

## TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

### PRESIDENT'S LETTER

Dear Members and Friends,

I hope this edition of the T.I.C. Bulletin finds you well and business prospering. It is hard to believe that we are already half way through 2014 with the Fifty-fifth General Assembly in New York City just over three months away. Before you know it, we will once again be raising a glass and toasting friends, old and new.

I am pleased to say that the preparations for the upcoming General Assembly are proceeding as planned as always guided by Emma Wickens, the T.I.C. Secretary General. Sometimes at this point we are still chasing a few abstracts for the technical sessions; however, at this point in time, we are on-plan and adjusting the agenda to allow for the full complement of presentations. Within this edition of the Bulletin you will find the titles of all the papers we have accepted.

One paper I would like to highlight is entitled "Reconciling Antitrust Rules with Trade Associations". This paper, which will be presented by the T.I.C. legal counsel Luc Houben Esq., of Jones Day, is very timely as trade associations continue to come under more and more scrutiny by governmental trade commissions. Any time competitors gather in one place there can be concern regarding the exchange of sensitive information. The T.I.C. meetings are no different. Considering this high level of scrutiny, combined with increased concern by corporations, it is imperative that we, as a longstanding trade association, are in full compliance with the law regarding this issue. Bringing this matter to the forefront and discussing it in the General Assembly is a necessity in our efforts to make certain our members, and prospective members alike, are well aware of the regulations regarding such matters and the potentially severe penalties that corporations and individuals are subject to should they decide to disregard the law. Whether intentional or unintentional, breaching the legal boundaries on this matter can have severe consequences. And while the T.I.C. is represented by its legal counsel at every General Assembly and Executive Committee meeting, it really comes down to personal responsibility. Stated differently, it is up to each member and guest to understand the law and act in a manner that will not negatively impact any other member or the viability and good standing of the T.I.C. I ask all members to attend this most important presentation so that we are all on common ground regarding our understanding of this issue.

In closing, I will once again remind you to mark your calendars, if not already done, and start to make your plans for GA55 in New York City, especially those of you who require visas.

Sincere regards,

Dr Daniel F. Persico (Dan)  
President

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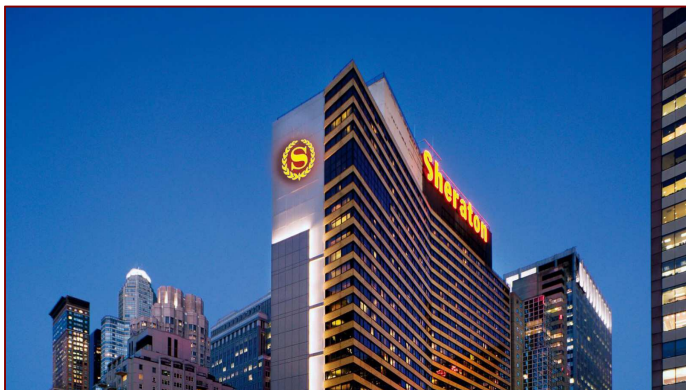
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### FIFTY-FIFTH GENERAL ASSEMBLY

The Fifty-fifth General Assembly and associated technical meeting of the T.I.C. will be held in New York City, U.S.A., from Sunday October 12th to Wednesday October 15th 2014. The conference will take place at the Sheraton New York Times Square Hotel, where a block booking of bedrooms has also been reserved.

On Sunday October 12th, the registration desk will be open from 10a.m. to 1p.m. and 2p.m. to 5p.m. All participants are invited to a Welcome Reception that evening, from 6p.m. to 8p.m.

The formal General Assembly of the association will be held from 8.30a.m. till 9.30a.m. on Monday October 13th and will be followed by technical presentations until mid-afternoon, with a break for a buffet lunch.



The Sheraton New York Times Square Hotel

Companies wishing to apply for membership at this General Assembly are reminded that their completed application forms should be returned to the T.I.C. by September 13th at the very latest. For any further information on becoming a member, please refer to the following page of our website: <http://tanb.org/applmemb>

On Monday evening, all participants are invited to a Gala Dinner to be held in the Metropolitan Ballroom of the hotel.

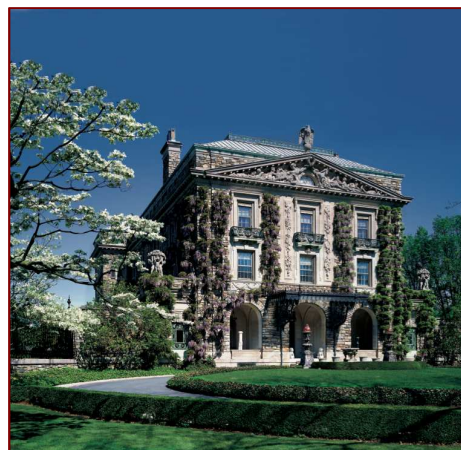
A second technical session will be held on Tuesday October 14th, breaking for a buffet lunch and ending mid-afternoon.

The full technical programme is published here below.

On Wednesday October 15th, delegates will be given the opportunity to visit the facility of Hi-Temp Specialty Metals, located in Yaphank, on Long Island.

Tours for accompanying persons are also being arranged for Monday and Tuesday. The first day will take participants to Kykuit, a splendid estate which was the home to four generations of the Rockefeller family. This six-story stone house and its elegant terraced gardens will reveal collections of sculptures, tapestries, automobiles and horse-drawn carriages. After lunch, the group will discover the Union Church of Pocantico Hills and its stained glass windows by Matisse and Chagall, also commissioned by the Rockefeller family. The second day, the group will discover New York City: the 'top of the rock' viewing platform on the 65th floor of the Rockefeller Center, a behind-the-scenes tour of the Metropolitan Opera and New York State Theater, the 9/11 Memorial, the financial district then a guided tour of the highlights of the Museum of Modern Arts.

