TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

BULLETIN No. 55 AUGUST 1988 THIRD QUARTER

International Symposium on Tantalum and Niobium

The Symposium will be held in Orlando, Florida, on November 7th, 8th and 9th 1988, with registration and a social event to celebrate the opening of the conference on November 6th.

SUNDAY NOVEMBER 6th

Registration : delegates should collect their papers and badges from the T.I.C. registration desk as early as possible.

Evening : Welcome cocktail party (dinner at leisure).

MONDAY NOVEMBER 7th

Twenty-ninth General Assembly of the Tantalum-Niobium International Study Center : attendance limited to delegates of member companies.

Opening of Symposium : the President of the T.I.C. will declare the conference open.

Presentation of papers, with breaks for lunch and, during the afternoon, for coffee.

Evening : Banquet dinner, all participants and their ladies are invited.

TUESDAY NOVEMBER 8th

Presentation of papers, followed by an afternoon open for informal discussions.

Evening : casual party, with cash bar and a large TV so that delegates will have the opportunity to meet each other and to see the results of the Presidential Election as they are declared, with the subsequent discussions and celebrations as the next President of the United States is elected.

WEDNESDAY NOVEMBER 9th

Presentation of papers, with pauses for coffee and lunch.

At 5.30 p.m. closing ceremony of the Symposium, by the President of the T.I.C.

Evening : the possibility to go out into the town of Orlando for dinner and entertainment.

The Symposium will be held at the Stouffer Orlando Resort, 6677 Sea Harbor Drive, Orlando, Florida 32821, U.S.A., where delegates will also stay. A large number of rooms has been booked for the group at special rates, and reservations can only be made through the T.I.C.

Pre-registration before October 1st is essential; forms and information are obtainable from the Secretary General of the T.I.C., 40 rue Washington, 1050 Brussels, Belgium. Invitations have been sent to the nominated delegates of member companies, and information has been sent to member companies and all who have contacted the T.I.C. to request this. The Symposium is open to participants from non-member companies : everyone interested is welcome and should send for information without delay.

Tours for spouses and accompanying persons are being arranged, including a visit to Cypress Gardens, where the annual chrysanthemum festival should be at its height, and a boat trip on the canals and lakes of Winter Park.

Orlando has many attractions, and those who are able to spend a few days there before or after the meeting will find much to interest them, such as Sea World, the Walt Disney World Magic Kingdom and EPCOT Center (Experimental Prototype Community of Tomorrow), golf on a choice of renowned courses, tennis on one of the numerous courts available, or a trip to the Kennedy Space Center. Information may be obtained through the T.I.C. and our agents are ready to offer travel arrangements. The weather should be mild and pleasant, the hotel is splendid and we believe that delegates will find both the programme and the setting for the meeting are most appealing.

TWENTY-NINTH GENERAL ASSEMBLY TO BE HELD AT 9.00 A.M. ON MONDAY NOVEMBER 7TH 1988 AT THE STOUFFER ORLANDO RESORT, ORLANDO, FLORIDA.

AGENDA

1. **Voting proxies**
2. **Address by the President of the T.I.C., Mr Hans-Jürgen Heinrich**
3. **Minutes of the Twenty-eighth General Assembly (held in Brussels on October 20th 1987)**
4. **Membership : applications, resignations**
5. **Financial matters : approval of audited accounts for the year ending June 30th 1988**
6. **Report of Executive Committee**
7. **Report of Technical Officer**
8. **Statistics**
9. **Statutory elections**
10. **Forthcoming General Assemblies**
11. **Other matters**

Technical programme

The programme of more than thirty technical papers for the symposium is intended to reflect the range of interests of the T.I.C. membership, with particular emphasis on applications for tantalum and niobium and new developments in the industry. It is divided into four sections : marketing aspects of tantalum and niobium; production of raw materials; processing technology; and applications. The technical programme will cover both tantalum and niobium. The majority of the speakers represent companies actively involved in the tantalum/niobium industry. Further details of the technical programme may be requested from the T.I.C.

1. MARKETING ASPECTS OF TANTALUM AND NIOBIUM

Historical development of the tantalum/niobium industry. Statistical survey and market reviews of tantalum and niobium. New developments.

2. PRODUCTION OF RAW MATERIALS

Mining and beneficiation of tantalum and niobium ores worldwide. Tantalum's association with tin production. Ore deposits.

3. PROCESSING TECHNOLOGY

Extractive metallurgy and high-purity compounds. Chlorination and niobium metal production. Tantalum capacitor-grade powder and mill products. Recycling of tantalum. Melting processes.

4. APPLICATIONS

Established and newer uses : tantalum electronic capacitors; niobium in HSLA, stainless and tool steels and cast iron; niobium-based superconductors; tantalum and niobium in high-temperature alloys; ceramic dielectrics containing tantalum and niobium oxides; tantalum and niobium based alloys for anti-corrosion applications; niobium-based aerospace materials under development; and niobium in catalysis.

T.I.C. statistics

QUARTERLY PRODUCTION ESTIMATES

(quoted in lb Ta_2O_5 contained)

MB quotation :	*US $ 30*	*US $ 40*	*US $ 50*
2nd quarter 1988	275 550	305 000	471 900
3rd quarter 1988	280 550	375 000	506 900
4th quarter 1988	280 550	395 000	516 900
1st quarter 1989	280 550	405 000	526 900
2nd quarter 1989	286 550	410 000	539 400

Note : These estimates were based on information received to date and do not necessarily reflect total world production.

