

The International Symposium on Tantalum and Niobium, Orlando, November 1988

This event, organised by the T.I.C. and held at the Stouffer Orlando Resort from November 7th to 9th 1988, was an outstanding success. More than 180 delegates were present, accompanied by some fifty ladies, making the attendance the largest ever recorded at a T.I.C. meeting, and one which covered a wide range of interests. Besides participants from companies which are producers, processors and consumers of tantalum and niobium, which were well represented, there were also delegates involved in research, government organisations, the specialist press, consultancy and trading. More than one-third of the participants came from organisations outside the T.I.C. membership.

Orlando was an excellent venue for the Symposium. Not only was the Stouffer hotel a magnificent setting for the conference, but Orlando, America's tourist capital, offered many interesting attractions for those attending. Ladies' tours visited Cypress Gardens and took a boat trip on the lakes of Winter Park, as part of the programme. The social events which complemented the technical sessions included a banquet on the evening of Monday November 7th.

The papers, numbering thirty-six in all, discussed almost every aspect of the tantalum and niobium businesses, from raw materials and refined products to the applications. When published, the Proceedings will surely be an invaluable source of information for anyone with interests in either tantalum or niobium. The T.I.C. is indebted to the authors for their efforts in preparing the papers, also to the session chairmen for ensuring the smooth running of the Symposium.

INDUSTRY OVERVIEW

Chairman: Mr Hans-Jürgen Heinrich, Gesellschaft für Elektrometallurgie

AN HISTORICAL PERSPECTIVE OF TANTALUM AND NIOBIUM
Mr Lawrence S. O'Rourke, Raw Materials Contractor

THE TANTALUM AND NIOBIUM MARKETS: TRENDS IN SUPPLY, DEMAND AND APPLICATIONS

Mr Andrew Jones, Tantalum-Niobium International Study Center

AN OVERVIEW OF THE TANTALUM INDUSTRY

Mr John Linden, Greenbushes Ltd.

THE NIOBIUM MARKET — A PERSPECTIVE

Dr Harry Stuart and Dr Friedrich Heisterkamp, Niobium Products Company

UNITED STATES GOVERNMENT STOCKPILE PROGRAMME

Mr Robert M. O'Brien, Defense National Stockpile

RAW MATERIALS

Chairman: Mr Paul de Goederen, Thailand Smelting and Refining

GEOLOGY OF TANTALUM AND NIOBIUM DEPOSITS

Dr Richard Gaines, Consultant

PYROCHLORE OCCURRENCES AS POSSIBLE NIOBIUM-TANTALUM RESOURCES IN GREENLAND

Mr Karsten Secher, Geological Survey of Greenland

A REVIEW OF THE BENEFICIATION OF TANTALUM ORES

Mr Richard O. Burt, Tantalum Mining Corporation of Canada

MINING AND PROCESSING OF PYROCHLORE-BEARING ORE AT NIOBEC MINE

Mr Noël Ayotte and Mr Ghislain Goyette, Niobec Mine/Cambior

TANTALUM IN TIN SLAGS: A REVIEW

Mr Roderick J. Tolley, Datuk Keramat Smelting

SYMPOSIUM PROCEEDINGS

The Proceedings will be published shortly in the form of a hard-cover book. The price will be US\$ 100 per copy; payment may be sent with the order, or a pro forma invoice may be requested.

Copies should be ordered from the T.I.C., 40 rue Washington, 1050 Brussels, Belgium.

(All delegates who attended the Symposium will be sent a copy of the Proceedings without further payment; the cost was included in the participation fee.)

PROCESSING

Chairman: Mr Keith Garrity, Fansteel Inc.

MODERN EXTRACTION OF TANTALUM AND NIOBIUM WITH SPECIAL EMPHASIS ON THE PRODUCTION OF HIGH-PURITY COMPOUNDS

Dr W.-W. Albrecht and Dr W. Rockenbauer, Hermann C. Starck Berlin

EXTRACTION OF NIOBIUM METAL BY CHLORINE PROCESS

Mr Toshiya Sugai and Mr Ryoichi Watanabe, Toho Titanium Company

JUDGING THE QUALITY OF TANTALUM POWDERS USED IN THE MANUFACTURING OF SOLID TANTALUM CAPACITORS

Dr Terrance B. Tripp, NRC Inc.

TOTAL QUALITY CONTROL IN CAPACITOR-GRADE TANTALUM PRODUCT MANUFACTURING

Dr Jesse H. Chen, Mr R.M. Bergman and Mr L.E. Huber, Cabot Corporation

TANTALUM MICRO-ALLOYS

Mr Charles Pokross, Fansteel Metals

THE ROLE OF ELECTRON-BEAM, PLASMA AND VACUUM ARC MELTING FOR THE PRODUCTION OF TANTALUM, NIOBIUM AND THEIR ALLOYS

Mr W. Dietrich, Mr G. Sick, Dr H. Stumpp and Mr H. Weingärtner, Leybold

RECYCLING OF TANTALUM

Dr Meinhard Aits, Gesellschaft für Elektrometallurgie

STEELS

Chairman: Dr Harry Stuart, Niobium Products Company

THE TECHNOLOGY OF MICROALLOYING WITH NIOBIUM IN HSLA STEELS

Dr J. Malcolm Gray, Microalloying International, and Mr Geoff Tither, Niobium Products Company

NIOBIUM IN TOOL STEELS

Dr J.R.C. Guimaraes, Companhia Brasileira de Metalurgia e Mineração

NIOBIUM IN CAST IRON

Dr Carl R. Loper, University of Wisconsin

THE USE OF NIOBIUM AND TANTALUM IN STAINLESS STEELS

Professor Anthony J. DeArdo, University of Pittsburgh

ELECTRONIC CAPACITORS

Chairman: Mr Robert W. Franklin, AVX Limited

FUTURE DEMAND FOR TANTALUM CAPACITORS

Mr David E. Maguire, KEMET Electronics Corporation

T.I.C. statistics — niobium

These production and shipment data, to be updated on a quarterly basis in the future, have been compiled from information supplied by most of the companies which produce or process niobium.