An invitation will be sent to the nominated delegate of each member company in the second half of July. Others who would like to attend should contact the T.I.C. Secretary General.



The Kykuit estate house

## TECHNICAL PROGRAMME

The following papers are expected. The announced presenter is the first author listed, unless otherwise specified. The papers are shown in alphabetical order of first author (not in running order).

### **Better Sourcing Program: an independent, flexible and cost-effective solution supported by the CFSI to validate conflict-free tantalum supply chains worldwide**

by Benjamin Clair, Better Sourcing Program

### **Delivering a conflict-free supply chain: Intel's journey**

by Carolyn Duran, Intel Corporation

### **New method for producing high CV/g tantalum powder**

by James Fife, KEMET Blue Powder Corp.

### **How high CV can go in tantalum capacitors**

by Yuri Freeman and Philip Lessner, KEMET Electronics

### **Critical materials supply chains: a public policy perspective**

by Jeffery Green, J.A. Green & Company

### **Reconciling antitrust rules with trade associations**

by Luc Houben and Yvan Desmedt, Jones Day

### **How is Rwanda implementing 'conflict minerals' legislations and what are the perspectives on tantalum and niobium?**

by Evode Imena, Ministry of Natural Resources, Rwanda

### **Development of polymer tantalum capacitors**

by Takashi Kono, NEC TOKIN Corporation

### **Getting to conflict-free: next steps in weeding out conflict minerals from supply chains**

by Sasha Lezhnev, Enough Project

### **Biomedical porous tantalum synthesized via 3D wire frame and chemical vapour deposition**

by Lu Dong, He Jilin, Wang Li, Marko Huttula, Li Bin, Shi Wenfeng and Cao Wei, CNMC Ningxia Orient Group  
(presented by Jiang Bin)

### **The genesis of tantalum and niobium - an African journey**

by Ramez Nasser, Universal Mining Group

### **An update on the Dodd Frank legislation and industry feedback**

by Ron Oleynik and Paolo Mastrangelo, Holland & Knight, LLP  
(both presenting)

### **Mineração Taboca: a reliable and long term supplier of tantalum and niobium units to the industry**

by Itamar Resende, Mineração Taboca

### **Conflict-Free Sourcing Initiative forecast: where are we and where are we going?**

by Michael Rohwer, Conflict-Free Sourcing Initiative (CFSI) / Electronic Industry Citizenship Coalition (EICC)

### **There's no statistics like show statistics**

by Ulric Schwela, Tantalum-Niobium International Study Center

### **NioCorp - the next niobium supplier**

by Mark Smith, NioCorp Developments Ltd

## **NEW HIGH PRODUCTIVE ELECTRON BEAM MELTING SYSTEM FOR BULKY REFRACTORY METAL MATERIALS**

Paper presented on October 14th 2013, as part of the Fifty-fourth General Assembly of the T.I.C., held in York, England. Paper written by Jochen Flinspach, Dieter Kaufhold and Arno Niebling from ALD Vacuum Technologies GmbH, a member of the AMG group.

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### **ABSTRACT**

ALD Vacuum Technologies GmbH, the engineering company of AMG, is introducing a new electron beam melting system for the consolidation of niobium and tantalum bulk material into easy to handle plates. The material is melted in a crucible system placed on a cart within a vacuum chamber. Evaporated metal is collected on condenser screens inside the chamber. The refined material consolidated to plates is easily accessible and handled by driving the cart outside the melt chamber. The produced plates can be either used directly after cutting into pieces as alloy component or as input material for further refining in additional EB melting furnaces.

Besides this new system, ALD is a well-known supplier of electron beam melting systems to the tantalum and niobium producers. ALD's products start from laboratory size systems in the 60 kW range to big production systems of > 6 MW installed melting power. Own process know-how gained on ALD's in house EB melting service can be transferred during system start up to new entries into the melting business.

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### **PAPER**

Since the beginning of the industrial use of electron beam technology for melting refractory metals in the late 1950s, ALD Vacuum Technologies GmbH and its predecessors Leybold-Heraeus and Leybold have been strongly involved in the design and manufacturing of electron beam melting systems including furnace and gun systems.

One of the first production furnaces built in 1964 is still in operation in France for the production of hafnium. Almost all niobium and tantalum producers in the western hemisphere and in Asia are using ALD equipment for the production of their high purity metal.

## STANDARD ELECTRON BEAM MELTING EQUIPMENT FOR REFRACTORY METALS

Main components of a refractory metal EB melting system are:

- Vacuum chamber for operation under high vacuum down to  $10^{-6}$  mbar
- Vacuum system consisting of mechanical pumps, diffusion pumps and turbomolecular pumps
- Electron beam gun system (typically two gun system for niobium and tantalum)
- Feeder systems like bar feeder magazine and electrode feeder
- Ingot withdrawal system (typically with two ingot cans to allow one ingot to cool down while the second one is melted)
- Control system for vacuum pumps and mechanical drive
- Control system for electron beam guns and beam deflection.

The flexibility of the energy source, the electron beam, allows a variety of melting techniques which prove to be very useful for melting metals with melting points above 2000°C.

## STANDARD MELTING TECHNIQUES FOR REFRACTORY METALS

### HORIZONTAL DRIP MELTING

Standard production for high purity niobium and tantalum metal starts with ATR (niobium) or 'Green' (tantalum) bars which are melted by horizontal bar melting.

### VERTICAL DRIP MELTING

Further refining is achieved by remelting the resulting ingot from the first horizontal melt several times by vertical drip melting to achieve lowest gas and metallic impurity content.

