BULLETIN N° 81
ISSN 1019-2026

TIC

TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

PRESIDENT'S LETTER

Dear Friends,

With some luck the arrival of the first TIC Bulletin in 1995 will be accompanied not only by the first signs of spring, but also by further signals of continued improvement in the world economy. The most well-known economic indicators point to favourable growth rates - at least for 1995. Let us hope that these predictions are correct this time.

Prices for most metals increased dramatically in 1994. Contrary to this general trend, tantalum and niobium prices remained stable during the same period. This situation has certainly been welcomed by producers as it provides a reliable calculation basis, which in many cases is a prerequisite for successful long-term development. Today's profits are derived from products and ideas that were developed in the past. Therefore, it must be our goal to further innovation in the tantalum and niobium fields in order to pave the way for the success of generations to come and to secure a stable and enduring position.

In his book, "Lincoln on Leadership", the author Donald T. Phillips explains how the principles of Abraham Lincoln can be applied to executive strategies. In the face of seemingly insurmountable obstacles, Lincoln always persevered. We, too, must persevere in pursuing our long-term goals. To quote one of Lincoln's principles: "When the occasion is piled high with difficulty, rise with it. Think anew and act anew".

Our bi-annual meeting will be held in Brussels on April 25th, 1995, and I hope as many members as possible will attend. Those not able to join us should rush their suggestions for topics of discussion to the Secretary General. After all, new ideas are an important stimulus for the continued success of our association !

Sincerely,

Peter Kählert,
President

SUMMARY

INTERNATIONAL SYMPOSIUM ON TANTALUM AND NIOBIUM

The Tantalum-Niobium International Study Center is pleased to announce that in September 1995 it will hold an International Symposium on Tantalum and Niobium in Goslar, Germany.

This charming medieval town, at the foot of the Harz Mountains, was a borough more than a thousand years ago, and owed its fame and wealth to the rich mines of silver, copper and lead in the nearby Rammelsberg. Part of the sturdy defences of walls and gates still shelter the cobbled streets and picturesque half-timbered houses roofed with local slate: the history and architecture of this delightful place have been distinguished by its inclusion in the Unesco World Heritage List.

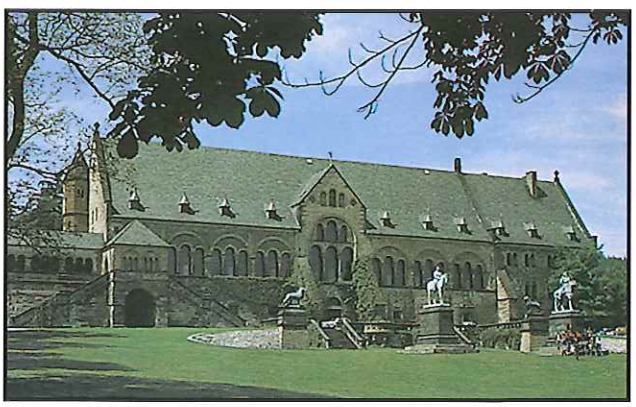
It is our good fortune that Goslar is also the home of H.C. Starck GmbH, which is hosting our meeting as part of its 75th Anniversary celebrations, and offering a plant tour of its metallurgical works as part of the programme. Metals still contribute to prosperity here - but our modern day interest is in niobium and tantalum, undiscovered in the days of the Knight Ramm who is said to have discovered the silver mine.

The technical programme for this conference, printed below, is remarkably broad and varied, ranging from raw materials resources through processing to consumption and use of the products in communications, aeronautics and space exploration.

The main conference will take place in the Hotel Der Achtermann, where delegates will also stay. On Sunday, September 24th the registration desk will be open in the Hotel, and the Symposium will begin with a cocktail party to welcome the participants.

On the evening of Tuesday, September 26th, all the delegates and their partners are cordially invited to a gala medieval banquet in the Kaiserpfalz, the Emperors' Palace, completed in 1056, as

Kaiserpfalz



guests of H.C. Starck GmbH & Co KG, to celebrate seventy-five years of the company's foundation.

A tour of the H.C. Starck plant is offered on the morning of Thursday, September 28th, concluding the conference.

Sightseeing for those accompanying the delegates will include an extensive tour of the Harz mountains, visiting Quedlinburg and Wernigerode, a guided walk round the historic heart of Goslar, and a fashion show at a silk-painting studio in Clausthal-Zellerfeld.

In May, we shall send invitations and full details to member companies and to those who have already asked specifically for this information. The Symposium is open to all, pre-registration is essential and space is not unlimited: if you would like to be sure of your invitation please let us know of your interest.