RAW MATERIAL PRODUCTION

(quoted in thousand lb Nb₂O₅)

	Ore concentrates	Occurring with tantalum raw material	Total
1980	43 315.6	1056.0	44 371.6
1981	42 497.4	925.0	43 422.4
1982	30 843.6	923.0	31 766.6
1983	24 233.8	907.3	25 141.1
1984	43 199.2	858.8	44 058.0
1985	46 126.8	753.8	46 880.6
1986	45 482.2	575.0	46 057.2

The response from the companies asked to report was 14/18 and included these producers :

Cia. Brasileira de Metalurgia e Mineração
Cambior
Mineração Catalão de Goiás

PROCESSORS' SHIPMENTS

(quoted in thousand lb Nb)

	HSLA-grade ferroniobium	Compounds/alloy additive	Metal/alloys	Total
1980	13 695.8	1493.9	365.1	15 554.8
1981	13 546.7	1777.6	299.1	15 623.4
1982	12 332.7	1557.0	387.8	14 277.5
1983	7 814.8	1857.4	461.3	10 133.5
1984	12 549.2	2055.4	587.0	15 191.6
1985	13 302.8	3082.0	468.0	16 852.8
1986	10 924.9	2256.2	453.9	13 635.0

The response from the companies asked to report was 18/19 and included these processors :

Cia. Brasileira de Metalurgia e Mineração
Cabot Corporation - Electronics and Refractory Metals
Mineração Catalão de Goiás
Fansteel
Greenbushes
W.C. Heraeus
Kennametal
Metallurg Group
Mitsui Mining & Smelting
NRC
Hermann C. Starck Berlin
Teledyne Wah Chang Albany
Treibacher Chemische Werke
Vacuum Metallurgical Company

Capacitor statistics

EUROPEAN TANTALUM CAPACITOR SHIPMENTS

(thousands of units)

3rd quarter 1988	163 231
(Data from ECTSP)	

JAPANESE TANTALUM CAPACITOR PRODUCTION AND EXPORTS

(thousands of units)

	Production	Of this, exports
3rd quarter 1988	914 788	254 522
(Data from JEIDA)		

US TANTALUM CAPACITOR SALES

(thousands of units)

3rd quarter 1988	US shipments	Exports	Total
Foil	286	4	290
Metal-cased	27 751	8 430	36 181
Molded	86 632	10 786	97 418
Dipped	92 015	20 584	112 599
Chips	40 837	6 566	47 403
Wet slug	2 199	164	2 363
Total	249 720	46 534	296 254

(Data from EIA)

The Electronic Industries Association (EIA) has released revised data for the 1st and 2nd quarters 1988 :

1st quarter 1988

	US shipments	Exports	Total
Foil	320	5	325
Metal-cased	30 610	9 587	40 197
Molded	88 732	17 852	106 584
Dipped	104 765	17 134	121 899
Chips	31 087	11 478	42 565
Wet slug	2 384	253	2 637
Total	257 898	56 309	314 207

2nd quarter 1988

	US shipments	Exports	Total
Foil	277	7	284
Metal-cased	30 866	9 710	40 576
Molded	87 146	16 648	103 794
Dipped	95 176	23 355	118 531
Chips	35 054	9 582	44 636
Wet slug	2 498	256	2 754
Total	251 017	59 558	310 575

WORLD TANTALUM CAPACITOR SHIPMENTS

(millions of units)

Because of the EIA revisions, previous data are amended as follows :

1st quarter 1988 1294.4

2nd quarter 1988 1326.0

(Data compiled by combining regional and export data)

FURTHER OPPORTUNITIES FOR GROWTH IN SOLID TANTALUM CAPACITORS

Mr William Millman, AVX Limited

ANALYSIS OF Ta₂O₅ LAYERS IN ORDER TO QUALIFY TANTALUM POWDERS

Mr Hans K. Schmidt and Mr Ramon Capellades, Componentes Electronicos

THE UTILIZATION OF NIOBIUM AND TANTALUM OXIDES IN CERAMIC CAPACITOR DIELECTRICS

Dr John Piper, KEMET Electronics Corporation

APPLICATION OF Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN) DIELECTRIC MATERIALS IN CERAMIC MULTILAYER CAPACITORS

Dr Mike S.H. Chu and Dr Alan Rae, TAM Ceramics

ALLOYS AND COMPOUNDS

Chairmen : Mr C.E. LeRoy, Teledyne Wah Chang Albany
Mr Conrad L. Brown, Trans Refractory Inc.

NIOBIUM IN THE SUPERCONDUCTING SUPER COLLIDER
Dr Rae Stiening, SSC Central Design

MECHANICAL BEHAVIOUR OF NIOBIUM AT CRYOGENIC TEMPERATURES - TEST RESULTS AT 4.2K
Dr Michael Hörmann, W.C. Heraeus

APPLICATIONS OF TANTALUM AND NIOBIUM IN THE CHEMICAL PROCESSING INDUSTRY
Mr Paul E. Sullivan, NRC Inc.

TANTALUM'S EFFECT ON NICKEL-BASE SUPERALLOYS
Dr Richard J. Quigg, Cannon-Muskegon Corporation

NIOBIUM DEVELOPMENTS IN ADVANCED MATERIALS FOR THE AEROSPACE INDUSTRY
Mr Edward A. Loria, Niobium Products Company

CURRENT STATUS AND FUTURE DEVELOPMENTS OF THE NIOBIUM AND TANTALUM CONTAINING SUPERALLOYS
Professor John K. Tien, Columbia University in the City of New York

CATALYTIC APPLICATIONS OF NIOBIUM
Professor Israel E. Wachs, Lehigh University

DEVELOPMENTS IN FINE-FILAMENT NbTi SUPERCONDUCTING MATERIALS AND THEIR APPLICATIONS
Dr E. Gregory, Mr T.S. Kreilick and Dr J. Wong, Supercon Inc.

PREPARATION OF SnNb SUPERCONDUCTORS AT TWCA
Dr David Smathers, Teledyne Wah Chang Albany

THE GROWTH OF EXCELLENCE IN A SPECIALTY METALS AND MATERIALS COMPANY
Dr Donald R. Muzyka and Mr Rick L. Balthaser, Cabot Corporation

A panel discussion during the afternoon of Monday November 7th considered the subject of "Stability in the industry". The panel was chaired by Dr George J. Korinek, NRC Inc., and taking part were Mr Keith Garrity, Fansteel Inc.; Mr Michael Herzfeld, Somink; Mr John Linden, Greenbushes Ltd.; and Mr Peter Maden, Sprague Electric Company. Contributions were invited and received from the floor.