### ELECTRON BEAM COLD HEARTH REFINING

To increase the refining area during melting and decrease the number of remelting steps cold hearth refining is applied. In this case, material is fed horizontally or via a vibratory feeding system into a water-cooled copper trough. The liquid material flows to the outlet lip and enters into the water-cooled copper mould. This production method is applied on a large scale for titanium and on a smaller scale for vanadium, zirconium, hafnium and niobium.

## MATERIAL PREPARATION FOR ELECTRON BEAM MELTING

For first melt material, material preparation is a prerequisite for a successful melting operation. Material has to be suitable for vacuum which means free of strong degassing or decomposing matter like oil, hydrogen and plastic.

Companies using scrap material as input have their own proprietary know-how on how to treat material before use in the EB melting.

## ALD'S NEW REFRACTORY METAL CONSOLIDATOR

ALD has provided in the 40 years of industrial use of electron beam technology a significant number of standard EB systems for high purity material.

The secondary market for scrap material not going to be reintroduced into the high purity material chain (like for sputter targets) but targeting the alloy market does require a different melting system.

Alloy components are typically used as chunks in the lower kg range. Melting ingots and breaking then the ingots down into smaller chunks involves quite a lot of work (saw cutting, shearing, cleaning...) and material loss.

Therefore it would be useful to have a system for producing a material shape easy to bring into the chunk form. This is what ALD calls a consolidator.

The basic principal is to melt the material not into an ingot but to produce plates by electron beam melting, which can be easily cut into chunks without material loss.

The furnace consists of:

- Fully water-cooled melt chamber
- Melt chamber cart system with plate crucible assembly
- One electron beam gun
- Vacuum system
- Control system.

## **FURNACE OPERATION**

The furnace can be operated directly at the furnace or more conveniently by remote control from a separate control room with a camera system for observation of the melt process.

Installed on the water-cooled chamber walls are condensate shields to collect any metal evaporated during melting (e.g. aluminium from ATR niobium).

There is enough space on the cart system to place several plate crucibles to increase productivity (e.g. 3 times 100 kg tantalum per load).

Before starting the process, material is loaded into the plate crucibles. Then the melt cart is driven into the melt chamber and evacuation is started.

When the vacuum level has dropped down to the operation level (typically  $< 10^{-3}$  mbar) the EB gun is started and the material is liquefied along the plate crucible. This melting process is controlled by the ESCOSYS deflection computer system which was developed by ALD and its predecessor Leybold.

After this first melting, the furnace is cooled down, vented and the furnace and crucibles can easily be accessed by driving the melt cart outside of the melt chamber for cleaning of evaporated metallic impurities.

Then the plates are turned upside down and the furnace is closed again and evacuated. After melting the back side, the material is sufficiently purified for alloy addition.

The resulting plates can be easily sheared down to chunk size.

## **TECHNICAL FEATURES OF THE ALD CONSOLIDATOR**

Number of plates per run: up to 3

Gun power installed: 600 kW

Vacuum level: down to  $10^{-5}$  mbar

Throughput in 24 hours melting operation: 300/600 kg niobium/tantalum

Utilities:

- Cooling water for melt chamber, crucibles and EB gun
- Argon for EB gun and enhanced cooling
- Compressed air for actuating valves

Space requirement: 15 m x 12 m x 7m

## **ALD ELECTRON BEAM MELTING IN HOUSE FACILITIES AND ALD EB MELTING SERVICE**

In 2001 ALD installed again an in house furnace to be able to do customer independent test runs with new components and to have a reference furnace to show to interested customers.

The furnace at the Hanau (Germany) location can perform all of the above mentioned standard melting techniques and plate consolidation on a pilot scale.

ALD's own EB process know-how gained by many years of operation of the in house facility is contributing to continuously improve the melting equipment.

In order to keep the in house installation busy, ALD also offers the electron beam melting service on a toll base to customers who have not decided yet to invest in their own melting capacity. The demanding shape of material supplied by various customers has led to some very unique solutions for processing refractory metal material into refined ingots.

While electron beam melting is mainly used for pure material it could be shown that it can also be successfully used for the production of alloys from virgin metal components by proper arrangement and melting technique.

For further information please refer to ALD's brochure of the electron beam melting service available on the internet:

[http://web.ald-vt.de/cms/fileadmin/pdf/prospekte/EB\\_Service\\_Onlineversion.pdf](http://web.ald-vt.de/cms/fileadmin/pdf/prospekte/EB_Service_Onlineversion.pdf)

# NOVEL HIGH VOLTAGE TANTALUM POWDER FOR NEW APPLICATIONS

Paper presented on October 15th 2013, as part of the Fifty-fourth General Assembly of the T.I.C., held in York, England. Paper written by Marcel Hagymási, Helmut Haas, Christoph Schnitter and Holger Brumm from H.C. Starck GmbH.

## INTRODUCTION

As a leading technology company, H.C. Starck observed in the recent years an increased demand in high voltage (HV) capacitors in the market. New electronic applications in the fields of flat panel displays, telecommunications like new LTE standard, automotive as well as medical devices are the main drivers for the need of HV tantalum capacitors with increased energy densities. To meet the requirements for making these new devices, suitable tantalum powders have to fulfil different demands on pore size distribution, primary particle size and homogeneity, chemical purity and physical properties in order to ensure high capacitance, open pore structure for infiltration as well as electrical and mechanical stability. To follow these market needs, H.C. Starck is continuously developing new tantalum powders with focus on formation voltages in the range of 60-200 V. The simple question 'What is high voltage for tantalum capacitors?' is difficult to answer since there is no uniform or clear definition for 'high voltage'. This depends on the applications and the consumer: Asian producers use capacitors with working voltages mainly of 16-25 V while western producers (EU/US) prefer rated voltages of 35-75 V. However, new types are continuously entering into the market so that these old classifications are no longer valid. It is reported from AVX for example that the development of new tantalum polymer capacitors enables a voltage rating of 125 V<sup>1</sup>. Also the limitation of too high ESR is already solved by using special anode designs<sup>2</sup>.