PRODUCTION AND SHIPMENTS

(quoted in lb Ta_2O_5 contained)

1st quarter 1988

	Production	*Shipments*
Tin slag (over 2 % Ta_2O_5)	240 063	220 096
Tantalite, other	200 860	24 392
Total	440 923	244 488

Note : The response from the companies asked to report was 16/16 and included these producers :

Datuk Keramat Smelting
Greenbushes
Malaysia Smelting
Mamoré Mineração e Metalurgia
Metallurg Group
Tantalum Mining Corporation of Canada
Thailand Smelting and Refining

4th quarter 1987

Material grade	*Production*	*Shipments*
Tin slag (over 2 % Ta_2O_5)	271 331	187 279
Tantalite, other	78 875	123 689
Total	350 206	310 968

Total for 1987

Material grade	*Production*	*Shipments*
Tin slag (over 2 % Ta_2O_5)	662 821	534 728
Tantalite, other	222 803	228 276
Total	885 624	763 004

PROCESSORS' SHIPMENTS

1st quarter 1988

Product category	*lb Ta contained*	*lb Ta_2O_5 equivalent*
Tantalum oxide/K_2TaF_7	19 959	26 945
Alloy additive	41 863	56 515
Carbide	144 266	194 759
Powder/anodes	257 253	347 292
Mill products	98 823	133 411
Scrap, ingot, unworked metal and other	16 310	22 018
Total	578 474	780 940

Notes :

1. The response from the companies asked to report was 17/18 and included these processors :
   Cabot Specialty Metals - Electronics
   Fansteel
   W.C. Heraeus
   Kennametal
   Metallurg Group
   Mitsui Mining and Smelting
   NRC
   Showa Cabot Supermetals
   Hermann C. Starck Berlin
   Treibacher Chemische Werke
   Vacuum Metallurgical Company
   V-Tech
2. Reports were made in lb tantalum contained.

Capacitor statistics

EUROPEAN TANTALUM CAPACITOR SHIPMENTS

(thousands of units)

1st quarter 1988	174 573

(Data from ECTSP)

JAPANESE TANTALUM CAPACITOR PRODUCTION AND EXPORTS

(thousands of units)

	Production	*Of this, Exports*
1st quarter 1988	794 173	228 807

(Data from JEIDA)

U.S. TANTALUM CAPACITOR SALES

(thousands of units)

1st quarter 1988

	U.S. shipments	*Exports*	*Total*
Foil	305	6	311
Metal-cased	32 488	10 041	42 529
Molded	104 221	19 568	123 789
Dipped	106 355	21 263	127 618
Chips	32 821	12 917	45 738
Wet slug	2 397	258	2 655
Total	278 587	64 053	342 640

(Data from EIA)

Miniaturised impressed-current corrosion protection systems : an application for platinum-clad niobium

The conclusion of an article from Bulletin no. 54 by Dr. Robert Baboian, Texas Instruments Inc.

FIELD TRIALS AND SERVICE PERFORMANCE

Field trials were conducted in areas having documented corrosion failures where tanks had failed in less than three years. They included sites with well waters, waters with high concentrations of sulphides or chlorides, and acid waters. Impressed-current corrosion protection systems conforming to production specifications were installed at each site. Water conditions, protection currents and tank potentials were measured periodically at selected sites. These potentials were all in the protection region for steel indicating that the proper protection current was being supplied by the mini-ICCP system.

Table I
Field Evaluation of Mini-ICCP in Hot Water Storage Tanks

Location	Source of water	Water resistivity ohm cm	pH	Protection current mA	Tank potential (volts vs. S.C.E.)
Reheboth, MA	Well	8000	5.5	14	−1.08
Reheboth, MA	Well	3200	4.9	17	−1.13
Attleboro, MA	Reservoir	3500	7.1	9	−0.95
Johnston, R.I.	Well	7100	6.9	15	−0.102
San Diego, CA	Reservoir	1000	8.4	16	−1.32

A typical potential profile for a hot-water storage tank showed that the protection was distributed throughout the inside tank wall. The absence of tank failure after five years at sites where failure had previously occurred with magnesium anodes after only three years provided conclusive evidence of the effectiveness of the mini-ICCP system in the increasingly aggressive hot-water storage tank environments now encountered.

Table II
Typical Potential Profile of Hot Water Storage Tank with Mini-ICCP Protection*

Tank depth (cm)	Tank potential (volts vs. S.C.E.)
Top	−1.20
10	−1.20
25	−1.31
50	−1.25
75	−1.05
Bottom	−1.03

*1 Year service, 15 mA protection current, 3500 ohmcm water, pH = 5.2

SUMMARY

Advances in electronics and materials technologies have led to the development of miniaturised impressed-current protection systems. The system described here was developed for the protection of glass-lined steel hot-water storage tanks. It consists of a platinum-clad niobium anode strip, which extends the full length of the tank, and an electronic control unit. The stability of platinum-clad niobium has been well documented so that the design of the anode for long life is ensured. The control unit was designed to provide optimum cathodic protection current for the tank in all water conditions. Service performance of the mini-ICCP system has shown that problems encountered with other protection methods are overcome with this device. The system has applicability in other environments including water pumps, valves, water-cooled devices and a wide range of plant equipment where small protection currents and inexpensive miniaturised circuitry is necessary.

Lithium niobate and tantalate in acoustics and electro-optics

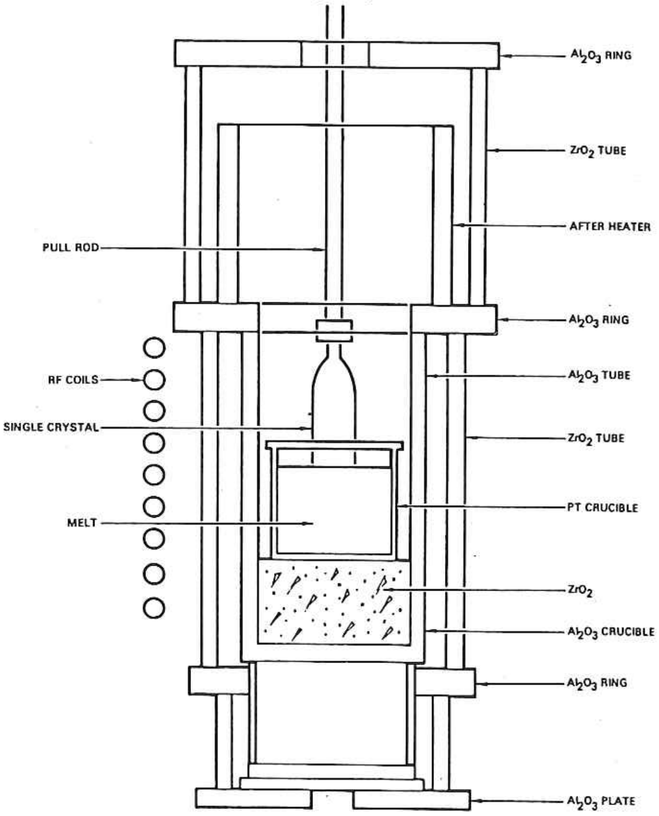
Lithium niobate and lithium tantalate (hereafter referred to as "LN" and "LT" respectively) are compounds used in acoustic and electro-optic applications as well as in a number of related but less common ones. In acoustics, LN and LT act as convertors of electrical energy into mechanical (acoustic) energy and vice versa, i.e. they are piezo-electric materials. Electro-optics uses LN and LT because the refractive indices of the two materials vary with an applied external voltage. These phenomena enable LN and LT to be applied in a wide variety of specialized devices — too many and too complex to be covered adequately in this article. Of the two materials, LN is by far the more widely used, primarily because of its lower cost, though some of its properties are more favourable as well.

