COMPARISON OF TANTALUM AND NIOBIUM SOLID ELECTROLYTIC CAPACITORS

This paper by Dr Yuri Pozdeev, Vishay-Sprague, Dimona, Israel, was presented at the meeting held by the T.I.C. in Xian, China, in October 1997

## ABSTRACT

This paper deals with a comparative investigation of tantalum and niobium solid electrolytic capacitors. Niobium is attractive for the replacement of tantalum in solid electrolytic capacitors because it is lighter and cheaper than tantalum. These two metals, tantalum and niobium, have much in common in their crystalline structure and physical and chemical properties. Nevertheless, the electrical properties of Ta and Nb capacitors are different. In particular, most Nb capacitors are characterized by an increase of the direct current leakage during Life Test. This causes parametric failure of the Nb capacitors. On the other hand, the direct current leakage of Ta capacitors does not change significantly for a long time, but then increases sharply for some samples. Hence, rare catastrophic failures are typical for Ta capacitors. Meanwhile, the properties of high CV Ta capacitors with low and high rated voltage approach the properties of Nb capacitors. The physical nature of these phenomena is discussed.

## 1. INTRODUCTION

Solid tantalum capacitors with porous anodes sintered in vacuum from fine Ta powder have the greatest capacitance per unit of volume compared with other capacitors. They possess also high reliability and good AC characteristics. Meanwhile, cost and weight per unit of capacitance for tantalum capacitors are higher than for other capacitor types, for example, aluminum capacitors.

Tantalum and niobium are neighbors in the 5a group of the Periodic Table of Elements. They have the same type of crystalline lattice as well as almost identical atomic radius and lattice parameter (Table 1). However, the atomic mass and the density of niobium are about half those of tantalum. This is the reason why Nb capacitors' weight is less than that of tantalum capacitors. Less ground metal consumption causes Nb capacitor cost reduction.

The capacitance  $C$  per unit of anode surface can be approximately expressed as  $C = \epsilon/d$ , where  $\epsilon$  is the low frequency dielectric permeability and  $d$  is the thickness of the anodic oxide film formed on the surface of the anode. The value of  $d$  is in direct proportion to the formation voltage  $V_f$ , thus  $d = aV_f$ , where  $a$  is the formation constant. From Table 1 one can see that the ratio  $\epsilon/a$  for  $Ta_2O_5$  film is almost identical to this same ratio for  $Nb_2O_5$  film. The  $V_f$  value is chosen in the same manner for both Ta and Nb capacitors, depending on the rated voltage. That is why  $C$  value and thereby volumetric efficiency are about the same for both Ta and Nb capacitors using similar powder grades.

## 2. RESULTS AND DISCUSSION

Utilization of Nb as ground metal for solid electrolytic capacitors is limited by the instability of the direct current leakage (DCL) during high temperature processing and electrical loading. For example, Figure 1 presents typical Life Test results for Ta and Nb capacitors manufactured by the same 'tantalum' process from similar powder grades. In this Figure DCL values after Life Test are shown versus initial DCL values before Life Test. For Ta capacitors (Figure 1a) most of the experimental points lie in the vicinity of the diagonal, which demonstrates high DCL stability. For Nb capacitors (Figure 1b) the experimental points are shifted upwards with respect to the diagonal, that means DCL increase during Life Test. This leads to parametric failure of the Nb capacitors.

There are two major degradation processes which are responsible for an increase in DCL in both Ta and Nb

PROPERTIES	Nb	Ta
Atomic number	41	73
Atomic radius, A	1.47	1.47
Atomic weight	92.91	180.95
Density, g/cc	8.57	16.6
Crystalline structure	BCC*	BCC*
Lattice parameter, A	3.294	3.299
Melting temperature, °C	2468	2996
Formation constant at 20°C, A/V	24	16
Dielectric permeability of pentoxide	41	27