The tantalum powders obtained by the Mg reduction process developed by H.C. Starck provide a unique combination of high purity and excellent macro- and microstructural homogeneity. In the past, these powders were mainly used for low forming voltages up to 60 V and high capacitance ranges. The extension to higher voltage applications was limited since bigger pores > 400 nm could not be generated with the existing process. By using a new advanced production process it is now possible to overcome this limitation thus allowing production of such tantalum powders with average pore sizes up to 1 µm combined with an improved microstructural homogeneity for high voltage applications. This enables the formation voltage range of Mg reduced powder to be extended from 50 V up to 200 V while still providing maximum capacitance and excellent leakage currents. The properties of these new tantalum powders will be compared to those of existing high voltage powders in order to show the improved pore structure and particle homogeneity as well as the resulting capacitance behavior.

## REQUIREMENTS ON POWDER MICROSTRUCTURE

H.C. Starck is continuously developing new high voltage powders for different applications. The main target is to improve the capacitance and/or the pore size distribution in comparison to already existing powders in order to develop new capacitor types made of these powders. Our internal classification concerning high voltage includes three different anodization ranges:

1. High voltage: 60-100 V
2. Highest voltage: 100-200 V
3. Ultra high voltage: > 200 V

To provide a proper powder for each range, several requirements have to be met which will be discussed subsequently:

1. Suitable large primary particle size
2. Sufficiently strong sinter necks: between primary particles as well as between different agglomerates
3. Sufficient large pore size diameter
4. Good homogeneity of 1. – 3.
5. High purity.

The first important characteristic of a HV powder is sufficient particle size to provide enough tantalum that can be formed into Ta<sub>2</sub>O<sub>5</sub> during anodic oxidation. Furthermore, the remaining tantalum core requires a minimum size in order to ensure good conductivity within the formed anode which influences the final capacitance. Based on theoretical simulations<sup>3</sup> with a simple cylindrical model it was already shown that a 100 V anodization with a remaining tantalum core of at least 50 nm requires a minimum particle diameter of 322 nm. Particles with smaller sizes will be totally converted to oxide which means a total capacitance loss. Sinter necks, defined as the smallest connection between adjacent primary particles, also require such a minimum size in order to ensure a good electrical pathway through the anode structure otherwise additional loss of active capacitor surface can occur. This is not only a pure powder property because pressing and sintering also has a significant impact on neck formation and primary particle size. Higher press density increases the contact area between adjacent agglomerates. Additionally, anode sintering increases and strengthens all sinter necks and particle size. However, it is not the aim to have maximum particle size since too big particles have low surface area and therefore low capacitance. The microstructural challenge is to find the optimum particle size that results in highest capacitance which is different for each given voltage.

<sup>1</sup> J. Petrážilek, T. Zedníček, M. Uher, I. Horáček, J. Tomáško, L. Djebara: *Next Generation of High Voltage, Low ESR Tantalum Conductive Polymer Capacitors*, CARTS Europe, Munich, 2010

<sup>2</sup> I. Horáček, T. Zedníček, S. Zedníček, T. Karnik, J. Petrážilek, P. Jacisko, P. Gregorova, I. Pinwill: *High CV Tantalum Capacitor – challenges and limitations*, CARTS USA, Jacksonville, 2009

<sup>3</sup> M. Hagymási, H. Haas, C. Schnitter, H. Brumm: *High Voltage Tantalum Powder – Challenges and Opportunities for new Powder Generation*, CARTS Europe, Nice, 2011



Pore size distribution is the next important parameter that has to be taken into account. The importance of pore structure has several reasons. Pores are required for providing space for the growing  $Ta_2O_5$  film, the higher the anodization voltage the higher the required pore space should be in which the oxide can grow. The pore size distribution after anodization is affected by the initial pore size. If the anodized pores are too small they will adversely affect the cathode impregnation process which can cause additional capacitance loss. In the worst case, small pores will be totally filled with  $Ta_2O_5$  so that further oxide growth cannot occur and impregnation with cathode material is prevented. Too big formed pores ensure on the one hand good impregnation but on the other hand this will also lead to capacitance dissipation since these pores can be regarded as 'waste' of space for tantalum surface area. The minimum required formed pore size distribution is not known and depends also on cathode material as well as the impregnation process itself which is different for each capacitor producer.

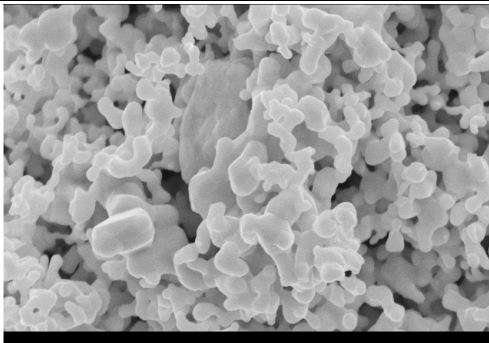
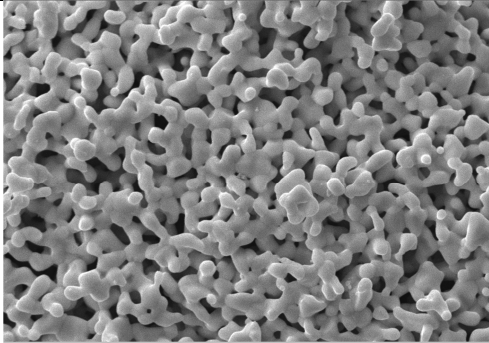
An important but difficult to determine parameter is the high microstructural homogeneity. It is well known that small particles have higher specific surface area than large particles <sup>4</sup> but show an increased surface area loss and therefore a capacitance loss with increasing anodization voltage. This is another reason to provide a tantalum powder with uniform primary particle size which will have lower and more uniform capacitance loss during anodization than a heterogenous powder with comparable initial surface area.