TECHNICAL PROGRAMME (PRELIMINARY)

Monday, September 25th 1995

T.I.C. General Assembly

Coffee Break

Tantalum/Niobium - Overview

Welcome Speech	P. Kählert	President, T.I.C.
Overview of Tantalum	Dr Korinek	T.I.C.
Overview Raw Material Availability	J. Linden	Gwalia
Overview of Niobium	Dr H. Stuart	Nb Products

Lunch Break

Ta/Nb - Processing

Hydrometallurgical Processing of Ta/Nb Compounds - Present State of the Art -	Dr Eckert	HCST
The Control and Recovery of MIBK in the Solvent Extraction of Tantalum and Niobium	Dr P.M. Brown	Cabot
CBMM's New Operation	R. DeScuccio/ M. Souza	CBMM
NiNb by Reading Process	B. Higgins	Reading Alloys

Coffee Break

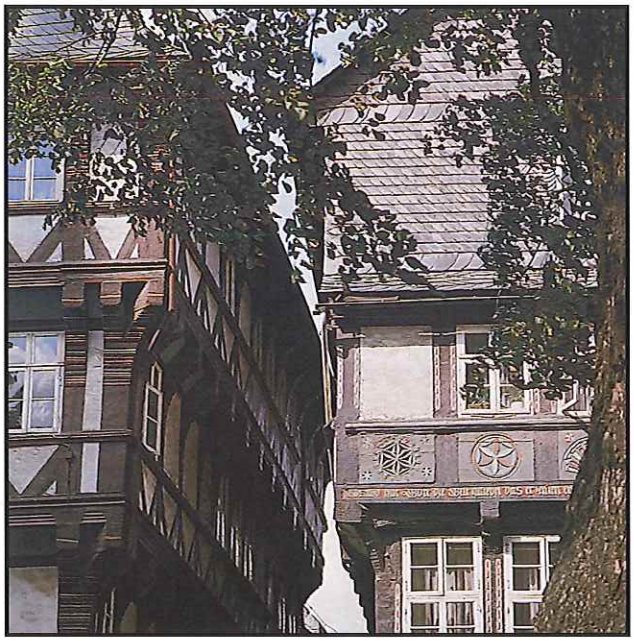
Niobium in Steels

Review of the Technology of Microalloying in Automobile and Pipeline Steels	Dr H. Stuart/ Dr F. Heisterkamp	Nb Products
Using Niobium in Modern Stainless Steels	Prof A.J. DeArdo	Univ. of Pittsburgh
Niobium in Castings, Forgings and Long Products	Dr G. Tither	Nb Products

Tuesday, September 26th 1995

Ta/Nb in Electronics

Vehicle Electronics - Competition and Innovation	Dr Raith	Mercedes-Benz
Outlook for Ta Capacitor Market	D. Maguire	Kemet Electronics



Houses in Goslar

History and Future View on the Development of Tantalum Capacitor Technology	K. Morimoto	NEC

Coffee Break

Approaching the Limits? The latest Developments in Solid Ta-Capacitors	W.A. Millman	AVX
Ta-Powders and Ta-Wires for Capacitors	Dr Tripp	HCST Inc.
A Review of the Role of Nitrogen in Tantalum Capacitor Processing	Dr Hongju Chang	Cabot
Ta-Paste Technology	Dr Hünert	HCST
Useage and Supply of Ta-materials for the Change from Leaded Capacitors to Surface Mount Technology	D. Zogbi	Consultant (Paumanok Publications)

Lunch Break

Material Requirements of Future Information and Communication Systems	Dr Schmidt	Bosch
Recent Development of Non-active Integrated Components in Multi-layer Modules	Dr Mussler	IBM
The Use of Ta/Nb-Compounds in the Electronics Industry	Dr Reichert	HCST

Coffee Break

Preparation and Properties of Functional Components	A. Schönecker/ F. Schlenkrich	IKTS, Dresden
Dielectric Characterization of Ferroelectric $Pb_3(Mg_2Nb)O_9$ Relaxor Ceramic	Dr Hennings	Philips GmbH
$LiNbO_3$ and $LiTaO_3$ Single Crystals for Surface Acoustic Wave (SAW) Applications	Dr Willibald-Riha	Siemens

Wednesday, September 27th 1995

Ta/Nb - Compounds and Applications

Ta/Nb Oxides in Glass for Modern Optical Systems	H. Morian	Schott
Properties and Performance of $YTaO_4$-Phosphors	Dr Zegarski	DuPont
Catalysis by Niobium and Tantalum Oxides	T. Ushikubo	(Mitsubishi Kasei) Mitsubishi Chemical
Coffee Break		
Fused Salt Electrolysis of Niobium	Dr Mori	Montanuniv. Leoben
Solubilities of $TaCl_5$ and $NbCl_5$ in Aprotic Solvents	Dr Drobot	Moscow State Academy
Ta- and Nb-Electrorefining and Electroplating	Dr E. Polyakov	Kola Science Center
Ta-Containing Hard Alloys for Surface Technologies	Prof Lugscheider	RWTH, Aachen
Lunch Break		
Oxidation Protection of Nb- and Ta-based Components in Space Application	Dr Rödhammer	Plansee
Tantalum as a Material of Construction for the Chemical Process Industry - A Critical Survey	Dr Gramberg/ H. Diekmann	Bayer
Modelling of the Forming of Ta-Parts with Finite Elements Code	C. Thiebaut	C.E.A.
Coffee Break		
Role of TaC in Hard Metals	NN	
New Materials for Jet Engines	Dr Malik	Lufthansa
Nano-sized Ta-Powders	Prof Winter	HCST
Closing Remarks	P. Kählert	President, T.I.C.