PRODUCTION AND STARTING MATERIALS

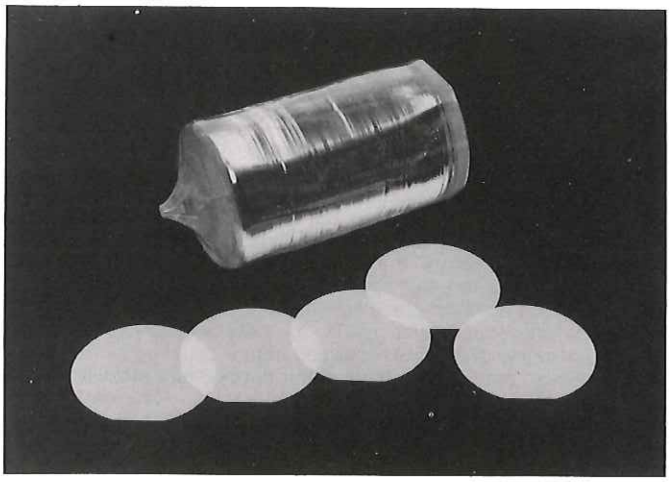
Both materials are transparent, moderately hard and dense and resemble clear glass. They are "grown" as single crystals from the molten state by the Czochralski process which uses exceptionally pure oxides and lithium carbonate as starting materials. The apparatus consists of a platinum crucible surrounded by a refractory housing. A radio-frequency induction coil heats the reagents until they melt (at 1253 °C for LN and 1650 °C for LT). A rotating seed crystal, with the orientation desired in the new crystal, is lowered to the surface of the melt and then slowly withdrawn, bringing with it some of the frozen liquid which becomes a new layer of solid single crystal. More material freezes onto this crystal as the seed is continuously raised.

The dimensions of the "boule", as the resultant cylindrical single crystal is known, are limited to 75 mm diameter by 125 mm length — an improvement from the 1970's when the maximum dimensions were 15 mm diameter and 20 mm length. This improvement has been achieved by refining the process parameters and has reduced the cost of producing LN and LT. Further refinements in the future could increase the scale of production and so reduce costs still further — obviously, this could open up new areas of usage. In 1987, Crystal Technology introduced 125 mm diameter boules.

The Czochralski method for producing LN and LT single crystals

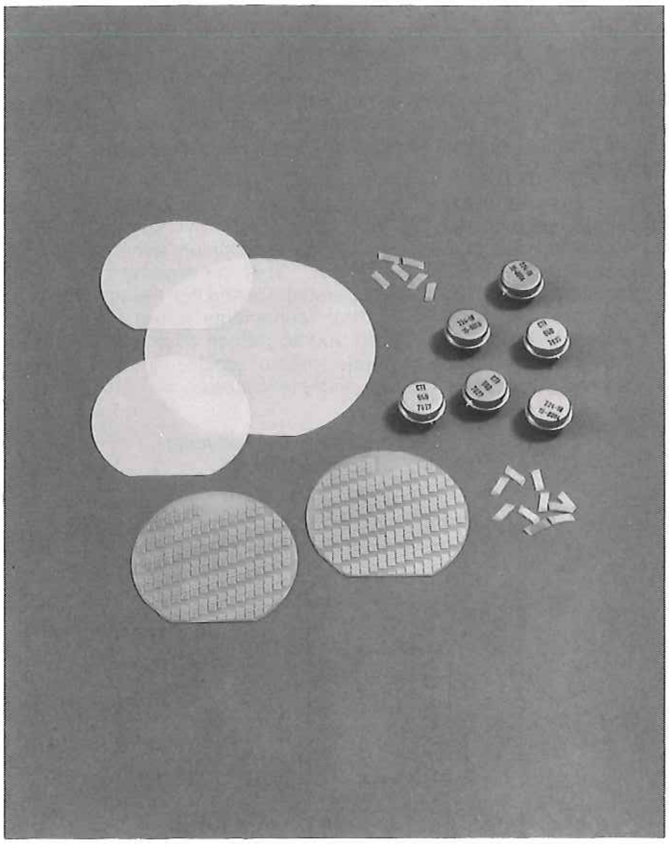


LN ($LiNbO_3$) boule and wafers



The boule is then "poled" by slow cooling through the Curie temperature to align the domains in a certain orientation to the crystal axes (analogous to the way in which a ferro-magnetic material is magnetically polarised). It is then rounded and sliced into circular wafers, normally $\frac{1}{2}$ or 1 mm thicknesses, which are polished on one side. Eventually these wafers will be sectioned into minute pieces suitable for fabrication into acoustic or electro-optic components.