The following companies supported the Symposium with sponsorship :

Anglovaal Limited
AVX Limited
Cabot Corporation
Datuk Keramat Smelting
Fansteel Metals
Greenbushes Limited
Mallory Capacitor Company
Mamoré Mineração e Metalurgia
Metallurg group companies :
Metallurg
Gesellschaft für Elektrometallurgie
Companhia de Estanho Minas Brasil
Mitsui Mining and Smelting
NEC Corporation
Niobium Products Company/Companhia
Brasileira de Metalurgia e Mineração
NRC Inc.
Sassoon Metals and Chemicals Inc.
Showa Cabot Supermetals
Hermann C. Starck Berlin
Tantalum Mining Corporation of Canada
Teledyne Wah Chang Albany
Thailand Smelting and Refining Company
Toho Titanium Company
Vacuum Metallurgical Company
V Tech

Twenty-ninth General Assembly

The Twenty-ninth General Assembly of the Tantalum-Niobium International Study Center was held in Orlando, Florida, USA, on Monday November 7th 1988, and almost all member companies were represented.

The association expressed its appreciation of the work done by Mr Hans-Jürgen Heinrich, Gesellschaft für Elektrometallurgie, during his year as President, particularly the organisation of the Symposium.

Dr Harry Stuart, Niobium Products Company, was elected President for the coming year. Mr Rod Tolley, Datuk Keramat Smelting, retired from the Executive Committee, and the T.I.C. thanked him for his service as President and Committee member. Mr Paul de Goederen, Thailand Smelting and Refining, joined the Committee, and the other members were re-elected.

Membership totalled 63 companies, after the election of three applicants - Elders Raw Materials, Iscor and Mineração Catalão de Goiás; eight companies ceased to be members.

The Assembly approved the audited accounts for the year ended June 30th 1988, and debated the level of membership fees for the year beginning July 1st 1989. It was confirmed that the quarterly Bulletin would continue to be sent free of charge.

It is planned that the Thirtieth General Assembly will be held in October 1989.

MEMBERSHIP

The following three companies were elected to membership by the Twenty-ninth General Assembly :

Elders Raw Materials Limited,
100 First Stamford Place,
Stamford, CT 06902, USA.

Iscor Limited,
P.O. Box 450,
Pretoria, 0001, South Africa.

Mineração Catalão de Goiás Ltda.,
Praça da Republica 497 - 12º Andar,
Bairro : Vila Buarque,
São Paulo - SP,
CEP 01045, Brazil.

At the same Assembly, the following companies ceased to be members :

Howmet
Axel Johnson Ore and Metals
Mallinckrodt
Murex
Nigerian Mining Corporation
Perangsang International
RefineMet International
Rohco Industria Quimica

President's letter

As we embark on the final year of the decade of the 1980s we can all feel confident in the state of our association. The T.I.C. membership reflects a wide diversity of interests in two metals which, although they are part of a chemically similar family, find applications which are more dissimilar than similar. Despite this, it is my belief that the activities of our association, exemplified by the "Bulletin", are of great benefit to all our members. Our recently held International Symposium in Orlando was a resounding success with participation from the great majority of members and the proceedings of the Symposium should provide a reference source for anyone interested in research, market development and marketing of niobium and tantalum.

It is my earnest ambition that the time of my Presidency will reflect a continuation of the past successes of the T.I.C., and solidify our base for the future.

Harry Stuart
President

Trends affecting tantalum and niobium usage in cemented carbides

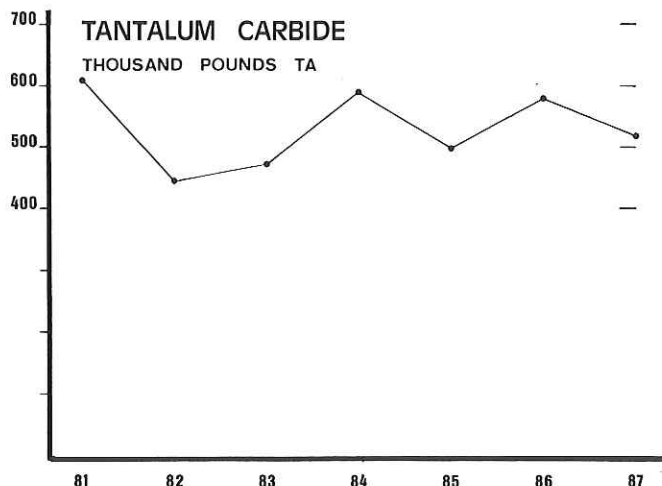
Cemented carbides are composed of refractory metal carbides, mainly tungsten but also tantalum, niobium and titanium, in a cobalt binder phase. Estimated demand in the market economy countries is about 13000 tonnes of tungsten carbide a year, with Western Europe accounting for 5500 tonnes, USA 4500 tonnes, Japan 2500 tonnes and "others" 500 tonnes. Carbides are the most important tungsten application (55 % of total demand), the second-most important one for tantalum (30 % of demand) but a minor one for niobium (5 % of non-ferrous demand). Most tantalum and niobium carbides are used in metal-cutting tools for machining steel and cast iron.

Tantalum usage in cemented carbides was widely discussed at the T.I.C. Stockholm meeting in 1984 (see *Bulletin* issues No. 39-41), and there have been no major developments since then. Tantalum carbide is added to turning and milling tool grades for two separate reasons :

- in small quantities to inhibit grain growth;
- to improve the properties, specifically thermal shock resistance, hot hardness and resistance to "cratering" and oxidation.

Niobium is also used in cemented carbides, but always in association with tantalum in mixed compositions. The primary reason for its use is cost reduction, not for any particular beneficial effect on tool properties. Normal TaC:NbC ratios are 90:10, 80:20 and 60:40.

The demand trend for tantalum carbide since 1981 has two distinct periods: from 1981 to 1983, when high tantalum prices caused extensive substitution, and from 1984 to the present, a period of relative stability in demand.



Between 1981 and 1982, shipments declined by just over 25 %. Apart from total substitution, mixed carbides containing tantalum, niobium and other metals were increasingly used as a partial substitute for pure tantalum carbide. Recycling of carbides increased to displace demand for the virgin product. Also, coated inserts being introduced at the time needed less tantalum in the substrate.

Lower tantalum prices after 1981 stabilized these trends towards substitution and recycled materials. From 1984 to 1987, carbide shipments remained between 0.5 and 0.6 million lb Ta — the movements during this period were mostly effects of the general economic conditions within the cemented carbide industry. In 1988, carbide sales (annualized from data for the first two quarters) showed an increase of 20 % from 1987, but this was due to the healthy state of cemented carbide shipments, not to any particular trend favouring tantalum usage. Two leading tool manufacturers, Kennametal (USA) and Sandvik Coromant (Sweden), both reported large increases in sales for the first half of 1988.