\* BCC – Body Centered Cubic

Table 1: Selected properties of niobium and tantalum

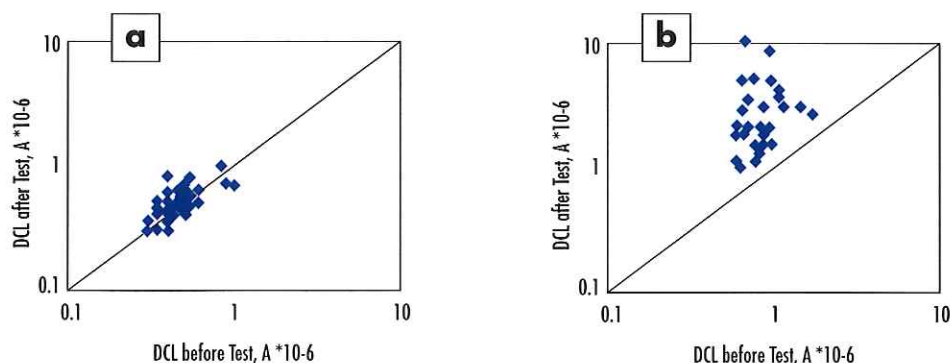


Figure 1: Typical 1000 h Life Test results for Ta (a) and Nb (b) capacitors, manufactured by the same 'tantalum' process

capacitors<sup>3,4</sup>. The first is the process of oxygen extraction from the  $\text{Me}_2\text{O}_5$  film by Me anode (Me: Ta, Nb). This process is originated by lack of thermodynamic equilibrium of the Me and  $\text{Me}_2\text{O}_5$  pair. Conductivity of the reduced  $\text{Me}_2\text{O}_{5-x}$  film becomes greater with increasing oxygen deficit  $x$  because oxygen vacancies act as donor centers, injecting current carriers into the dielectric. The second degradation process is amorphous  $\text{Me}_2\text{O}_5$  film crystallization initiated by the lack of thermodynamic equilibrium of the amorphous state. Crystallization leads to amorphous matrix disruption and thereby to DCL increase.

Although the nature of the degradation processes is identical for both Ta and Nb capacitors, the rates of degradation in these two capacitors are quite different<sup>3</sup>. This causes different consequences of the degradation processes for Ta and for Nb capacitors, in particular, different DCL behavior during Life Test as is shown in Figure 1.

### Oxygen Transport

One of the main reasons for different degradation rates in these capacitors is higher Nb activity to oxygen absorption with respect to Ta. This is originated by more heat of oxygen dissolving in Nb than in Ta<sup>5</sup>. As a result the process of oxygen extraction from  $\text{Nb}_2\text{O}_5$  film by the Nb anode in a Nb capacitor is more intensive than the same process in a Ta capacitor. Due to low reduction rate, the oxygen deficit created in  $\text{Ta}_2\text{O}_5$  film could be completely compensated by the oxygen stream from the  $\text{MnO}_2$  cathode, which possesses solid electrolyte property. Hence, dynamic equilibrium of oxygen content in  $\text{Ta}_2\text{O}_5$  film is provided, allowing Ta capacitors to show stable DCL values during Life Test.

In the Nb capacitor the rate of oxygen extraction from  $\text{Nb}_2\text{O}_5$  film by the Nb anode is actually higher than feasible oxygen supplying to this film by the  $\text{MnO}_2$  cathode. In this case the oxygen deficit  $x$  in reduced  $\text{Nb}_2\text{O}_{5-x}$  film increases in the course of time, leading to an increase in DCL. This is not a monotonous process. Low manganese oxide phases ( $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}$ ) appear in the vicinity of the  $\text{MnO}_2/\text{Nb}_2\text{O}_5$  interface, suppressing further oxygen diffusion from  $\text{MnO}_2$  cathode to reduced  $\text{Nb}_2\text{O}_{5-x}$  film<sup>6</sup>. This leads to accelerated

increase in  $x$  and thereby to accelerated increase in DCL and capacitor failure.