Finally, metallic elements like Fe, Cr, Ni and non-metallic impurities like carbon were often described to have a negative influence on both wet and solid leakage and can cause increased breakdown losses <sup>5,6,7</sup>. Therefore, high powder purity is regarded as a must for high voltage applications since the negative effects will be increased with increasing formation voltage <sup>8</sup>.

## COMPARING EXISTING POWDER TYPES: WHERE ARE THE LIMITS?

In order to understand the required microstructural changes for new high voltage powders, table 1 shows a comparison of the strengths and weaknesses of existing powder types. Powders made by reduction of  $K_2TaF_7$  salt with Na (so called 'Na reduced powder') have two important microstructural advantages for HV applications. First, they have large primary particles up to several  $\mu m$  that still have a large tantalum metal core after anodization with high potential. Second, they provide sufficiently large pores up to 3  $\mu m$  in which the generated oxide film can grow. However, the main disadvantage is the coexistence of desired sufficient large primary particles and significantly smaller particles (a few hundred nm) which can be seen in the showcase of table 1. These small particles will be totally converted to oxide at higher voltages. This causes two losses at once: capacitance loss since the total converted area has no capacitance. Also, these 'dead' particles will block pores and hinder the infiltration of impregnation chemistries. Besides the non-uniformity of the primary particle size distribution, the higher impurity content of Na reduced powders (mainly Na, K, F as well as other metallic elements) causes higher leakage current or even breakdown during anodization.

**Table 1: Comparison of Na reduced and Mg reduced powders**

|                           | Na Reduced Powder   | Mg Reduced Powder  |
|---------------------------|---|--|
| Advantages                | Large pore size: up to several $\mu m$<br>Large primary particle size               | Very homogenous primary particle structure, High purity                              |
| Disadvantages             | Heterogeneous primary particle structure<br>Higher impurity level                   | Small pores (< 400 nm)<br>Too small primary particle size                            |
| Main Focus (Past)         | Low capacitance<br>High voltage (> 50 V)  | High capacitance<br>Low voltage (< 50 V)   |
| Microstructure (showcase) |  |  |

The powder production by Mg vapour reduction of high purity  $Ta_2O_5$  (so called 'Mg reduced powder') is a key competence of H.C. Starck and combines several advantages which are important for HV. Using high purity oxide as precursor is the reason for the superior purity of Mg reduced powders. The most important benefit is the very homogeneous primary particle size

<sup>4</sup> H. Haas, M. Hagymási: *Tantalum capacitor anodes providing highest capacitances: Where are the limits?*, CARTS Europe, Nice, 2011

<sup>5</sup> W.D. Westwood, N. Waterhouse, P. S. Wilcox: *Tantalum Thin Films*, Academic Press, London, 1975

<sup>6</sup> G.C. Wood, C. Pearson: *Dielectric breakdown of anodic oxide films on valve metals*, Corrosion Science, Vol. 7 issue 2, pp 119-125, 1967

<sup>7</sup> C.J.B. Fincham: *Properties of Tantalum Oxide in Electrolytic Capacitors*, Proceedings of the fourth Electrical Insulation Conference, Washington, 1962

<sup>8</sup> Y. Pozdeev-Freeman, A. Gladkikh: *The Effects of Thermal Treatment on the Dielectric Properties of Anodic Films on Tantalum and Niobium: Crystallization*, CARTS, 2003

distribution. The showcase of the microstructure pointed out that the powder has a significantly more uniform primary particle size distribution than the Na reduced powder; the primary particle and the neck sizes show no large deviation. This will cause higher capacitance for powders with same initial surface areas since particles that are too small causing higher capacitance loss during anodization simply do not exist. However, the main reason why Mg reduced powders could not be used in the past for HV applications is that the pore size as well as primary particle size itself were too small for anodization. For anodization voltages > 60 V most of the tantalum was already formed to oxide and especially the small pores were already closed with Ta<sub>2</sub>O<sub>5</sub>. Due to the small microstructure, the Mg reduced powders were mainly used for high capacitance applications at low voltage range (< 25 V), while only the Na reduced powder could be used for HV applications.

## HVMC: NOVEL MG REDUCED HIGH VOLTAGE POWDER

The well-known relationship between capacitance and anodization voltage for different powders in figure 1 demonstrates that there is a limit that can currently not be exceeded. It was therefore the aim of H.C. Starck to push this limit for the anodization range of 50-200 V by 10-20 % to higher capacitances. Since the growth rate as well as the dielectric constant are constant for tantalum, improved capacitance behavior can only be reached by tailoring of the microstructure. It was already mentioned that Mg reduced powders when compared to Na reduced powders have a superior microstructural homogeneity which is the key parameter for increasing the capacitance value at a given formation voltage. By calculating the structure and therefore the theoretically possible capacitance maximum, different models have been used to predict the optimum particle size<sup>3,4</sup>. Moreover, intensive microstructural investigations on existing powders were accomplished in order to check the potential for further powder optimization. Finally, H.C. Starck was able to overcome the main hurdles preventing the use of Mg reduced powder for HV applications. By implementation of major process changes, both pore size distribution and primary particle size distribution for Mg reduced powders can now be shifted to higher values while maintaining the microstructure homogeneity. The pore structure of the new H.C. Starck powders which are named 'High Voltage Medium Capacitance' (HVMC) is exemplarily shown in figure 2. The standard high capacitance (150k  $\mu$ FV/g) powder has a very small pore size peak of 150 nm while the HVMC pore size peak can be adjusted from 350 to 1000 nm. This has an impact on the final application voltage: powders with a pore size peak between 350 and 600 nm can be used for anodization voltages up to 100 V (high voltage range) while the powders with larger pores up to 1000 nm can be subjected to higher anodization voltages  $\geq$  100 V (highest voltage range).