LN wafers and filters



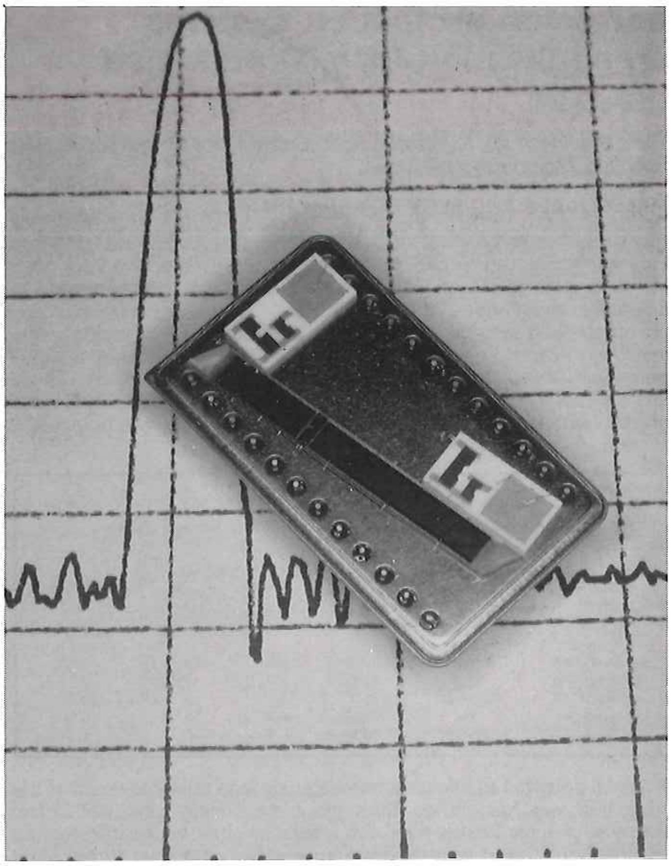
Exceptionally high purities are required of the starting materials for LN and LT production, especially the niobium and tantalum oxides since they account for around 95 % by weight of the final material. LN is produced in two grades : the more usual "acoustic-grade" specified by one manufacturer as containing less than 15 ppm iron and 5 ppm of other transition metals; and "optical-grade" containing less than 5 ppm iron and 1 ppm of other transition metals. Similar high qualities are required of LT. Iron contents are important since the element has an especially deleterious effect on the properties of the final material. The oxides used as starting materials are nominally specified as having "99.99 % purity", though the maximum contents of individual elements are obviously more significant; at Hermann C. Starck Berlin, these oxides are produced by a chlorination route. The oxide and lithium carbonate are rected together prist to being melted in the Czochralski apparatus.

In the West, there are two major producers of LN and LT materials : Crystal Technology, U.S.A.; and Pilkington Electro-optic Materials, U.K. There are thought to be a number of producers in Japan, one of whom is Hitachi Metals. The worldwide market is perhaps between 10 and 20 tonnes Nb_2O_5 for acoustic-grade LN and less than one tonne Nb_2O_5 for optical-grade LN; the equivalent market in LT is probably at least one order of magnitude less.

ACOUSTIC AND ELECTRO-OPTIC APPLICATIONS

Most LN is used to make surface acoustic wave (SAW) devices for IF filters in colour TV sets, the component which splits the incoming signal into its audio and visual components. The signal is transmitted into and out of the mounted LN substrate by metal electrodes produced as a series of lines on the substrate surface by vapour deposition; the geometry of these electrode lines controls the device's characteristics. Before this application in consumer electronics, the major market for acoustic-grade materials lay in military electronics for delay lines and encoders/decoders, for example. LN tends to be favoured because of its lower cost and higher coupling factor (lower energy losses), but LT does have better temperature stability and is used for digital radio links in civil communications. New markets are being created for SAW devices (using acoustic-grade LN) in expanding areas of electronics such as video recorders, video games and cable TV.

SAW filter with LN substrate



The major market for optical-grade LN lies in Q-switches for lasers. A market which shows some potential for growth is integrated optics, primarily in telecommunications using fibre optic technology. However, this market could be restricted in the future if materials such as gallium arsenide gain widespread acceptance. These materials are used for "true" integrated optic devices, i.e. laser and photodetector mounted on the same chip; LN substrates are used only for "hybrid" assemblies, i.e. discrete sources and detectors.

SUMMARY

Lithium niobate and lithium tantalate are piezo-electric materials with applications in acoustics and electro-optics. They are produced as single crystals by the Czochralski method using high-purity niobium/tantalum oxide as a starting material. The major use for lithium niobate (the more widely applied of the two specialty materials, primarily for reasons of cost) is to make IF filter substrates for TV sets. A promising market lies in integrated optics.

LITERATURE

1. "Lithium niobate — a material to influence product design", T. Weardon, "New Electronics" (20.3.84).
2. "Niobium compounds in acoustics and electro-optics", R. Rice, "Niobium '81".
3. Product literature from Crystal Technology Inc.

(Photographs courtesy of Crystal Technology, Palo Alto, California, U.S.A.).

Andrew Jones
Technical Officer

Powder-metallurgy techniques for the capacitor industry

This article has been extracted from a paper "Powder-metallurgy techniques in the electronics industry" by Dr James C. Wang, Kemet Electronics Corporation, presented at the Annual Powder Metallurgy Conference 1987 and published in the Proceedings.

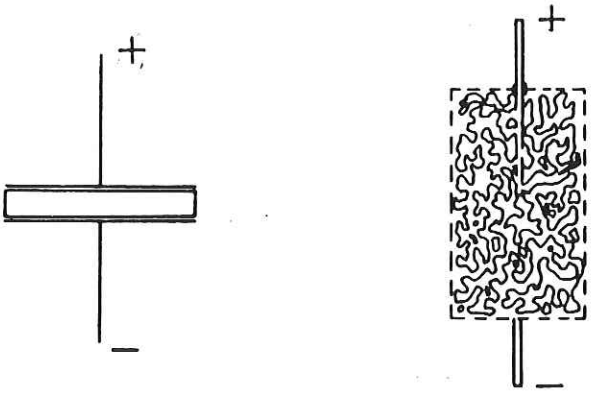
Powder metallurgy is widely used in the appliance, automotive and aerospace industries for making structural components. Little attention is given to the powder-metallurgy techniques used in the electronics industry. Powder metallurgy is used for fabricating raw materials, such as conductive materials for lead frames, and is used for making components such as capacitors used in electronic circuits. This paper discusses some of the special powder-metallurgy techniques used by the capacitor industry.