The oxygen transport in the Ta (Nb) capacitor is schematically shown in Figure 2. In this Figure stream 1 conforms red-ox reaction at Me/ $\text{Me}_2\text{O}_5$  interface, stream 2 conforms diffusion of oxygen ions through  $\text{Me}_2\text{O}_5$  film and stream 3 conforms red-ox reaction at the  $\text{MnO}_2/\text{Me}_2\text{O}_5$  interface. From Figure 2 one can realize the nature of galvanic cell property (current generation) inherent in Ta and Nb capacitors at elevated temperatures. According to its definition, for this property two red-ox reactions separated by an ion conductor are required<sup>7</sup>. This phenomenon allows the experimental determination of the oxygen ion current  $I_i$  through  $\text{Me}_2\text{O}_5$  film. The value of  $I_i$  is equal to the short circuit current  $I_{sc}$  in the external circuit (Figure 2).

Figure 3 shows the temperature dependence of the short circuit current for Ta and for Nb capacitors with the same CV and the same  $\text{Me}_2\text{O}_5$  film thickness. One can see that the Ta capacitor has higher activation energy of oxygen transport as well as lower  $I_{sc}$  values at equal temperatures with respect to the Nb capacitor. This is experimental evidence that oxygen transport through the anodic oxide film in the Nb capacitor is more intensive than in the Ta capacitor. As a result the balance of oxygen content in anodic oxide film is maintained for a long time in the Ta capacitor. Meanwhile, oxygen deficit  $x$  in  $\text{Nb}_2\text{O}_{5-x}$  film increases in course of time in the Nb capacitor, leading to increase in DCL and capacitor failure.

### Crystallization

Crystallization of the amorphous anodic oxide film in the Nb capacitor is also more intensive than in the Ta capacitor. This is because of higher Nb activity to oxygen absorption as well as due to lower Nb melting temperature and higher formation constant (Table 1). The absorption of oxygen from residual atmosphere in the vacuum furnace leads to Nb anode supersaturation with oxygen and thereby to the local precipitation in the anode of oxide phase particles. These particles are incorporated in the  $\text{Nb}_2\text{O}_5$  film during its formation and act as crystallization centers for amorphous matrix.

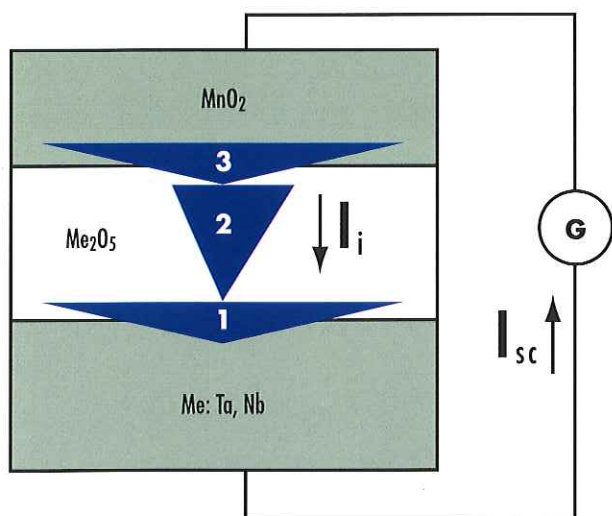


Figure 2: Scheme of oxygen transport in Ta (Nb) capacitor

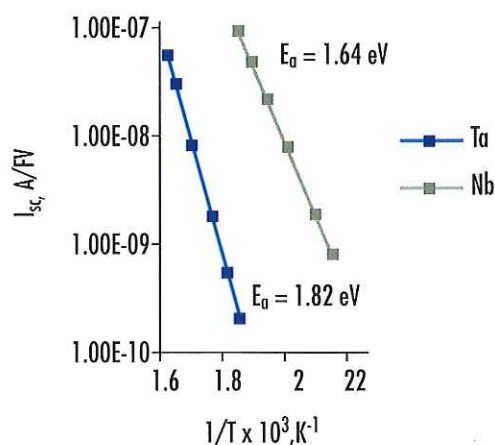


Figure 3:  $I_{sc}$  dependence on inverse temperature



The lower melting temperature of niobium causes excessive Nb anode shrinkage with respect to Ta anode at equal sintering temperatures. That is why for the same CV, Nb anodes should be sintered at lower temperatures than Ta anodes. For a given temperature range the rate of oxygen absorption becomes greater with decreasing sintering temperature<sup>4</sup>. This is the additional reason for Nb anodes becoming super-saturated with oxygen during sintering.