IMPROVING THE PROPERTIES OF PMN CERAMICS

by A. Hoppe and K. Reichert, H.C. Starck GmbH & Co. KG, and F. Schlenkrich, Fraunhofer Institute for Ceramic Technologies and Sintering Materials.
Presented by Dr Hoppe at the T.I.C. meeting in Japan, October 25th 1994.

INTRODUCTION

Because of their very good dielectric and electrostrictive properties, complex lead perovskites of the general composition $Pb(B'B'')O_3$ (B': Mg, Zn, Ni, Fe; B'': Nb, Ta, W) are playing an increasingly more important role in electroceramics, where they are used in components such as capacitors and actuators. A complex process is required for their production, which can only be mastered by the optimal sequence of each individual step. If properly directed, the process leads to materials with extraordinarily good properties.

A typical example of this group is lead magnesium niobate ($Pb_3Mg\ Nb_2O_9$). A main problem in the production of PMN ceramics is the reproducibility of the dielectric properties. On the one hand, there is the possibility that an undesirable pyrochlore phase will form in addition to the perovskite phase [1], and on the other, PbO evaporation above 800°C cannot be controlled. These problems can be solved by varying the processing route or the PMN composition and/or by selective doping. Despite the doping agents, the dielectric properties remain the same or, in some cases, are even clearly improved.

EXPERIMENTAL PROCEDURES

A modified ceramic process developed by the company H.C. Starck GmbH & Co. KG was used to synthesize the lead magnesium niobate powder. This process allows PMN synthesis by either the columbite method [2] or via the direct synthesis (see figure 1) [3]. The calcined powder was pressed in the form of disks and sintered at 850°C, 900°C, 1000°C, 1100°C and 1200°C in a closed crucible. In order to compensate for PbO loss during sintering, this step was sometimes performed in a PbO atmosphere.

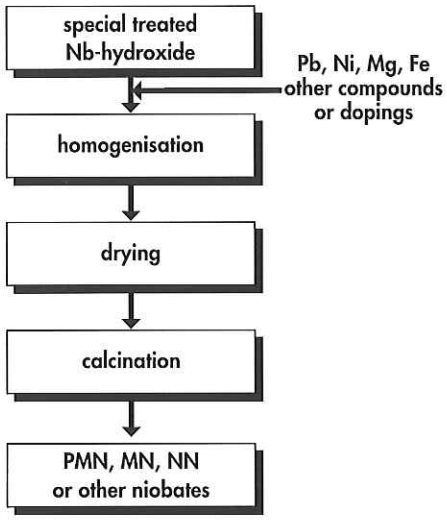


Figure 1 : HCST-procedure for the production of niobates

RESULTS AND DISCUSSION

A. Influence of the processing route on powder properties

Numerous processes have been developed for the synthesis of complex lead perovskites with the aim of obtaining perovskite-structured substances free from phase shift. These can be classified in traditional ceramic and nonconventional processes, such as the sol-gel process, coprecipitation, physical drying processes, etc. [4-7].

Using the ceramic method, it has not been possible to synthesize powder free from pyrochlore phase directly from the corresponding oxides and carbonates so that a two-step process, the so-called columbite method, was developed to overcome this problem [4]. With this method, binary oxides expressed by the formula MNb_2O_6 are formed in a preliminary reaction. These are then converted with the help of lead compounds according to the equation

$$Nb_2O_5 + M(II)O \rightarrow MNb_2O_6$$
$$3PbO + MNb_2O_6 \rightarrow Pb_3M(II)Nb_2O_9$$

Wet chemical processes have proved to be better for the production of complex perovskites. The coprecipitation method [8, 9]

generally yields highly reactive intermediates, which react even at low temperatures to form perovskites free from pyrochlore phase. The sintering behavior and the dielectric properties of these fine powders are superior to those obtained by the conventional procedure. However, these wet chemical processes have been extremely uneconomic up till now.

The H.C. Starck process as described above has a number of advantages compared to other processes. This process makes PMN synthesis possible by either the columbite method or via a direct synthesis [2, 3]. The powders thus obtained are characterized, for example, by a high phase purity and a narrow grain size distribution. One of the biggest differences or advantages lies in the reactivity of the intermediate powders with PbO compared to all other processes. As demonstrated in Table 1, the $MgNb_2O_6$ from the H.C. Starck method shows the highest reactivity with lead compounds. The perovskite already began to form at 600°C. In the case where the powders were calcined at 650°C for two hours, the pyrochlore phase was measured at only 10 percent. Surprisingly, these types of niobates also show a higher reactivity compared to very homogeneous powders, like the sol-gel niobates obtained from a wet chemical process.