Traditionally, capacitors were made of two pieces of parallel conducting metal plates, separated by a sheet of paper impregnated with oil, wax or dielectric resin. Without changing materials, i.e. the dielectric constant is the same, one can increase the capacitance by increasing the area of the plates, decreasing the separation of the plates, or both. The thickness of a paper is typically 50 μm so there is only limited room for reducing the separation. The only option is to increase the area. A thousandfold increase in capacitance requires a thousandfold increase in material consumption, and the weight of a capacitor could be in the order of kilograms.

A large increase in capacitance without a large increase in size, weight and material consumption can be achieved by changing the plate construction to a porous slug. One can sinter powder into a porous slug which serves as the anode. A very thin (500-5000 Å) dielectric is formed onto the porous surface in situ by anodizing the pore surface to oxide. A conductive electrolyte solution is subsequently infiltrated into the pores, serving as the cathode or negative plate. Alternatively, a suitable solution is infiltrated into the pores and then thermally decomposed into a semi-conductive, solid compound coated on the anodized dielectric film. Using this construction, a 10^4 increase in capacitance is obtained without any increase in volume, weight and material usage. This type of capacitor is called an electrolytic capacitor.

Tantalum powder is generally chosen for making the porous slug, because its anodized oxide film has excellent dielectric properties.

Plate construction vs porous slug construction



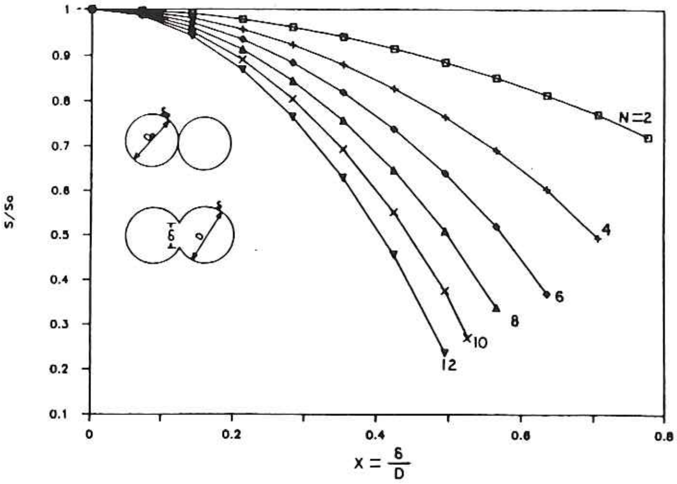
CAPACITANCE AND SINTERED SURFACE

For electrolytic capacitors, sintering is solely to impart mechanical strength to the porous body and to form an electrically conducting path. Any decrease of surface area and any closure of pores are to be avoided. Even the narrowing of the pore opening is undesirable because it restricts the subsequent infiltration process.

The capacitance of an electrolytic capacitor depends on the sintered surface area. One apparent way to maximize the surface area is to decrease the powder size. Since the cost of tantalum is approximately \$ 100 per pound, use of fine powder is very attractive. Besides, fine powder can provide large surface in a small volume, helping miniaturization. The benefits of fine powder can easily be erased unless other factors are addressed.

The loss of surface area to sintering is important. Consider a spherical powder of diameter D_o with a specific surface area (surface per unit weight) of S_o. As the neck grows, according to Knudsen's model, the center-to-center distance between particles decreases and the particle diameter increases. At a sintering parameter (neck to particle size ratio) equal to X, the particle diameter is D and the specific surface area is S. The fractional surface retained is plotted.

Sintered surface as a function of co-ordination number and sintering parameter



So the effort spent in producing fine powder can easily be defeated if the co-ordination number is high (i.e. a high green density) or the sintering parameter is large (i.e. well sintered). Immediately, we see a dilemma. To achieve mechanical strength, one must use either a high green density or a low green density with more sintering. Either way, the loss of surface area is unavoidable. Fibrous powder can greatly improve the situation and also produce an open-pore structure after sintering, allowing easy infiltration of the cathode.

Since fibrous powder is still a laboratory material, flakes are frequently used to provide some improvement. Because no sintering models are available for flakes, the analysis of sintering still uses theories developed for mono-sized spherical powders.

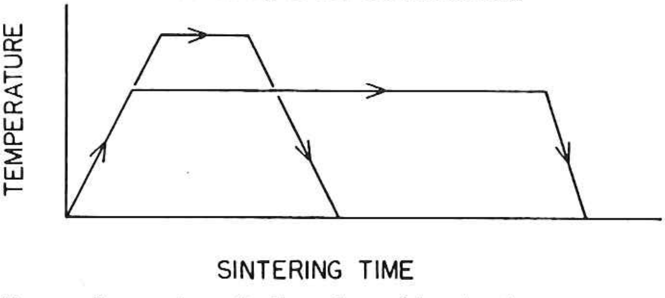
SINTERING THEORY AND ACTUAL PRACTICE

In the early days of tantalum capacitor manufacture, only coarse powders were available. The sintering temperature was around 2000 °C or higher, and the sintering time was long. It was believed that the high temperature and long time were needed to clean the powder by vaporizing the unstable volatile impurities. Impurities were thought to result in poor dielectric films and high electric current leakage.

Currently, powders of less than 0.5 μm equivalent diameter (0.5 m^2/g specific surface) are routinely used and even finer powders are being made in laboratory quantities. With the current powders, high-quality capacitors can be obtained using lower sintering temperatures around 1600-1700 °C and can be flash sintered in just a few minutes. It is postulated that with the small particle size, the distance needed for impurities to diffuse from the center of the powder to the surface is reduced. As a result, the diffusion time is decreased quadratically with the decreasing particle size. However, the reduction in temperature reduces the diffusion rate exponentially, more than enough to offset the size effect, without considering the reduction in the sintering time. Besides, only the top surface layer (approximately 5000 Å) is anodized into dielectric film, so the diffusion distance is constant regardless of the particle size. Therefore, a different explanation seems necessary.