The difference in formation constant between Ta and Nb means that for the same formation voltage the thickness of the Nb<sub>2</sub>O<sub>5</sub> film is about 1.5 times that of the Ta<sub>2</sub>O<sub>5</sub> film. It is well known that susceptibility to crystallization of the amorphous films becomes greater with increasing thickness<sup>2</sup>. That is why the upper limit for rated voltage in Nb capacitors is less than that of Ta capacitors.

### Failure Mechanism

Despite the lower rate of the degradation processes in Ta capacitors versus Nb capacitors, rare failures occur for Ta capacitors too. Actually they are sudden sharp DCL increases (catastrophic type)<sup>8</sup>. For most events these failures are initiated by local penetration of either silver or graphite (top cathode coatings) through pores and cracks in the cathode to the Ta<sub>2</sub>O<sub>5</sub> film (Figure 4). In areas of such penetration the inherent capacitor healing effect is blocked, which leads to deterioration of the Ta<sub>2</sub>O<sub>5</sub> film and further electrical breakdown. As the integral surface of these areas is negligible compared with the complete anode surface, the DCL practically does not change before breakdown. The moment of time when such failure will occur depends on the existence of latent defects in the Ta<sub>2</sub>O<sub>5</sub> film below silver (graphite) areas (Figure 4).

The experimental evidence of this failure mechanism was obtained by means of a scanning electron microscope (SEM). The small areas of either silver or graphite penetration to the anode surface were detected by SEM on cross sections of the failed capacitors. Typically these areas are located in places where there is thinning of the MnO<sub>2</sub>, or big pores or cracks, caused by inadequate cathode deposition. After the cathode was stripped, a burnt spot was revealed on the anode surface around the breakdown channel.

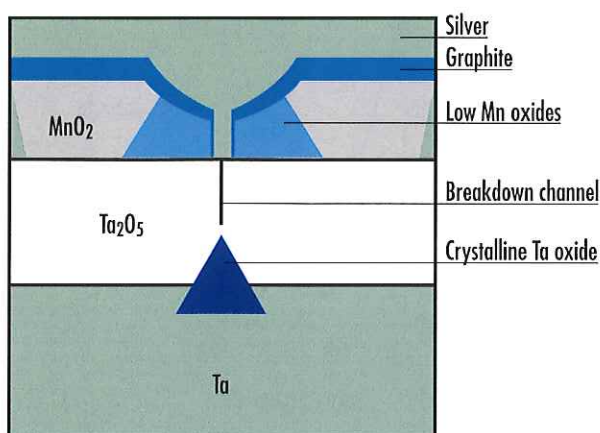


Figure 4: Scheme of failure mechanism in tantalum capacitor caused by silver penetration to the Ta<sub>2</sub>O<sub>5</sub> film.

### Special Properties

The above discussion deals with differences between Ta and Nb capacitors. Meanwhile, two cases were detected in which Ta capacitors demonstrated properties typical of Nb capacitors. The first case relates to Ta capacitors manufactured from high CV powder. As the radius of powder particles becomes smaller with increasing CV, anode activity to oxygen absorption increases and sintering temperature decreases, as for the regular Nb anode<sup>4</sup>. Utilization of high CV anodes is especially difficult for either high or low rated voltage capacitors. Relatively thick Ta<sub>2</sub>O<sub>5</sub> films formed on these anodes for high rated voltage capacitors have enhanced susceptibility to crystallization. Thin Ta<sub>2</sub>O<sub>5</sub> films in low rated voltage capacitors are transparent to oxygen diffusion, because the diffusion stream becomes greater with decreasing film thickness. All these phenomena cause DCL increase in Ta capacitors during high temperature processing and electrical loading similar to Nb capacitors.