There are significant regional variations in the use of mixed Ta-Nb carbides as opposed to straight tantalum carbide. In Europe, about 90 % of tantalum consumed in cutting tools is in mixed carbides, whereas the US figure is only about 20 %. Europe accounts for around 55-60 % of total tantalum carbide consumption. It was reported by Borchers (see *Bulletin* no. 39, August 1984) that the niobium content of Ta-Nb mixed carbides in European shipments (non-recycled) was 30-35 % from 1981 to 1983; today's figure is just under 25 %, indicating a slight trend towards increasing tantalum contents of mixed compositions. In Japan, there is a TaC:NbC usage ratio of about 4:1; mixed carbides have gained significantly there since 1983. Niobium contained in worldwide carbide shipments (non-recycled) can be estimated to have been around 110-120 000 lb in 1987. This implies a worldwide TaC:NbC ratio of about 4.5:1.

Carbides are normally produced by a two-stage carburization of the oxide at 1600-2000 °C, followed by a vacuum treatment. Producers of tantalum and tantalum-niobium carbides include: Kennametal Inc. (USA); London & Scandinavian Metallurgical Co. Ltd. (UK), a Metallurg Group company; Mitsui Mining & Smelting Co. Ltd. (Japan); Hermann C. Starck Berlin (West Germany); and Treibacher Chemische Werke (Austria). The last-named company has formed a joint venture with Greenbushes Ltd. (Australia) to manufacture and market tantalum and tantalum-niobium carbides. A Brazilian company, Brassinter SA, produces carbides for the domestic market.

Since the mid-1970s, a recycling industry has developed to recover metal carbides from scrap. Recycling has supplied 25-30 % of tantalum carbide requirements in recent years; this percentage seems unlikely to increase significantly in the future since practically all available cemented carbide scrap is already being treated. There are two main processing routes:

- the **zinc process**, which uses "hard" scrap (solid material) as raw material and preserves the original composition of the mixed (W-Ta-Nb-Ti)C phase;
- **chemical methods** (based on nitric acid, for example), which are used to treat "soft" scrap (sludges, sweeps and powders) and produce a tantalum/niobium oxide sludge suitable for processing by solvent extraction.

For the tool manufacturer, recycled carbide grades containing tantalum and niobium offer cost savings of 20-30 % over non-recycled material. Therefore the use of recycled carbides is really dependent on the availability of suitable scrap and is not tied to the price of tantalum carbide to any great extent. A significant part of the recycled material is probably not included in T.I.C. statistics, hence the total usage of tantalum carbide (as opposed to T.I.C. shipments) was probably around 0.7 million lb in 1987.

The substitution trends noted in 1984 towards recycled and mixed carbides have stabilized since then, due largely to low tantalum prices in the mid-1980s. Tantalum carbide shipments in the first half of 1988, when annualized, were higher than those in 1981, because of recent increased activity in the metal-working industry. Over the past few years, however, changes have occurred in the market for cemented carbide tools: shipments have shown almost no real growth due to such factors as auto components being produced at near net shape and also in smaller sizes, so requiring fewer machining operations than previously. Opportunities for growth in tantalum carbide demand will be limited in the future.

On the other hand, despite alternatives to cemented carbides, such as ceramics and cermets, receiving much attention, they have failed to capture a significant share of the tool market, except in Japan. The attempts to replace tantalum in this application with other refractory metals have had limited or no success in the 1980s.

LITERATURE

P. Borchers; "Production and properties of tantalum carbide and mixed carbides, influence of scrap reclamation"; T.I.C. Bulletin no. 39 (August 1984)

B. Kieffer, E. Lassner; "Reclamation of tungsten-containing scrap materials: economic and technical aspects"; Proceedings of 4th International Tungsten Symposium (September 1987)

Andrew Jones
Technical Officer

Improvements in the sodium reduction process to produce tantalum powder

This article was prepared by Dr W.-W. Albrecht, Hermann C. Starck Berlin

Commonly, tantalum powder is produced commercially by reducing potassium fluotantalate (K_2TaF_7) with liquid sodium. For application in solid tantalum capacitors, this powder is compressed into pellets, sintered to form stable porous bodies and subsequently anodised to form a dielectric oxide layer on the surface of these bodies.

Besides purity, flowability and green strength, surface area is one of the most important properties of tantalum powder: a higher surface area means a smaller particle size. Various processing techniques are therefore practised to achieve a uniform and fine particle size distribution of the powder generated by sodium reduction.

Two basic methods for reducing particle size are well known: controlling the nucleation at the beginning of the sodium reduction; and lowering the process temperature.

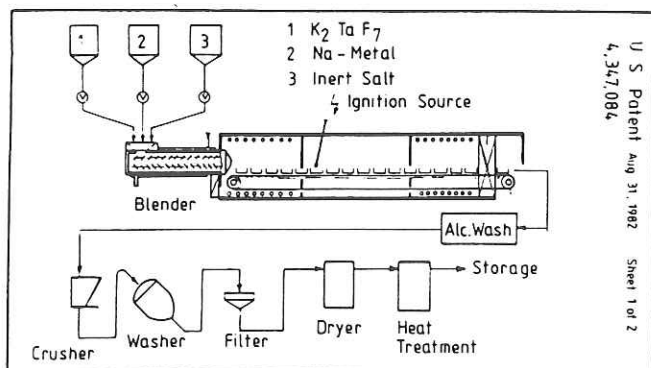
During the nucleation period in the early stage of sodium reduction, the grain size, and thus the surface area, of tantalum powder is controlled by the sodium feed rate, as well as by the addition of dopants. A high sodium feed rate tends to produce a very fine powder.

The sodium reduction of K_2TaF_7 is an exothermic process, i.e. the generated process heat tends to increase the temperature during the process and thus increase the size of the created fine tantalum particles. Reducing the process temperature, therefore, is essential and can be achieved in different ways:

- starting at a low temperature;
- adding inert salts, such as chlorides and fluorides, as dilutants;

- extracting process heat by forced cooling;
 - running the reduction continuously or incrementally instead of the usual batch process of several hundred kilograms of molten K_2TaF_7 .
- (The last item is described in U.S. patents 4231790 (PL-Process) and 4684399.)