The high sintering temperature and long sintering time for coarse powders could have been needed for structural reasons. A mechanically weak, porous slug can cause the anodized dielectric film to crack, resulting in high electric leakage. A given degree of mechanical integrity is brought about by a given amount of sintering which corresponds to a given sintering parameter. Sintering mechanism for tantalum in this temperature range is believed to be volume diffusion so that the time required to reach a given degree of structural integrity is proportional to the cube of the particle size. This seems to be a better explanation for the shorter sintering time required for finer powders. If the sintering mechanism is a combination of volume diffusion and surface diffusion, the powder size effect can be even more pronounced. Diffusion theory suggests that the time of sintering for surface diffusion is proportional to the fourth power of the particle size. However, in view of the exponential effect of the sintering temperature, the explanation proposed here may not be complete.

Flash sintering vs conventional sintering



The new fine powders offer the options of lowering the temperature, shortening the time, or both. From the production point of view, it is desirable to increase sintering temperature and shorten sintering time. However, with a short sintering time, a small variation in furnace dwell time constitutes a large variation in the amount of sintering, thus a large variation in surface area and capacitance. When the temperature is high, the amount of sintering taking place during the heating and cooling could be significant and may be an important portion of the total sintering, so the control of heating and the cooling rates also become important. Therefore, the compromise between throughput and batch-to-batch consistency must be considered in process design. This is particularly true for the sub-micron powders which allow flash sintering.

Currently, sintering conditions are arrived at by experience. For computer process design, a knowledge about the activation energy becomes imperative. The current knowledge on the activation energy of tantalum is scarce, and the reported values differ from investigator to investigator. The range of the reported value is from 530 KJ/mole to 335 KJ/mole.

To offer a more precise explanation for the low sintering temperature and short sintering time, or to experimentally verify which reported activation energy value is correct, fundamental research is needed, such as a detailed study of sintering mechanisms. But this is often beyond the scope of industrial research, so a joint effort between the industry and the academic community is highly desirable.

KINETICS OF SURFACE REDUCTION

Fine powder offers extremely high surface area. The finer the powder, the higher the surface area is and the faster the surface area is lost by sintering. It is essential to understand the mechanism and the rate of surface loss.

Every reaction can be described as :

$$\text{Reaction rate} = \text{Rate constant} \times (\text{Reaction source})^m$$

where "m" is the order of reaction. Therefore, using a simplified argument :

$$\text{Rate of surface loss} = K \times (\text{Surface})^m$$

It is clear that the finer the powder, the larger the surface area and, therefore, the faster the surface area is lost by sintering.

In the above simplified argument, it is assumed that the driving force for sintering is the amount of surface area present. This assumption works very well for the intermediate sintering stage. However, in the early stage of sintering (where most of the sintering of capacitors takes place) the origin of the driving force is more complicated. The free energy of a convex surface is higher than that of a flat surface; and the free energy of a concave surface is lower than that of a flat surface. The sharper the curvature, the greater the free energy differs from that of a flat surface. It follows that the free energy of a surface arises from both the amount of the surface and the type (convex, concave or flat). In the early sintering stage, the neck radius is very sharp. The driving force is predominantly the urge to move atoms from the high-energy convex region to the low-energy concave neck. In other words, the neck growth is driven by the negative curvature of the neck rather than the amount of total surface area. A theoretical treatment shows that the surface reduction is at its highest rate at the earliest stage.

Theory can show that the rate constant, K, is inversely proportional to the cube of the powder size if the sintering is by volume diffusion, or to the fourth power if by surface diffusion. It can also be shown that the finer the powder, the faster the surface area is lost to sintering, imposing a difficult challenge to the use of even finer powders.

PRESERVATION OF SINTERED SURFACE

As mentioned before, the high surface area offered by the sub-micron powders can easily be lost in sintering. Therefore, some means of preserving the surface during sintering is needed.

Certain impurities can be added to help preserve the surface area during sintering : phosphorus, silicon, nitrogen and boron are used. The impurities can be doped through hydrometallurgy during the chemical reduction of the tantalum powder from ore concentrate. But the standard powder-metallurgy blending approach can also be used.

For example, elemental phosphorus and, particularly, phosphorus compounds can be doped by dry blending or wet blending before pressing. Wet blending can be accomplished by adding the dopant into a water-methanol solution and then wet blending with tantalum powder. The blended slurry is dried and homogenized in a twin-shell blender. After sintering, the resulting porous surface can be increased from a few percent to about 30 %, depending on the dopant concentration (based on phosphorus level). The increase in sintered surface is noticed at dopant levels as low as 20 ppm or less. At higher dopant levels (above 100 ppm), a further increase in sintered surface to 35 % is possible.

The maximum dopant level is 400 ppm, because the doping effect saturates at this level and the green strength starts to deteriorate. Incidentally, doping with $Ca_3(PO_4)_2$ also improves the flow characteristics.

The current explanation of the effects of these dopants on sintering is that they act as inhibitors, probably forming stable inert phases on the powder surface and retarding the atomic movement. Considering that a tiny amount of dopant (a few tens ppm) is distributed over a large surface area, their profound effect on preserving the sintered surface area is amazing. The precise mechanism responsible for this deserves more exploration. Furthermore, if the dopant is introduced chemically by hydrometallurgy, the amount of dopant required is further reduced to just a few ppm. Also, the dopant is probably uniformly distributed throughout the powder as an interstitial impurity, rather than being an inert phase concentrated on the surface. This puts the previous explanation in question; a more convincing explanation is needed. An accurate understanding of how a few ppm of impurities can have such profound effect on sintering may lead to a new understanding of impurity-matrix interaction during sintering. This new understanding could have practical applications to the making of both porous bodies and full-density parts.

APPLICATION OF ACTIVATED SINTERING

As the powder becomes finer and finer, the green density can be made lower and lower to achieve a given surface area per unit volume (known as volumetric efficiency of a capacitor). Since the powder is finer and the green density is lower, the lead wire inserted in the slug will have a lesser number of contacts and each contact will be smaller in size, resulting in weak bonding between the lead and the porous body.

Activated sintering is a logical choice to remedy the problem. Activated sintering of tantalum has not been extensively studied, but there are many publications on the activated sintering of other refractory metals.