The second case relates to Ta capacitors with welded type anodes (Ta lead wire is welded to sintered Ta anode). A thin shell enriched with Nb was detected around the welding zone in such anodes. Figure 5 presents the welded type Ta anode after its formation by  $V_f = 50$  V. One can see a dark hemispherical shell around the welding zone. High Nb content in this shell was measured by means of X-ray microanalysis. The anodic oxide film color inside the shell is dark red and outside the shell it is light yellow. According to the color scale, a ratio between the oxide film thickness inside the shell versus outside the shell is about 1.5:1. This ratio is the same for all  $V_f$  values and conforms to the ratio between Nb and Ta formation constants (Table 1).

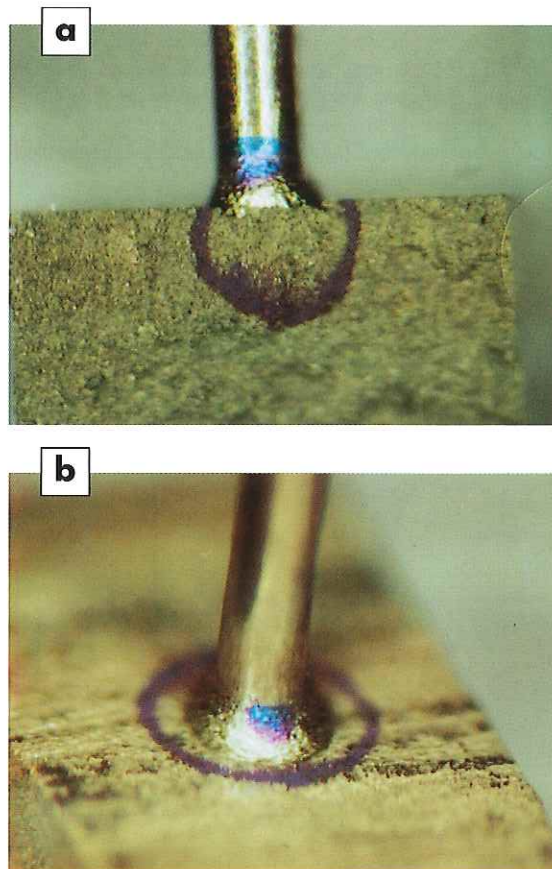


Figure 5: Top (a) and fracture (b) of welded type tantalum anode after formation of anodic oxide film ( $V_f = 50$  V)

The possible interpretation of this phenomenon could be the following. Niobium is the typical substitution impurity in tantalum. During the welding process a high-density current impulse can push Nb from the welding zone to a thin shell on its periphery. For giving technology Ta anodes after lead welding are subjected to high temperature annealing in vacuum. This second sintering provides redistribution of Nb and other impurities from the shell to the Ta anode volume (the Nb peak was not detected around the welding zone after the second sintering). Meanwhile, the second sintering has a negative consequence for Ta capacitors. The oxygen content in Ta anodes increases after a second sintering, this is especially pronounced for high CV anodes<sup>4</sup>.

### 3. CONCLUSION

Based on this study, the following two conditions are required for the proper manufacturing of Nb capacitors:

- Protection of the Nb anodes from super-saturation with oxygen
- Suppression of oxygen transport through the Nb<sub>2</sub>O<sub>5</sub> film and Nb/Nb<sub>2</sub>O<sub>5</sub> interface.

If these conditions are satisfied ('niobium' process), Nb capacitors with stable DCL and high reliability are produced. The preferable area for Nb capacitors includes moderate rated voltages and CV which is not very high. Besides that, 'niobium' process is useful for high CV tantalum capacitors because of the similarity in physical properties between conventional niobium and high CV tantalum capacitors.

### ACKNOWLEDGMENT

The author would like to express his appreciation to Mr P. Maden from Vishay-Sprague, Dr M. Belman from Vishay-Dale, Dr A. Palevsky, Dr A. Gladkikh and Dr M. Karpovsky from Tel-Aviv University for helpful discussions and for their collaboration in carrying out experiments.