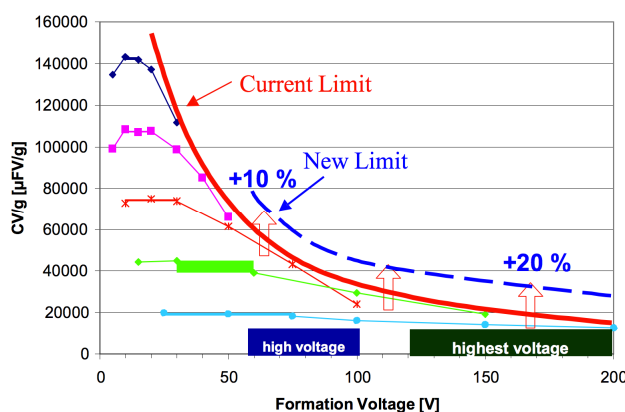


Figure 1: Capacitance vs voltage for different tantalum powders: pushing the limits by new HVMC powders

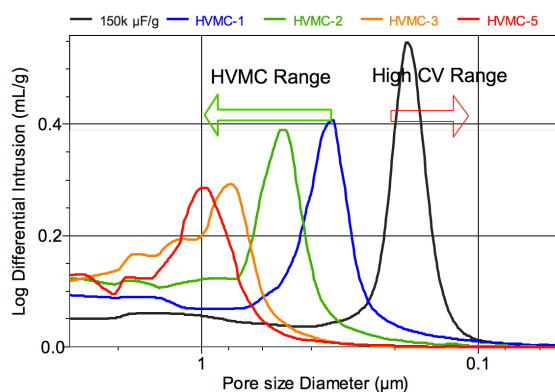
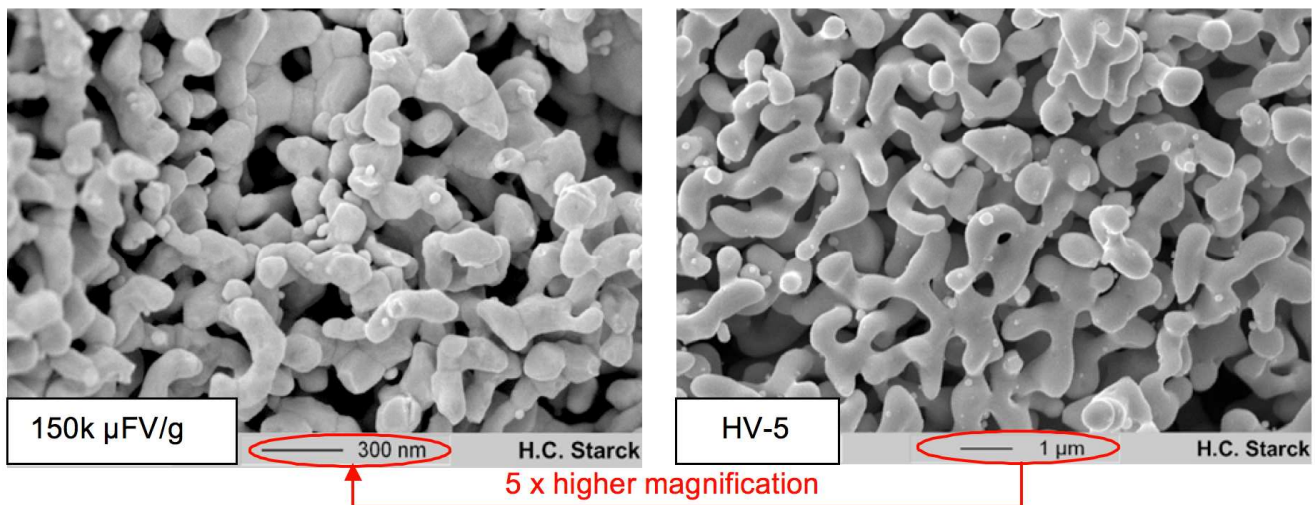


Figure 2: Characteristics of new improved HVMC powders: pore size distribution of different HVMC powders in comparison to standard Mg reduced 150k  $\mu$  FV/g powder

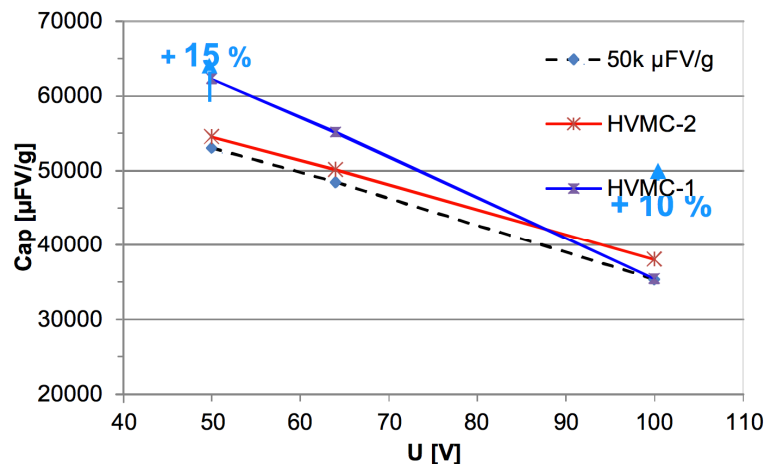


The homogeneous powder microstructure as key factor can be seen in figure 3 where the HVMC-5 powder is compared to high CV Mg reduced 150k  $\mu\text{FV/g}$  powder. It is easy to realize that the primary particle size of both powders is very uniform and shows no significant size deviation, all particles have nearly the same size. However, it has to be noted that the 150k powder picture has a 5 times higher magnification or with other words: the HVMC-5 powder is nearly 5 times coarser than the 150k powder without losing its unique microstructure.