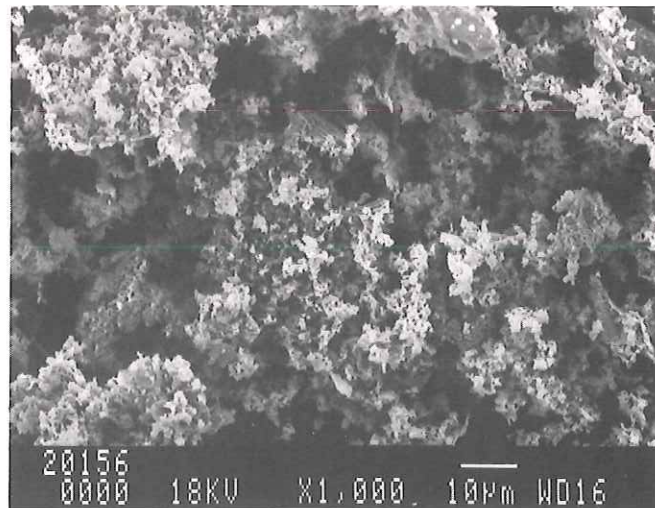
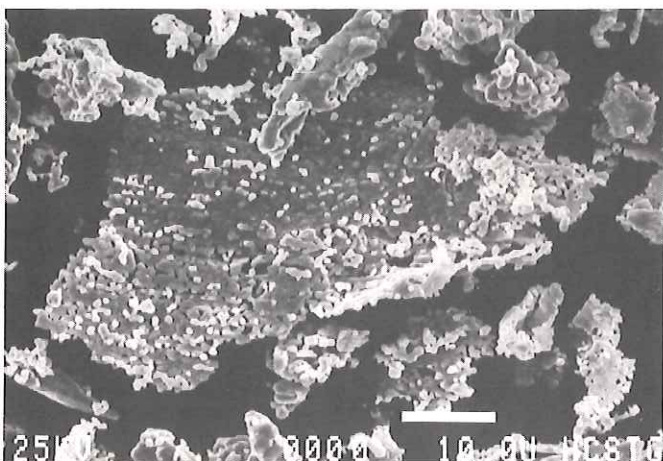
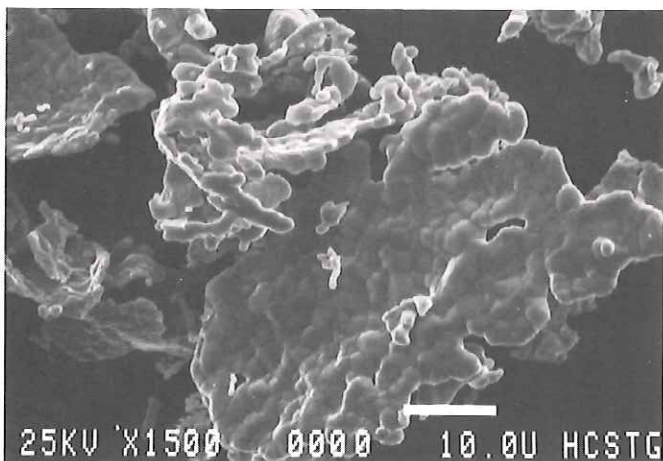
The influence of the process temperature on the shape and particle size of tantalum powder produced in the continuously operated "PL-Process" will be discussed.



Sodium reduction of K_2TaF_7
(PL-Process)

In this process, K_2TaF_7 , liquid sodium, and inert salts are mixed and then in the form of a paste put into tantalum-lined trays which then continuously pass through a furnace. These tantalum trays contain only small quantities of material. This continuous sodium reduction process is followed by the usual steps: crushing, washing and heat treatment of the tantalum powder.

If the PL-Process is operated at about 900 °C, coarse tantalum particles (flakes) are created which after thermal treatment lead to a capacitor-grade powder with about 12 000 CV/g. Reducing the process temperature to about 800 °C makes the flakes become flilgree, i.e. the particle size is reduced to about 1.5 μm . After thermal treatment this powder can be used up to 22 000 CV/g. A further reduction in temperature to below 600 °C completely decomposes the flaky structure of the metal.



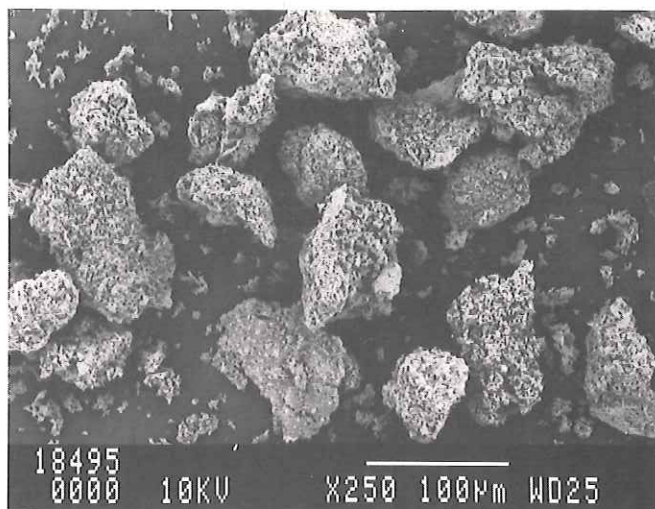
Tantalum particles produced by the PL-Process at temperatures of 900 °C, 800 °C and below 600 °C, respectively

Thus a very fine tantalum powder is generated with an average grain size (Fisher Sub-Sieve Size-FSSS) of 0.5 μm and a surface area (BET) of 2.2 m^2 . Such a powder can be used as feed stock for an additional heat-treatment process, generating a capacitor-grade quality (B 30-K) with outstanding properties.

Analysis (ppm) and characteristics of tantalum powder (B 30-K) of capacitance 30 000 $\mu FV/g$ (sinter condition: 1400 °C for 20 minutes)

H	< 100	Si	< 15
N	100	W	< 5
O	2400	Mo	< 5
C	70	Zr	< 2
Na	< 5	Ti	< 3
K	< 5	B	< 25
Ca	< 5	P	< 10
Mg	< 5	S	< 10
Fe	< 20	FSSS	1.7 μm
Cr	< 3	Scott Bulk	
Ni	< 3	Density	20 g/inch ³
Nb	< 5		

Very stable agglomerates contribute to the remarkable properties of this high-capacitance powder, such as: free flow (without binder); and excellent impregnation behaviour for manganese nitrate, i.e. low dry loss for finished capacitors.