		% Perovskite after calcination					
Composition	**Method**	600°C	650°C	700°C	800°C	900°C	1000°C
P+M+N	ceramic (4)	-	-	-	68,4	74	76,3
P+MN	ceramic (4)				98,9	98,5	98,2
P+M+N	sol-gel (8)	-	-	9	98	-	-
P+M+N*	sol-gel (10)	±45	±60	±80	±95	±98	-
P+M+N	single-step HCST	-	-		96	-	-
P+MN	HCST	3,4	90	94	99	-	-

Calcining conditions: 4h, * 120H and HCST 2h

Table 1

B. Influence of the PMN composition on the dielectric properties of PMN ceramics

It is well known from scientific literature that an excess of magnesium oxide in the PMN powder improves the dielectric properties in the resulting perovskite ceramics. The increase in the dielectric constant might be a combination of the effect of the grain size and the avoidance of the pyrochlore phase. The reason for the diminished pyrochlore phase is most probably a result of the higher homogeneity of the powder. As is generally known, the reactivity is particularly high between lead and niobium oxide. Since the mobility of the lead oxide is also very high, segregation is possible during the pyrochlore formation, which is known to occur first in PMN synthesis, so that the subsequent perovskite development is impeded. However, if excessive nonreactive and nonmobile magnesium oxide is added and it also bonds on the niobium oxide by a prereaction, a higher homogeneity will again be achieved in part, thus favorably influencing the formation of perovskites. On the basis of this assumption, one is able to produce perovskite powder free of phase shift from the single oxides by substantially increasing the magnesium content (by 30 percent) and by prolonging the mixing times.

Since extremely high homogeneity was achieved in the powder blends right from the beginning using the H.C. Starck process, one can produce perovskite powders free from phase shift without adding excessive amounts of magnesium oxide. As opposed to conventional ceramic powders, H.C. Starck PMN ceramics produced by the columbite method also show only a slight change in dielectric properties with the increase in the magnesium oxide content.

Unfortunately, the dielectric values published in scientific literature are usually not comparable since either the sintering temperatures or the measuring frequencies do not correspond or are not indicated. As can be seen in Table 2, the powders produced by the modified process are capable of being sintered at extremely low temperatures. Sintering densities of over 95 percent are already achieved at temperatures of 850°C. We are not aware of any other powders produced by the ceramic method with such extraordinarily good sintering properties. Powders produced by the columbite method are usually sintered at temperatures above 1200°C. Only the sol-gel powders have similarly good sintering capabilities. However, these powders have the disadvantages of having very low dielectric constants in this temperature range - for example 2992 at 900°C. Powders produced by the modified process are characterized by much higher dielectric constants of more than 12 000. Even hot-pressed powders cannot match these types of powders.

Composition	**Method**	**DC max**	**sintering condition**	**measuring frequency**
PMN	single crystal	15900		60 kHz
P+MN	columbite (11)	15900	1200°C	100 kHz
P+MN	columbite (11)	18200	1270°C	100 kHz
P+MN	columbite (11)	16400	1300°C	100 kHz
P+M+N	sol-gel (12)	2992	900°C	1 kHz
P+M+N	sol-gel (12)	9369	1000°C	1 kHz
P+M+N	sol-gel (12)	14550	1100°C	1 Khz
P+M+N	sol-gel (12)	15400	1200°C	1 kHz
P+M+N (13)	sol-gel/hot-pressed	6400	825°C	1 kHz
P+M+N (13)	sol-gel/hot-pressed	11200	900°C	1 kHz
P+MN	HCST	12000	1000°C	100 kHz
P+MN	HCST	13000	1100°C	100 kHz
P+MN	HCST	17300	1200°C	100 kHz
P+MN+M 5%	columbite (11)	17000	1200°C	100 kHz
P+MN+M 5%	columbite (11)	19400	1270°C	100 kHz
P+MN+M 5%	columbite (11)	17900	1300°C	100 kHz
P+MN+M 5%	HCST	12300	850°C	100 kHz
P+MN+M 5%	HCST	16200	1000°C	100 kHz

Table 2

C. Improving the properties of H.C. Starck PMN ceramics by doping

The dielectric constants measured at room temperature as a function of the sintering temperature are shown in Table 3. Here it can be clearly seen that a maximum dielectric constant can be achieved with H.C. Starck ceramics at a sintering temperature of 1000°C. The dielectric constants decrease slightly at lower and at higher sintering temperatures. In the case of all other powders known to us, the dielectric constant increases with the sintering temperature for the temperature range given in Table 3. The lower dielectric constant at sintering temperatures around 850 - 900°C can be explained by the fact that the grain was not yet fully developed. However, if the PMN powder is doped with alkali oxides or alkaline earth oxides, the dielectric constant values can be increased by 20 percent for this temperature range. The increases