### REFERENCES

- [1] Metals Reference Book. Editor C.I.Smithells. Butterworth. London. 1976
- [2] L.Young. Anodic Oxide Films. Academic Press. New York. 1961
- [3] B.T.Boiko, Y.Pozdeev et al. Thin Solid Films. 229 (1993) 207
- [4] Y.Pozdeev. Proc. 10th European Passive Components Symposium. Nice. 1996
- [5] E.Fromm and E.Gebhard. Gase und Kohlenstoff in Metallen. Springer. Berlin 1976
- [6] B.T.Boiko, Y.Pozdeev et al. Thin Solid Films. 130 (1985) 341
- [7] F.A.Kroger. The Chemistry of Imperfect Crystals. Holland. Amsterdam. 1964
- [8] Per-Olof Fagerholt. 17th USA Capacitor and Resistor Symposium. Florida. 1997

## NEW STRUCTURE OF SURFACE MOUNT TYPE TANTALUM ELECTROLYTIC CAPACITOR

### " THE LARGEST CAPACITANCE IN THE SMALLEST SIZE CASE "

These are the transparencies presented by Mr Takeshi Ohba, Matsushita Electronic Components, at the meeting in October 1997 in Xian, China.

1

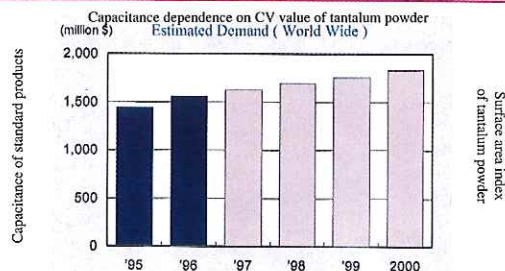
#### Characteristics of tantalum capacitors

- The largest capacitance per volume among all the existing capacitors

- ⇒ Contributes to the miniaturization, weight reduction and multi-functioning of hand-held electronic equipment.
- ⇒ The market demand on tantalum capacitors has been expanding in this Multi media age.

2

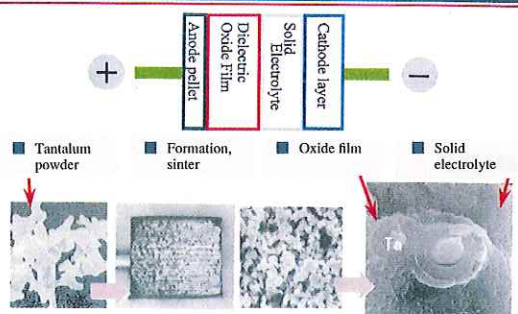
#### Demand on tantalum capacitors





3

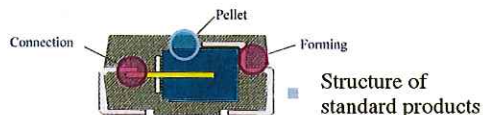
### Showing the principle of tantalum capacitors



5

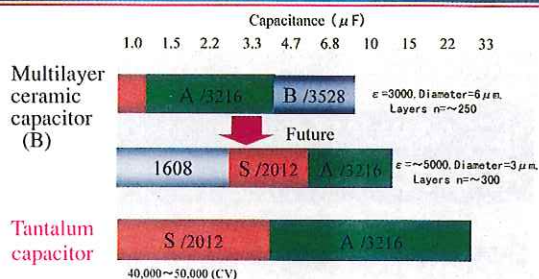
### Current technical issues concerning tantalum capacitors

- Slow down of higher CV tantalum powder development
- Only small improvement of volume efficiency
- Miniaturization of other types of capacitors