Agglomerated tantalum powder B 30-K

SUMMARY

Operating the PL-Process at a temperature below 600 °C creates a tantalum powder which in its heat-treated, de-oxidised version shows outstanding characteristics, such as:

- a capacitance of 30 000 CV/g, which at present seems to be the highest value available on the market;
- high purity, comparable to electron-beam-melted powders;
- free flowability and high crush strength, allowing binderless pressing on high-speed presses.

Mineração Catalão de Goiás

This article is based on company literature

Mineração Catalão de Goiás SA, a Brazilian producer of ferro-niobium, is a joint venture of two groups, Bozano Simonsen and Anglo American of Brazil, and entrepreneurs of Goiás state. The company holds mining rights over mineralized land near Catalão in south-east Goiás state. Production of pyrochlore concentrates was initiated in 1976; a year later, the company installed a metallurgical plant to produce ferro-niobium. With this facility, Mineração Catalão strengthened Brazil's position as the major producer of ferro-niobium, currently supplying 85 % of world demand.

Towards the end of 1975, during the initial phase of experimental pyrochlore production, Mineração Catalão carried out more than 5000 metres of diamond drilling and over 4000 metres of well excavation to delineate the areas of economic interest.

The existing mineralized body resulted from the action of severe climatic conditions on the original carbonatite and reaches a depth of over 80 metres. The material is decayed, earthy, friable and unconsolidated. Extraction is relatively simple and is performed by open-pit mining divided into blocks with a 25 x 25 metre base. Both mineral and overburden are removed mechanically with appropriate equipment which permits production of 1500 tonnes of ore a day.

The ore body occurs as an alkaline dome known as "Catalão 1". Pandaite is the main economic mineral: it is a member of the pyrochlore group, in which barium replaces sodium and calcium in the crystalline network. Ore reserves were 50 million tonnes Nb_2O_5 in 1987 with a grade of 1.05 % Nb_2O_5 .



Overview of the mine site

The homogenized ore is first processed by jaw and impact crushers before undergoing concentration. After passing through rod and ball mills, the ore is upgraded by magnetic separation and rougher and scavenger flotation. The pyrochlore concentrate is then leached, before being used as the feed material for ferro-niobium production. The company's aluminothermic reduction facility has a capacity of 2800 tonnes of ferro-alloy a year. This product, which is added to micro-alloyed steels, has the following basic specification.

Specification of ferro-niobium (Mineração Catalão)

Elements	Guaranteed maximum %	Typical %
Nb	60-70	66.00
Ta	1.0	0.5
C	0.15	0.10
Si	3.0	2.5
Al	2.5	1.5
S	0.15	0.06
Ti	1.0	0.20
P	0.2	0.14

Mineração Catalão's work force consists of 470 people. Its adequate and safe performance is insured by continuous investments in training and safety. Constant attention to the environment led to the construction of embankments and dams by using the overburden in order to retain plant refuse. Measures have also been taken and investments made to prevent air and effluent pollution.

The company is engaged in energy saving through the substitution of petroleum products with wood, a renewable resource. A wood gasification system supplies the equivalent of 600 tonnes of fuel oil a year. The gas is used in the process of pyrochlore leaching, the boiler, and the reactor and calcination furnaces. The company's forestation projects supply the necessary wood resources.



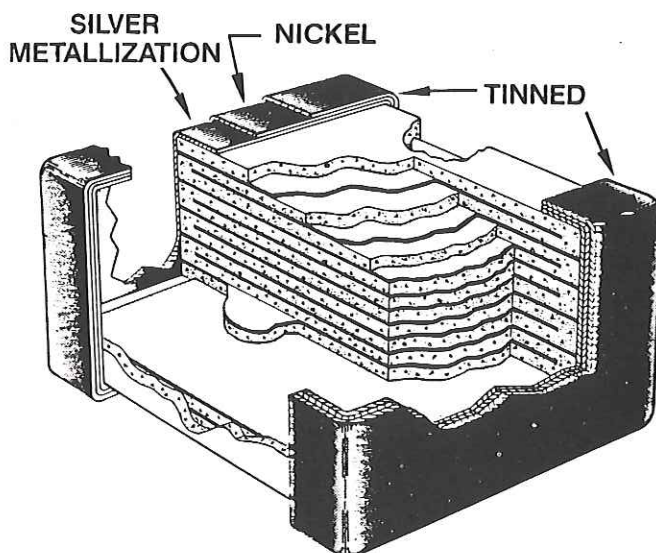
Production of ferro-niobium by thermite reaction

The utilization of niobium and tantalum oxides in ceramic capacitor dielectrics

This paper was presented by Dr John Piper, KEMET Electronics Corporation, at the International Symposium on Tantalum and Niobium, Orlando, November 7th-9th 1988

The multilayer ceramic capacitor (MLC) is a small electronic component used by the billions per month and using about five million kilograms of metal oxide materials annually.

Its construction consists of electrode plates, usually made of palladium or a palladium-silver alloy, interleaved in a co-sintered matrix of ceramic dielectric. The opposing plates store electrical charge, and the capacitors are typically used in applications to smooth out the flow of electricity. MLCs typically span the capacitance range 1 pF to 10 μ F. The range for tantalum capacitors is usually 1-1000 μ F, overlapping that of the MLC at the low end.



Construction of a multilayer ceramic capacitor

A reduction in the electrode area reduces the amount of palladium used and also increases manufacturing productivity. Reductions in the sintering temperature of the ceramic dielectric permit the use of more dilute palladium alloys, further reducing the amount of precious metal required — the dominant materials cost in the product. So the major requirements for the oxide dielectric material are a high dielectric constant and a low sintering temperature. Also, the dielectric constant has to be relatively stable over the temperature range of use of the capacitor. Dielectric stability requirements have been largely standardized to three types.