Sintering conditions	**DC 25°C undoped/doped**	**tan δ [10^{-4}] undoped/doped**	**density [g/cm³] undoped/doped**	**weight loss [%] undoped/doped**
2 h / 850	9744 / 11626	150 / 220	7,88 / 7,85	-0,48 / -0,41
2 h / 1000	12022 / 12758	170 / 195	7,93 / 7,94	-0,74 / -0,69
2 h / 1100	11202 / 12360	155 / 180	7,84 / 7,80	-0,97 / -1,01
2 h / 1200	9848 / 11851	110 / 170	7,86 / 7,82	-1,09 / -1,02
2 h / 1000 (o)	12258 / 12889	170 / 195	7,93 / 7,76	-1,01 / -0,90
2 h / 1100 (o)	10435 / 12275	125 / 175	7,87 / 7,85	-1,02 / -0,99

(o) = PMN was sintered without lead oxide atmosphere
PMN with excess of MgO

Table 3 : Dielectric properties of undoped and doped PMN-Ceramics

are not so dramatic for sintering temperaures of about 1000°C. The reason for this is probably the excess magnesium oxide, which mainly influences grain growth at temperatures above 1000°C. Excess magnesium oxide shows no effect at sintering temperatures below 1000°C, and hence the doping agent produces an effect. Table 3 also indicates that these powders can even be sintered without a lead atmosphere while still keeping their good dielectric properties.

CONCLUSION

The results discussed here show that by using the H.C. Starck process, i.e. a modified ceramic process, the synthesis of lead magnesium niobate powder and other $Pb(B'B'')O_3$ compounds leads to very highly reactive powders. With respect to their properties, these materials are superior to powders produced using either conventional ceramic or wet chemical processes. H.C. Starck PMN ceramics show extraordinarily high dielectric constants - especially at low sintering temperatures.

Initial tests have also indicated that dielectric properties can be significantly improved - mainly for sintering temperatures below 1000°C - by doping the niobate powders with alkali oxides or alkaline earth oxides.

References

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CERN TO BUILD POWERFUL ACCELERATOR

Recently the 19 member nations of CERN, the European Laboratory for Particle Physics, voted to proceed with the building of the most powerful particle accelerator in the world. The announcement was received with great satisfaction by the international community of particle physicists, since the CERN accelerator (called Large Hadron Collider - LHC) will help solve some of the problems which the cancelled SSC project in Texas had been designed to do.

The advantage of the LHC over the SSC is that it can be accommodated within the same tunnel between France and Switzerland as the Large Electron-Positron (LEP) collider.

The new collider is planned to be built in two stages. The first stage, to be completed by the year 2004, will generate particles at energies of 10 trillion electron-volts. This stage is funded by European members only. The second stage which would upgrade the LHC to 14 trillion electron-volts could be completed four years later, provided non-members such as the US, Japan, Russia and others contribute the additional funds needed.

The LHC project should be a significant consumer of Ti-Nb superconducting alloy.

TANTALUM CAPACITORS : IMPROVEMENTS TO VOLUMETRIC EFFICIENCY

By Mr James A. Fife of Cabot Performance Materials during the 1994 T.I.C. meeting held in Japan

This paper pertains to tantalum capacitors. In particular it deals with the problem of volumetric efficiency in tantalum capacitors. In the course of this discussion we will define what is meant by "volumetric efficiency", explain why it is important in the capacitor industry, and show that volumetric efficiency can be treated mathematically as a problem in packaging. We will further demonstrate that the shape of the tantalum particles in the capacitor anode is critical to the volumetric efficiency of the anode, and that there is one shape, the flat plate or flake particle, that gives the highest volumetric efficiency. Finally we will demonstrate how the mathematical analysis of volumetric efficiency has been used to design new powders at Cabot Performance Materials to provide increased volumetric efficiency under demanding conditions of high formation voltage, and in particular, how the tantalum powder products C250 and C255 were designed and made based upon this theory.

First, what is meant by volumetric efficiency? Volumetric efficiency in tantalum capacitors refers to the amount of capacitor function that can be packaged into a given volume. Volumetric efficiency is usually measured as microfarad volt per cubic centimeter. High volumetric efficiency provides two important advantages for the capacitor manufacturer: first, higher volumetric efficiency means higher package density which means that more parts can be processed in a given space or in a given unit operation. This provides for cost savings for the capacitor manufacturer because of less labor per part. The second benefit is through the extension of the range of parts offered in a given case size. This creates new markets by increasing the technical opportunities for electrical designers. The entire tantalum industry benefits from the technological advantage brought about by range extensions.

Before going into the details of the mathematical analysis of this important packaging problem I must first review the basic principles of any capacitor. For this we must consider the components of a generic parallel plate capacitor. In this configuration the capacitor is seen to consist of three components: the metal anode plate, the insulating dielectric layer, and a second conducting plate (see Figure 1). All capacitors contain these three basic components. In order to optimize the volumetric efficiency of this configuration we must assure that none of these components is present to an extent greater than the minimum required to achieve its purpose. This concept forms the basis of the packaging problem that must be solved.