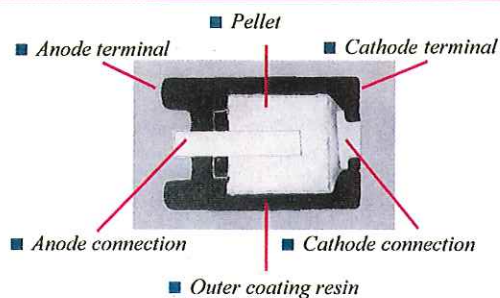
7

### Miniaturization trend of other types of capacitors



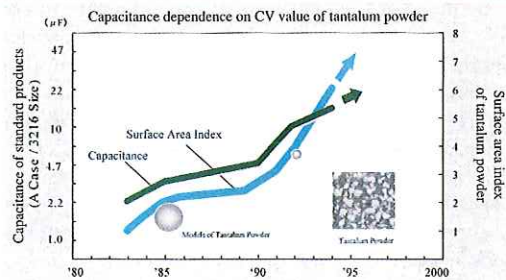
9

### New structure tantalum capacitor



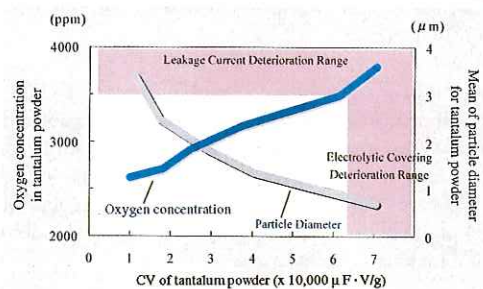
4

### Trend of increasing capacitance



6

### Technical issues of using higher CV tantalum powder



8

### Break-through

Needs break-through technology for further miniaturization



10

### Features of new products

- Standard product
- New product
- In the same case size
- 2.5 times larger cap.
- With the same w.v. products
- 60% less volume

11

### KE Series S Case (2012 Case Size)

10 $\mu$ F

□ Standard product

□ New product



■ A Case (3216)

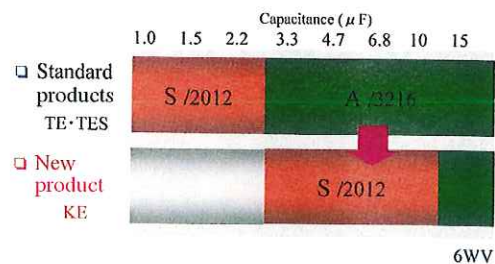
1.0mm

■ S Case (2012)

12

### Mounting area

- 50% less Area



13

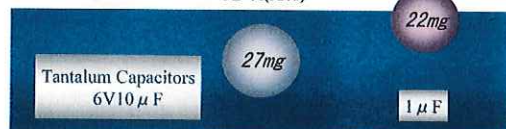
### Weight

- 50% less weight

□ New product  
KE S(2012)

Multilayer ceramic capacitor  
S(2012)

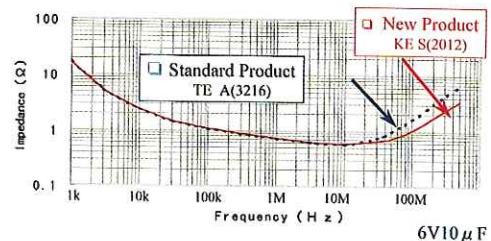
□ Standard product  
TE A(3216)



14

### Impedance characteristics

- Same performance as standard product
- Better characteristics at high frequency



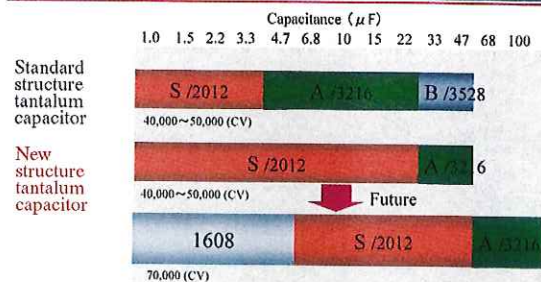
15

### Outlook for the new structure

- Drastic capacitance range increase without sacrificing characteristics.
- Additionally, new solid electrolyte realizes remarkable characteristics.

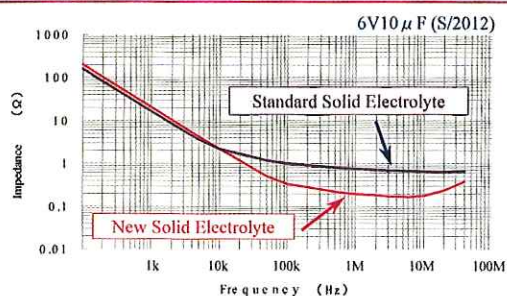
16

### Capacitance enlargement



17

### Higher characteristics with new solid electrolyte



18

### Conclusion

- Remarkable miniaturization, capacitance increases and characteristics improvement are possible with tantalum capacitors.
- The new structure is effective for satisfying market needs.