Ceramic capacitor designations

EIA designation	Temperature range	Permitted variation in dielectric constant (at 25 °C)
Z5U	-10 to +85 °C	+10 % to -56 %
X7R	-55 to +125 °C	±15 %
COG	-55 to +125 °C	±30 ppm per °C

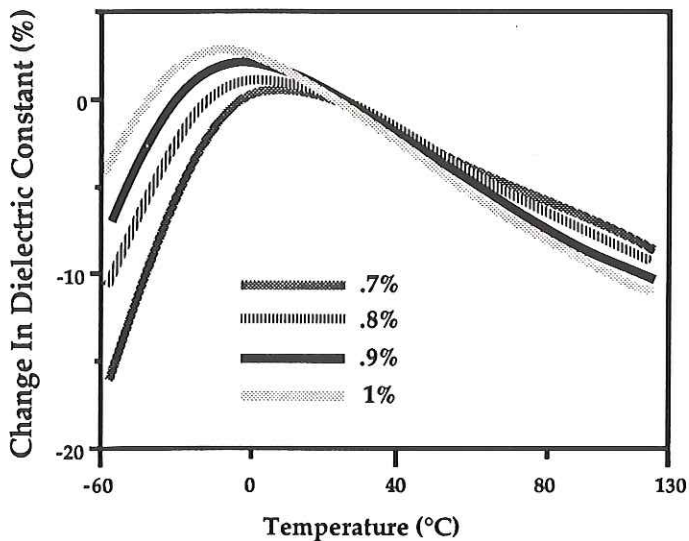
This paper is concerned with the X7R and Z5U dielectrics, where ferroelectric behaviour plays an important role, yielding very high dielectric constants. The dominant base dielectric material for X7R and Z5U MLCs is barium titanate, a ferroelectric compound with a perovskite crystal structure. Minor quantities of niobium and tantalum oxides are often used as additives. However, promising new dielectrics are being developed which use significant amounts of niobium or tantalum. They offer opportunities to expand MLC markets and meet future electronic design requirements, but their business success is very dependent on raw materials pricing.

NIONIUM AND TANTALUM IN BARIUM TITANATE DIELECTRICS

The traditional uses of the oxides are for the modification of the temperature coefficient of the dielectric constant and for grain size control.

A typical dielectric composition is: barium titanate 89 %, bismuth titanate 10 % and niobium oxide 1 %. Small amounts of other ingredients, such as manganese dioxide, are often added to improve secondary electrical characteristics of the dielectric.

The effect of niobium oxide on the temperature coefficient of the dielectric constant is quite dramatic. By changing the niobium content, a dielectric formulation can, for example, be adjusted to achieve the X7R characteristic.



Effect of niobium additions on the temperature dependence of the dielectric constant of a barium titanate X7R dielectric

In this application, niobium is as satisfactory as tantalum. There are alternative means of making the required adjustments, and the amounts used are small.

Control of the grain size of the sintered dielectric is important. Firing times and temperatures must be sufficient to intermix the various ingredients of the dielectric. Resulting grains must be large enough to develop the required ferroelectric behaviour, but very large grains adversely affect the capacitor's secondary electrical characteristics, including its long-term reliability. Additions of tantalum oxide, preferably in the range of 0.1–0.5 %, control excessive grain growth, particularly in dielectrics requiring high sintering temperatures.

During the past decade, the widespread introduction of sintering aids and liquid sintering assists in dielectric formulations has somewhat diminished this application, especially in the United States. This technique is, however, used extensively in a competitor to the MLC, the semiconductor grain boundary barrier layer capacitor, using compositions such as strontium titanate 96.6 %, tantalum oxide 2.0 % and copper oxide 1.4 %. In this very sophisticated dielectric, the grain boundary interface area within the ceramic becomes the electrode-dielectric interface, so the grain size is extremely critical.

COMPLEX PEROVSKITE DIELECTRICS

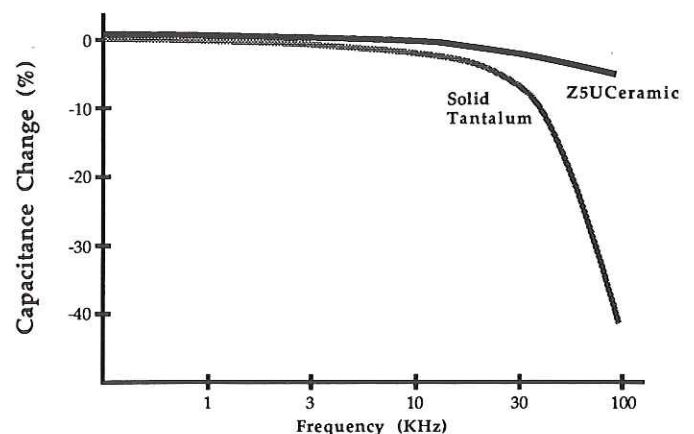
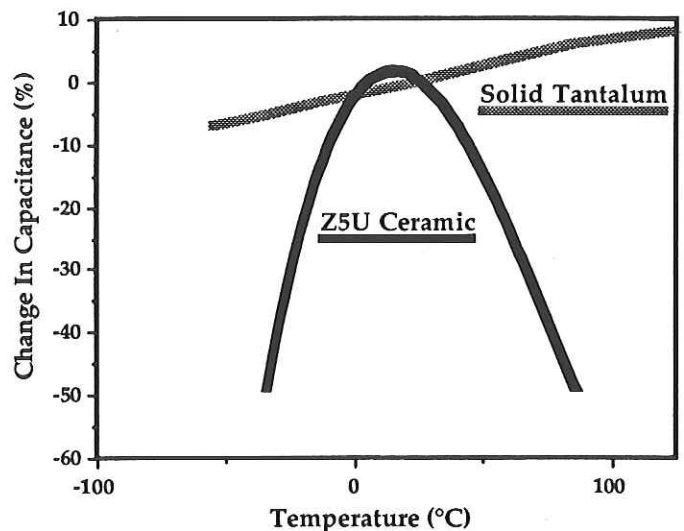
Starting in Russia in the late 1950s, numerous investigators studied ferroelectric perovskites containing lead and niobium or tantalum, such as: lead magnesium niobate, lead iron niobate, their solid solutions, lead nickel niobate, lead iron tantalate, etc. These materials were found to be similar to barium titanate and its solid solutions as they had a high dielectric constant, the temperature of which could be altered by additives, and promising secondary electrical characteristics. The sintering temperatures were, however, lower than those of barium titanate compositions.

Commercial capacitor dielectrics, based on these materials, only emerged in Japan and the West in the late 1970s. The niobium oxide contents varied from about 15 % to 25 %, but all achieved a high dielectric constant and a low sintering temperature compared to barium titanate dielectrics. A comparison between the two dielectrics includes the impact of reductions in sintering temperature on the amount of palladium required in the electrodes.