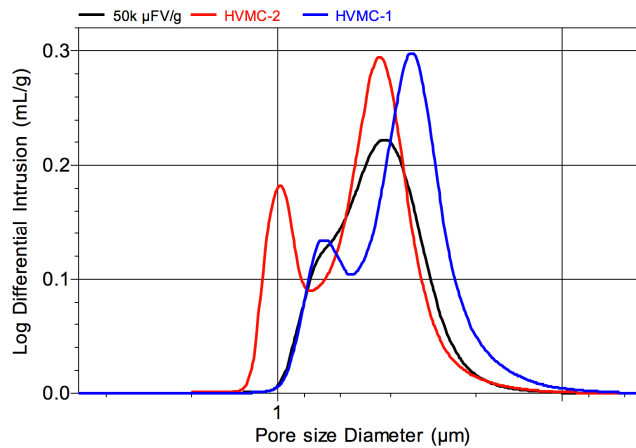
**Figure 3: Keeping the microstructure homogeneity: comparison of 150k  $\mu\text{FV/g}$  powder with HVMC-5, both from Mg reduction. Note the different scale!**

The advantage of these new powders is demonstrated in figure 4. It shows a comparison between anodes made from new HVMC powders to such made from the best in class 50k  $\mu\text{FV/g}$  Na reduced powder currently used for HV applications (reference powder 1). The anodes made from these powders have been formed in the range of 50-100 V (figure 4). Over the whole anodization range at least one HVMC powder gives higher capacitance than the reference powder. The capacitance increase is between 17 % at 50 V and 10 % at 100 V.



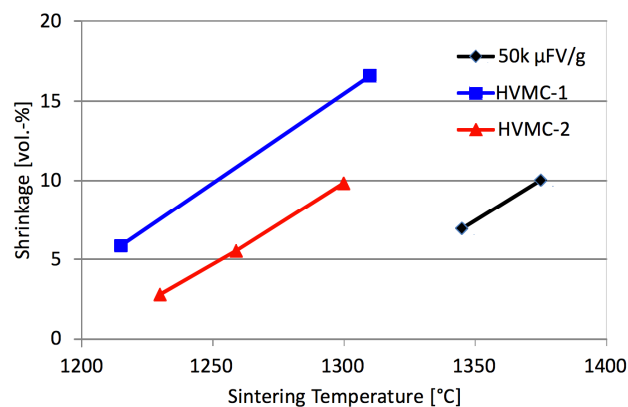
**Figure 4: Capacitance behavior of HVMC powders in comparison to best in class 50k  $\mu\text{FV/g}$  powder (50-100 V range)**

It was also mentioned that capacitance itself is not the only important property but also the pore size distribution has to be taken into account. Pores that are too small cause serious capacitance losses since the impregnation with cathode material is insufficient so that finally a significant anode area is not utilized. That is why not only the powder but also the sintered pellet pore size distribution has to be taken into account which is also influenced by the packing density of powder agglomerates and not only by powder porosity. Anodes made from the two new HVMC powders have a characteristically broad bimodal pore size distribution which supports the pellet impregnation: the bigger pores act first as a 'highway' for the cathode material which is afterwards distributed to the smaller pore areas. In contrast to that, the anodes made from the reference powder 1 show a smaller pore size distribution and no bimodal distribution. The anodes made from the HVMC-1 powder have smaller pores and therefore distinctly higher surface area than those made from the reference powder 1 resulting in 15% higher capacitance at 50 V formation. However, these smaller pores of HVMC-1 anodes are closed by tantalum oxide during anodization already at lower voltages than those made from the reference powder 1. Therefore the capacitance drop between 50 and 100 V is higher for the HVMC-1 anodes and at 100 V the anodes of both powders show the same capacitance. The HVMC-2 anodes have a higher porosity than those made from the reference powder 1 over nearly the entire range; furthermore the HVMC-2 anodes have even ~ 200 nm broader pore size distribution than the anodes made from the reference powder 1. A broader pore size distribution with a higher content of larger pores normally results in lower capacitance, however, the anodes made from the new HVMC-2 powder have in contrast to those made from the reference powder 1 even higher capacitance of up to +10%.



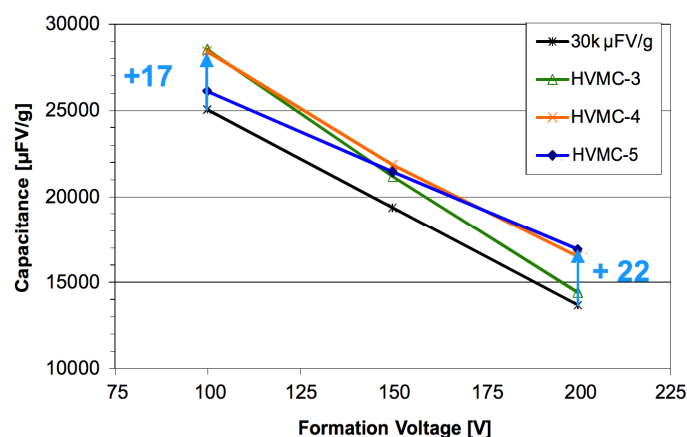
**Figure 5: Pore size distributions of sintered pellets: Na reduced 50k  $\mu$  FV/g powder vs new HVMC powders**