**Please note that the T.I.C. now has an e-mail address:  
tantniob@agoranet.be**

#### **MR PAUL LEYNEN**

Mr Paul Leynen, the second President of the T.I.C., died on May 7th 1998. He was one of the prime movers in founding the association, and in the months leading up to the first General Assembly he undertook many of the administrative tasks of drafting the statutes and establishing the credentials of the founding member companies. As the delegate of Zairetain, of the Geomines group, he was elected President of the T.I.C. in 1977, and in this role he brought together the first International Symposium, in Rothenburg ob der Tauber, and chaired that conference. He retired from the Executive Committee in 1981 due to poor health, and was presented with a specially made tantalum plaque in recognition of his work for the association.

#### **DR ED MANKER**

We were sorry to hear that Dr Ed Manker, who represented Niobec at the T.I.C. when that company joined the association in 1984, passed away recently.

#### **MEMBER COMPANY NEWS**

##### **CBMM**

Plans for increase of ferro-niobium production capacity

CBMM, parent company of our member Reference Metals, announced the signing of a letter of intent with Mannesmann Demag do Brasil for the supply of a 10.5 MVA electric furnace capable of producing 40 000 tpy of ferro-niobium from December 1999. The reason for the expansion is a growth in demand for ferro-niobium in its major markets in USA, Europe and Japan. CBMM plans to increase its ferro-niobium output this year to 26 000 tons, compared with 22 000 tons produced in 1997.

The installation of the new electric furnace for the treatment of the niobium concentrates which will replace the present leaching method will result in reduction of the production costs and will be more environmentally friendly. CBMM is the first company to use this process.

CBMM also announced that it will very shortly start up its new high-grade niobium oxide plant with a capacity of 150 tpy of Nb<sub>2</sub>O<sub>5</sub>. The output of this plant is intended mainly for the Japanese optical industry. CBMM possesses already a niobium pentoxide plant with a capacity of 2000 tpy which produces a material suitable for the production of vacuum-grade ferro-niobium and nickel-niobium.

##### **Gwalia**

Gwalia restructuring

We reported in T.I.C. Bulletin no. 93 on a planned corporate restructuring and consolidation of core assets of our member company Gwalia. It was later announced that this restructuring was approved by an overwhelming majority of 98% of the shareholders of Gwalia.

##### **Kemet**

Kemet receives President's 'E' award for export excellence

It was announced in Greenville, South Carolina on May 5th 1998 that Kemet Corporation had been awarded the President's 'E' award for export excellence. This award, which was created by Executive Order of the President on December 5th 1961, recognises persons, firms or organisations which contribute significantly in the effort to increase United States exports.

Kemet has demonstrated creative and effective solutions to export-related challenges such as customs delays, high air freight costs, lack of physical presence in the European Union, and indeterminate control over overseas inventory. As a result of the solutions implemented, exports have risen to 44.5% of Kemet's total sales.

##### **Sogem-Afrimet**

The delegate of Sogem-Afrimet to the T.I.C. is now Mr Mark Caffarey, President of the company.

##### **Lev Gubenko**

The fax number of member company Lev Gubenko is now +972 3 529 0035. Telephone numbers are +972 3 522 6022 and 6049.

##### **Cambior**

Cambior Inc. reported an improved financial and operating performance for the first quarter of 1998. Cambior produces niobium at the Niobec mine in Canada.

Tantalum-Niobium International Study Center,  
40 rue Washington,  
1050 Brussels, Belgium  
Tel.: (02) 649.51.58  
Fax: (02) 649.64.47  
Please note that there is no longer a telex line  
to 40 rue Washington

Claes Printing s.a. - Sint-Pieters-Leeuw