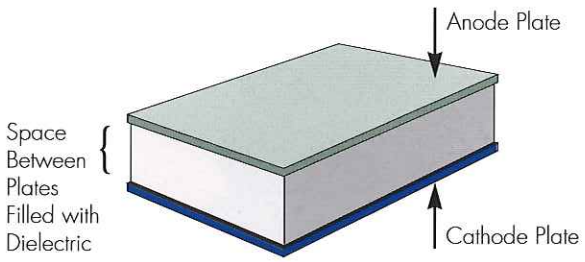

Figure 1 : Generic capacitor components

In a real tantalum slug capacitor the tantalum particles of the anode are of many different random shapes and sizes. If we examine the slug very closely we can see that on the microscopic level the structure of the anode resembles the simple generic model discussed above (see Figure 2). The same three components are found in repeating layers: the tantalum metal is the anode plate,

the anodic film is the dielectric layer, and the MnO_2 is the cathode plate.

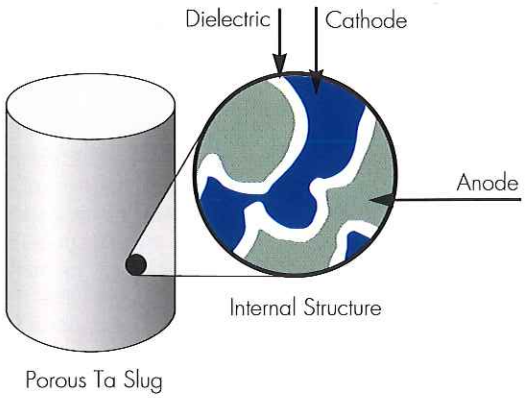

Figure 2 : Microscopic structure of tantalum slug capacitor

In order to analyze mathematically the packaging of these components in a real tantalum capacitor we will consider that the many particles in an anode are of simple geometric shapes that can be treated mathematically. Then we can compare the volumetric packing efficiency possible with various shapes to make an approximation to the behavior of the very complex mix of particle shapes and sizes in a real capacitor. The first idealized particle shape to be considered is the sphere (see Figure 3). In this model the spherical tantalum particles can be brought as close together as needed and their sizes varied to optimize the packing volumetric efficiency.

Figure 3 : Packed spheres

The second idealized particle shape is the rod shape or fiber particle. In this configuration the cylindrical fibers are considered to be bundled together so as to give a highly dense, efficient packing arrangement (see Figure 4).

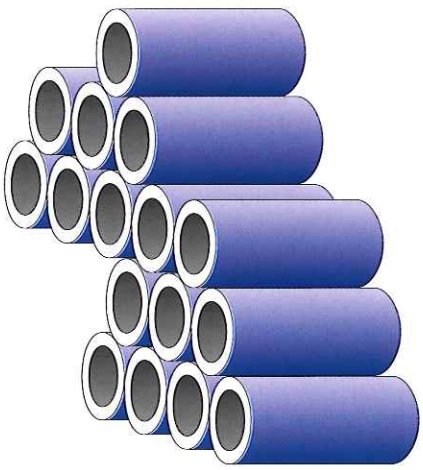

Figure 4 : Fiber structure

The third particle shape to be modeled will be the plate shaped flake particle. In this structure the plates will be stacked parallel to each other with gaps between to allow for the MnO_2 cathode.

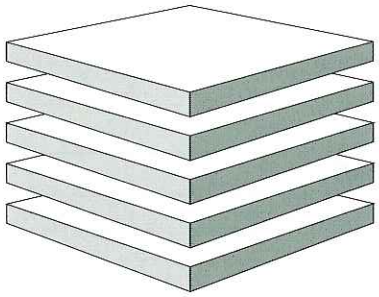

Figure 5 : Stacked plates with gaps between

In all three cases (spheres, cylinders and plates) there will be certain geometrical constraints on how closely we can imagine packing the particles. This constraint is to take into account the fact that in a real tantalum capacitor the manufacturing process and other electrical requirements for the finished capacitor will dictate that there must be a minimum gap left between the dielectric layers for the MnO_2. This gap cannot in general be allowed to be arbitrarily small and so leaving room for this gap causes an unavoidable reduction in anode density and thereby limits the volumetric efficiency achievable. The size of this MnO_2 gap is referred to in this analysis as the "impregnation parameter" or, when we consider it to be held to a given value, the "impregnation constant". When we calculate the packing density of the idealized particles we will always allow just enough space between the closely packed particles to ensure that we do not violate the requirement of maintaining this gap size. When we use this closest allowed packing density in our calculations we will always be obtaining the highest possible volumetric efficiency attainable for the given particle shape and size under consideration. In the case of the spherical particles the impregnation parameter is held equal to the longest diagonal distance between neighboring pairs of particles in the close packing arrangement. Similarly, in the cylindrical particles case the diagonal gap between neighboring cylinders is held equal to the impregnation parameter. Finally, in the plate shape particles the parallel plates are prevented from touching each other by exactly this impregnation parameter.