Transition metals (Group VIII) are found to be effective sintering activators for refractory metals. Group VIII elements have near complete d-shells which, when used as sintering aids, can modify the inter-atomic bondings of the neighboring refractory metal, resulting in easier atomic movement. Ni, Pd and Pt have been found most effective. Co is sometimes effective, especially for W, Mo and WC.

The only study on activated sintering of tantalum, to the author's knowledge, was conducted by German. From the activated sintering experience of other refractory metals, Ni, Pd and Pt were expected to have good activation effects on tantalum. However, the experimental results showed that only Ni provided the anticipated effect; Pd, Pt and other activators, such as Cu and Fe, seemed to show some marginal activation effect at lower temperatures.

From the fact that Ni-Ta forms a liquid phase at the sintering temperatures, while Pd-Ta and Pt-Ta do not form liquids, it has been pointed out that the mechanism for the Ni activation is perhaps due mainly to liquid-phase sintering and only slightly to the modification of atomic bonding.

An improved bonding between the lead wire and the porous tantalum body has been demonstrated using Ni-activated sintering. A Ni-coated lead wire is inserted into the green compact during pressing and is subsequently sintered. A stronger lead attachment is obtained when the coating thickness is 1000 Å, or thicker. The Ni coating cannot be too thick either; a Ni coating of 3000 Å, or thicker, results in a decreased strength and increased electrical leakage. The 1000 Å minimum thickness is about an order of magnitude higher than the commonly known threshold of 10-100 atomic monolayers. It could be that some of the Ni migrates from the wire to the surrounding powder, therefore, a thicker Ni source is needed. Otherwise, the Ni would be depleted and no activated sintering would be possible.

Other than Ni, Al has also been used as the activator for this purpose. The underlying mechanism is again probably liquid-phase sintering. An Al coating of 3600 Å on the lead wire increases the lead pull-out force from 2.2 kg to a wire-breaking force of 3.7 kg.

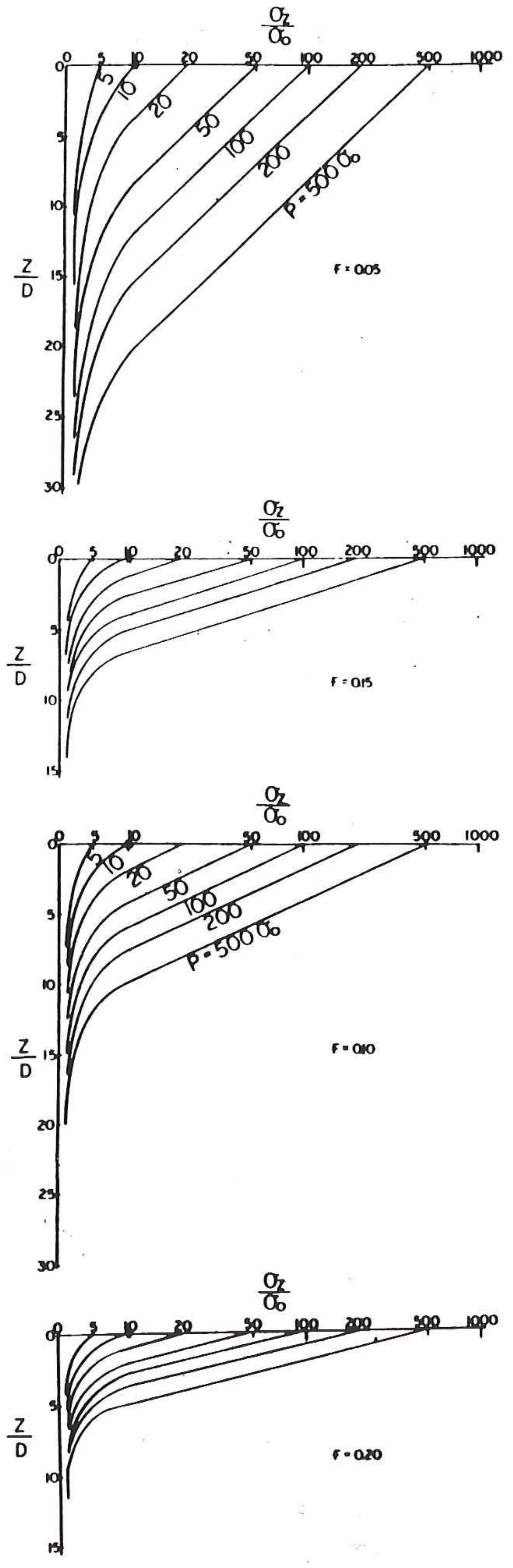
POWDER COMPACTION

In dry powder compaction, there is always some degree of non-uniformity in green density. This non-uniformity in density is due to a variation in compaction pressure within the compact, stemming from the friction encountered in compaction.