The higher capacitance with simultaneous better pore size distribution of the HVMC-anodes in comparison to the reference anodes made from Na reduced powder is a result of the improved homogeneous microstructure of the powder. Another significant difference to the reference powder 1 is the increased sinter activity of the HVMC powder as illustrated in figure 6. In order to achieve the same shrinkage value, the anodes made from the reference powder 1 require +75°C higher temperature than those made from the HVMC-2 powder and +130°C higher temperature than those made from the HVMC-1 powder. It is known that sinter activity also influences the ESR value, the better the sinter activity the better the anode-to-wire connection and the better (lower) the anode ESR value. Furthermore, the microstructure of sintered anodes influences the ESR value, a more homogeneous microstructure should result in improved ESR as well.



**Figure 6: Sinter activities of new HVMC powders and Na reduced 50k  $\mu$  FV/g powder**

The excellent properties of the new HVMC powders are further demonstrated in figure 7. This figure shows a comparison between anodes made from another set of new HVMC powders and anodes made from a 30k  $\mu$ VF/g Na reduced powder currently used for HV applications (reference powder 2). These HVMC powders with even bigger pore sizes have been developed in order to expand the anodization range for Ta powders from Mg reduction to 100 - 200 V.



**Figure 7: Capacitance behavior of new HVMC powders in comparison to standard 30k  $\mu$  FV/g powder (sinter density: 6.7 g/cm<sup>3</sup>) (100-200 V range)**

Again, anodes made from HVMC powder show higher capacitance than those made from the reference powder 2 over the entire anodization range, the capacitance increase varies here from +14% at 100 V to +22% at 200 V.

The HVMC-3 and HVMC-4 powders are recommended for 100-150 V formation range while the HVMC-5 powder is best for the 150-200 V formation range. Please note that the slope of the capacitance curve is also an indicator for the high voltage stability: the lower the capacitance decrease (negative slope) with increasing voltage the better the high voltage capability! The capacitance of HVMC-5 anodes shows the lowest negative slope of all powders which reflects its unique homogenous microstructure that is superior to current standard powders.

In general, the new HVMC powders offer several possibilities for capacitor makers:

1. Using the higher capacitance in order to provide higher capacitance for new capacitor codes
2. Reduce the powder amount in order to reach the same capacitance
3. Applying powders with same capacitance in order to have the benefit of improved pore structure (higher porosity, broader distribution) for improved ESR and better infiltration with cathode material (capacitance recovery).

Moreover, the improved homogeneous microstructure leads to very narrow breakdown, ESR and capacitance distribution with a low deviation which is important for high reliability applications. The current maximum pore size of the HVMC powders is not the final stage; further developments are running in order to extend the pore structure above 1 µm for additional voltage range extension beyond 200 V.

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## SUMMARY

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Tantalum powders for high voltage applications require an adapted microstructure to realize stable anodes with high capacitance and low leakage currents. Besides large primary particles, strong sinter necks and sufficient large pores also the homogeneity of these properties has to be taken into account. To improve the HV capability of tantalum powders, the microstructure has to be tailored.

It has been shown that the newly developed high voltage tantalum powder class HVMC extended the anodization range of Mg reduced powders up to 200 V. This could be achieved by simultaneously increasing the primary particle and pore size distribution up to 1 µm by keeping its high structural homogeneity. As a result, the new powders provide higher cap than current standard powders from Na reduction at a given formation voltage and/or better pore size structure which can support the subsequent anode impregnation.

## EXECUTIVE COMMITTEE

According to the Charter of the T.I.C., the Executive Committee may consist of between two and eleven people, plus the President. The Executive Committee is drawn from the membership, and committee members may be, but need not also be, the delegates of member companies.

The Executive Committee composition was approved by the T.I.C. members at the General Assembly on Monday October 14th 2013, and it currently consists of (in alphabetical order):

- |                              |  |
|------------------------------|--|
| - John Crawley               | <a href="mailto:jcrawley@rmmc.com.hk">jcrawley@rmmc.com.hk</a>                     |
| - Alan Ewart                 | <a href="mailto:adewart@alance.co.uk">adewart@alance.co.uk</a>                     |
| - David Gussack              | <a href="mailto:david@exotech.com">david@exotech.com</a>                           |
| - Dale Gwinnutt              | <a href="mailto:dalegwinnutt@elitematerial.com">dalegwinnutt@elitematerial.com</a> |
| - David Henderson            | <a href="mailto:dhenderson@rittenhouseir.com">dhenderson@rittenhouseir.com</a>     |
| - Jiang Bin                  | <a href="mailto:jiangb_nnec@otic.com.cn">jiangb_nnec@otic.com.cn</a>               |
| - Ian Margerison             | <a href="mailto:ian.margerison@metalysis.com">ian.margerison@metalysis.com</a>     |
| - William Millman            | <a href="mailto:bill.millman@avx.com">bill.millman@avx.com</a>                     |
| - Yasukazu Muto              | <a href="mailto:yasukazu.muto@hstarck.com">yasukazu.muto@hstarck.com</a>           |
| - Daniel Persico (President) | <a href="mailto:danielpersico@rc.jp.nec.com">danielpersico@rc.jp.nec.com</a>       |
| - Itamar Resende             | <a href="mailto:itamar.resende@taboca.com.br">itamar.resende@taboca.com.br</a>     |
| - Alexey Tsorayev            | <a href="mailto:tsorayeva@ulba.kz">tsorayeva@ulba.kz</a>                           |