In all three cases we will calculate the volumetric efficiency of any selected particle shape and size by first calculating the microfarad volt per gram of an isolated particle at the given forming voltage. Next we calculate the resultant size of the anodized particles taking into consideration that the outward size of a tantalum particle increases as it is anodized because the tantalum pentoxide coating is less dense than the tantalum metal consurned in the process. Next we combine the numerical size of the anodized particle and the assumed impregnation parameter to calculate the optimum density to achieve the highest possible volumetric efficiency. This will be the highest density that does not allow the particles to come closer together than the impregnation parameter. In all cases however we do not allow the density to exceed 50% of the theoretical density of solid tantalum metal. The next step is to correct the microfarad volt per gram for sintering losses as reflected in the sintered density by applying a microfarad volt yield factor that depends linearly on the sintered density; the higher the sintered density the smaller the fraction of the total microfarad volt per gram that is available. In the final step the volumetric efficiency (microfarad volt per cubic centimeter) is calculated as the product of the maximum density and the corrected microfarad volt per gram. Following the above procedure for various particle sizes while keeping forming voltage and impregnation parameter constant creates a graph whose maximum occurs at the particle size which gives the higest volumetric efficiency for the assumed conditions of formation voltage and impregnation parameter. This procedure is outlined in Figure 6.

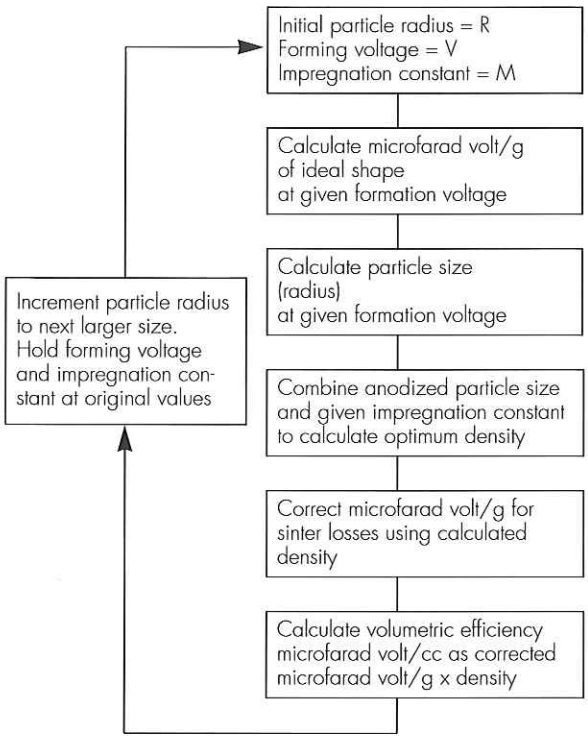

Figure 6 :
Mathematical model for optimizing particle size : flow chart.

Graphs of the data generated by the above procedure (see example in Figure 7) show microfarad volt per cubic centimeter versus particle size for standard formation voltages and constant impregnation parameter. Such graphs always show two characteristics:

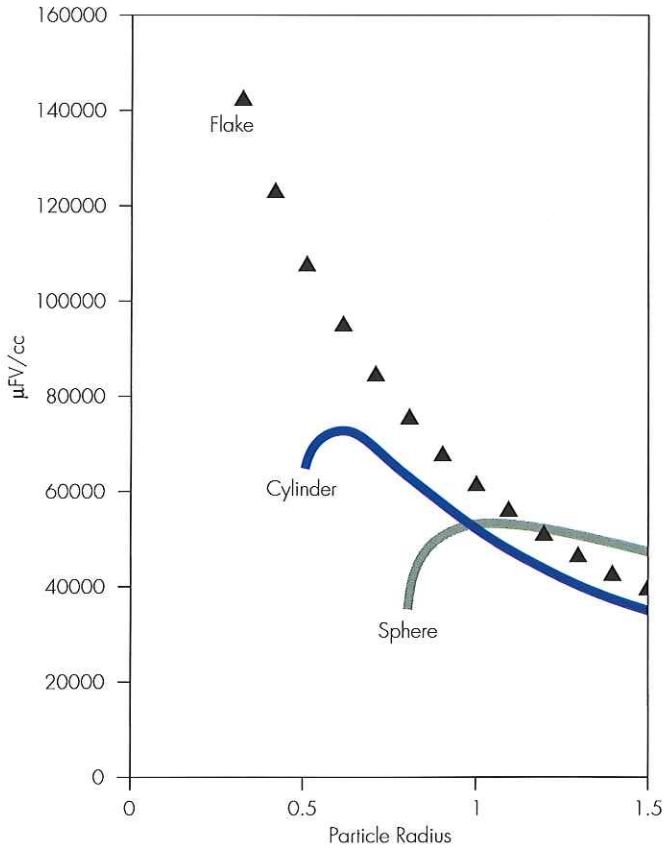

Figure 7 : Volumetric efficiency of flakes, cylinders and spheres formed to 150 volts with impregnation parameter of 0.75 micron