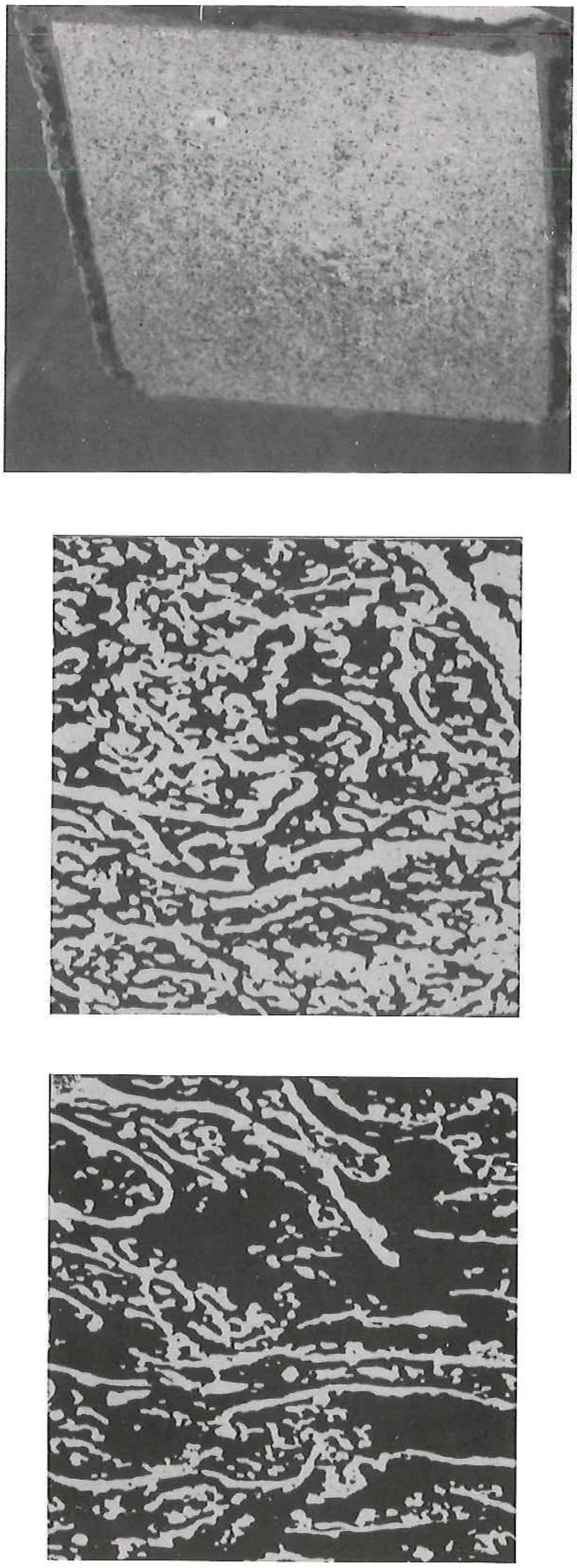
During compaction, the compaction pressure induces a die wall pressure. Because of the friction between the powder and the die wall, the compaction pressure decreases from the punch to the bottom of the compact. An analysis of the die wall friction indicates that the compaction pressure decreases exponentially along the compaction direction, as does the density.

The situation is uniquely severe in the capacitor industry. With increasing specific powder surface, powders become finer and flakier. As a result, friction becomes higher and compaction becomes more difficult. For example, the average density of the porous body (see photographs) is only 29 % of the theoretical, yet the non-uniformity in density is strikingly severe by any standard. In order to achieve a usable mechanical integrity, the bottom region of the compact must reach a certain density. In doing so, if a slight density increase in the bottom is required, the punch pressure will increase exponentially to a disproportionate level, leading to a dense compact in the top. Furthermore, the closure of the pores in the top region is foreseeable. Double-action compaction can provide some relief. However, as long as the miniaturization of capacitors and the increase in powder specific surface area continue, future difficulty is inevitable. This presents an area for more research into the wet-pressing technique and other advanced methods.

Pressure profiles along the axial direction for various die wall frictions and punch pressures (z, f, D, σ_z, σ_o and P are the distance below the punch, the frictional coefficient, diameter of the compact, compaction pressure at z, yield strength of the compact and the applied punch pressure, respectively.)



Density non-uniformity in a press-sintered capacitor (2.64 mm by 2.64 mm); plus enlarged views of top and bottom regions, respectively



INFILTRATION OF POROUS MATERIALS

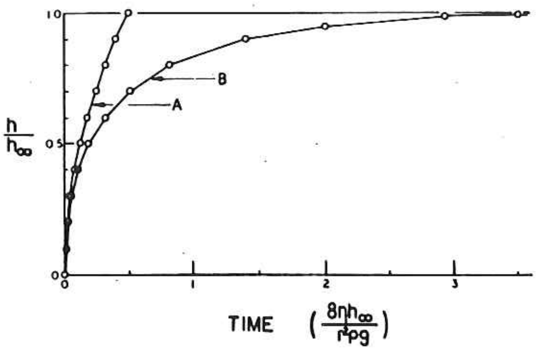
The infiltration of a porous capacitor by a liquid is very similar to the infiltration of porous bodies by molten metals.

The driving force for infiltration is to reduce the total free energy of the system, including surface energies and stored energies (kinetic energies, internal energies, potential energies) of all the components participating in the infiltration process. For infiltration to occur spontaneously, the free energy change must be equal to or less than zero. Assuming that infiltration occurs under mechanical equilibrium (very slowly) and there is no chemical reaction occurring, the kinetic and the internal energies can be omitted from consideration. Only the surface energy and the gravitational potential energy (weight of the infiltration column) need be considered.

If the free energy condition is not satisfied, infiltration is impossible. In this case, one can either modify or change the infiltrant, or one can use external pressure. Forced infiltration such as with a mercury porosimeter is unstable, however, and the infiltrant will be expelled once the external pressure is removed. Therefore, one has to choose an infiltrant which is compatible with the porous body.

Infiltration takes time. The primary forces for infiltration are capillary force (i.e. surface tension) and hydrostatic head, if present. These forces are consumed by the viscous drag and the weight of the capillary column. The excess force, if any, is to accelerate the infiltrant in the column. The infiltration time required is a quadratic function of the infiltration distance which has received wide acceptance by both researchers and practitioners because of its simplicity. However, it is only an approximation which may lead to serious errors (curve A). A more stringent analysis does not omit the weight of the infiltrant in the capillary (curve B).

Infiltration distance vs time



Curve A is valid only if the target distance for infiltration is less than 20 % of the equilibrium value. However, this distance can be exceeded if the infiltration distance is large (the parts to be infiltrated are big), or the maximum infiltration distance is small (low surface tension, high specific gravity, large pore size, or large contact angle). In addition, curve A predicts that it requires only a finite time to reach the final distance, while curve B indicates that it actually requires an infinite time.

Application of this model to porous materials must be done cautiously, because of the complicated nature of the infiltration path. Nevertheless, the concept and the basic features of the theory still apply qualitatively.

Non-ideal situations are often noticed. Air entrapment occurs as a result of the manner in which the infiltrant is directed inside the porous channels. The locations bypassed by the infiltrant form air pockets. The situation can be rectified by infiltration under vacuum, or by use of a long soaking time.

Theories tailored for porous media are needed to address the complicated capillary path, which is a network of channels, as well as the flow pattern and velocity field in the network. Until now, theories developed by chemical engineers have been transplanted by powder metallurgists. For further progress, efforts from the discipline of fluid mechanics are required.

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