one, the three different particle shapes produce distinctly separate curves that diverge as the volumetric efficiency approaches its maximum with decreased particle sizes; flake giving the highest maximum microfarad volt per cubic centimeter, cylinders the next highest, and spheres exhibiting the lowest. The second feature is that curves for the rounded spheres and cylinders show a broad breakdown behavior in the vicinity of their maximum microfarad volt per cubic centimeter values which adds a further restriction to the achievable volumetric efficiency because of the need to avoid operating near this electrical failure regime. Such a graph made for 150 volts formation and impregnation parameter of 0.75 micron shows a maximum volumetric efficiency for flakes of 120 000 microfarad volt per cubic centimeter, for cylinders we obtain about 75 000 microfarad volt per cubic centimeter, and spheres give us about 55 000 microfarad volt per cubic centimeter. Graphs like this one were used during the design phase of C250 development to guide the selection of the flake thickness and microfarad volt per gram for a product that would give optimum microfarad volt per cubic centimeter at 150 volts formation. The design considerations are to make a powder as high on the flake curve as possible whilst staying away from the termination of the curve at the very highest microfarad volt per cubic centimeter where the formation completely consumes the flake.

The calculation of the volumetric efficiency for flake particles is achieved through the use of four equations that are shown below. These equations are based upon the geometric concept of a flake anode unit cell (see illustration below) comprised of the basic components of the anode stacked as closely together as is possible in order to maximize the microfarad volt per cubic centimeter. The first equation gives the optimum sintered density as a function of flake thickness, impregnation parameter, and forming voltage. The second equation gives the microfarad volt per gram as a function of the sintered density (arrived at by equation 1) and the flake thickness (this equation amounts to "correcting" the microfarad volt per gram of the ideal flake to take into account the sintering losses associated with the densification of the pellet. In this equation we multiply the theoretical maximum microfarad volt per gram of the flake by a sliding yield factor which linearly decreases to zero as the sintered density approaches 100% dense - 16.6 g/cc). The volumetric efficiency, microfarad volt per dubic centimeter, is obtained by the third equation which is the product of the maximum sintered density from equation 1 and the corrected microfarad volt per gram from equation 2. The final equation, equation 4, gives the thickness of the residual metal of the flake after anodizing. This is to check on the consistency of the calculation so as to discard any combinations of flake thickness and forming voltage which would produce a negative residual metal thickness; i.e. cases wherein the flake would be completely consumed by the anodization process are not considered.

Eq 1	Anode Density	$D_s = \frac{16.6L}{L + M + 0.002V_f}$
Eq 2	Anode microfarad volt per gram	$C = \frac{-904\ D_s + 15000}{L}$
Eq 3	Anode microfarad volt per cubic centimeter	$E = \frac{249000M + 498\ V_f}{(L + M + 0.002\ V_f)^2}$
Eq 4	Residual thickness (after anodizing)	$T = L - 0.0014\ V_f$

Figure 8 : Volumetric efficiency equations for plates

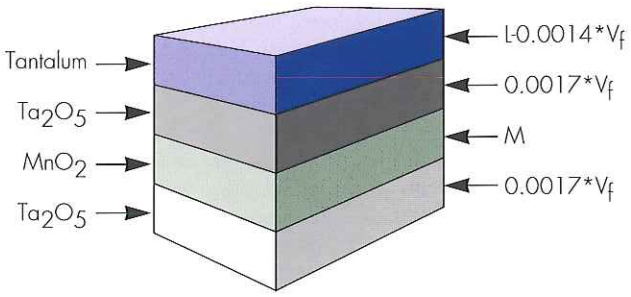

Figure 9 : Anode unit cell for maximum volumetric efficiency

In this diagram and in the equations in Figure 8 above L = flake thickness in microns prior to anodizing, M = impregnation parameter in microns, V_f = forming voltage, and D_s = sintered density in g/cc.

In conclusion we have discovered that maximizing volumetric efficiency is a problem in packaging that can be treated mathematically. The solution to this problem indicates that flake shaped particles give the highest volumetric efficiency because of the limitations that result from the thick anodic film at high voltages. Further we have seen how the equations for the volumetric efficiency of flake can be used to analyze and design tantalum capacitors with selected requirements for forming voltage and microfarad volt per cubic centimeter. Finally we show as an example how C250 and C255 tantalum powders were in fact designed at Cabot Performance Materials using these equations to achieve the maximum volumetric efficiency for applications requiring 150 volts formation.

CATALAO : ISO 9002

CATALAO RECEIVES ISO CERTIFICATION
Mineraçao Catalao de Goiás Ltda, of Sao Paulo, recently announced that it has established and implemented a Quality Management System according to ISO 9002. The certificate, issued by Bureau Veritas Quality International (BVQI) on behalf of the Dutch, British and American Councils of Certification, applies to the integrated production and distribution of standard grade ferroniobium.

Landscape near Nekoma Hotel

Mr and Mrs Hubert Hutton (President 1993-4) with Mr and Mrs Peter Kählert (President 1994-5) (right)

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