Comparison of barium titanate and lead niobate dielectrics

	Dielectric constant (Z5U)	Sintering temperature (°C)	% Pd required in electrode
Barium titanate technology	12 000 ↕ 7000	1300	100
Lead niobate technology	10 000-15 000	1100 ↕ 900	30 ↕ 0

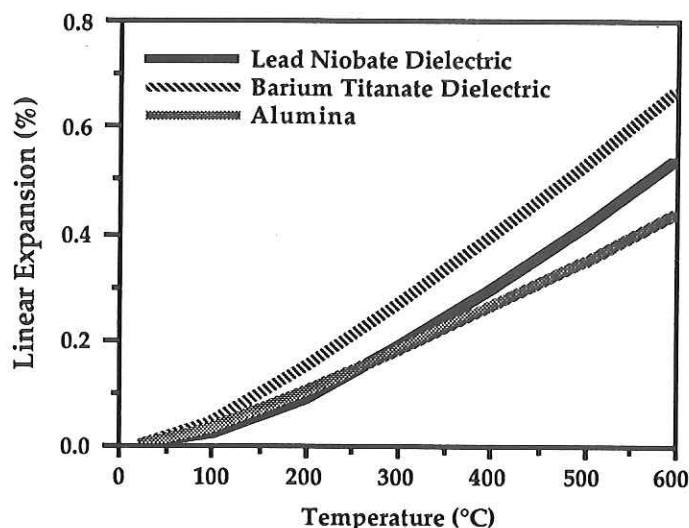
The impact is such that materials costs per capacitance unit between a lead niobate Z5U ceramic capacitor and a solid tantalum capacitor are about equal, as are the volumetric efficiencies of the finished components. The electrical characteristics differ in two major ways: the stability of the capacitance with temperature and with frequency.



Temperature and frequency dependencies — solid tantalum capacitor and niobate Z5U MLC

The importance of the two characteristics depends on the application. The use of tantalums in computers, as clock frequencies increase, will become more vulnerable to erosion by large-value ceramic capacitors than in military circuitry, which must operate at extreme temperatures. Switch-mode power supplies are an area where displacement has started. MLCs with capacitances up to 100 μ F are being marketed.

Another opportunity for lead niobate MLC technology is in applications where the capacitance function is built into the substrate which provides the circuitry and physical support for integrated circuit chips. The thermal expansion characteristic of lead niobate dielectrics is quite different from that of barium titanate dielectrics.



Thermal expansion of barium titanate and lead niobate dielectrics compared to alumina

Barium titanate has a consistently larger coefficient of thermal expansion (TCE) than alumina, the commonly used ceramic for multilayer substrates and integrated circuit chip carriers. At low temperatures, the TCE of lead niobate is less than that of alumina, causing the relatively weak capacitor dielectric to be under compression in an integrated structure with alumina.

Multilayer ceramic hybrid circuits with built-in layers of capacitance, using lead niobate technology, are being produced.

TUNGSTEN BRONZE DIELECTRICS

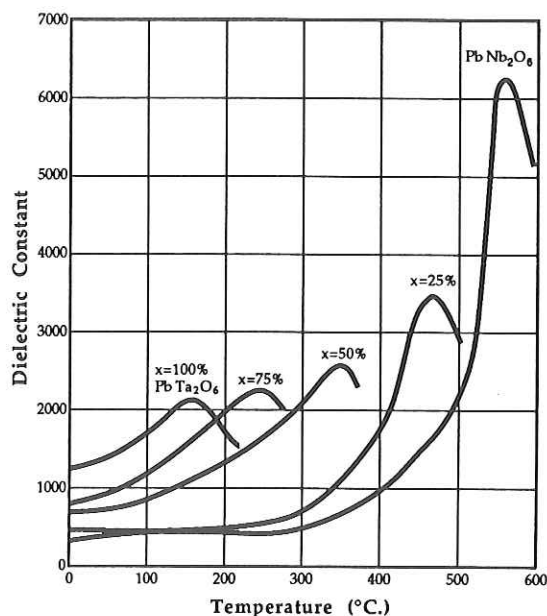
Early studies also found ferroelectricity and high dielectric constants in the tungsten bronzes with a composition of AB_2O_6 , where A and B are metals. Typical examples are $PbNb_2O_6$, $PbTa_2O_6$, $BaNb_2O_6$ and their solid solutions. The B-site of the tungsten bronzes can be occupied by a pentavalent element (Nb or Ta), or a mixture of compensating ions.

So the materials engineer has a wide range of compositions from which to develop a capacitor dielectric.

A-site metals :	Pb	Ba	Zr	Ca	Sr
B-site metals :	Nb	Ta	W	Zr	Ti

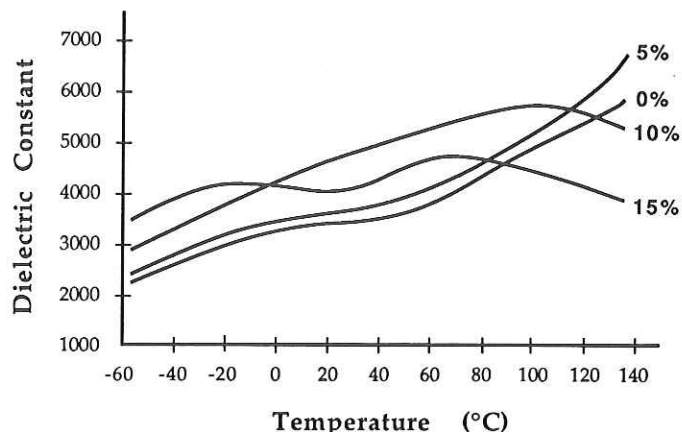
The presence of tantalum in the tungsten bronze crystal structure produces quite different properties from niobium.

Tantalum's high cost relative to the metals commonly used in ceramic dielectrics, including niobium, prohibits its use as a large percentage of the composition, so other ways to improve low-temperature performance were sought with some technical success. But the addition of tantalum is still often needed to meet X7R temperature stability requirements.



Effect of replacing niobium with tantalum on dielectric constant of composition $(1-x)PbNb_2O_6 \cdot xPbTa_2O_6$ (M.H. Francombe and B. Lewis; Structural, dielectric and optical properties of ferroelectric lead niobate; Acta Cryst., 11,701 [1958])

Tantalum price and price instability considerations appear to have had a chilling effect on commercialization of tungsten bronze capacitor dielectrics despite their substantial technical promise. In KEMET analyses, the cost-performance trade-off between tantalum-containing tungsten bronze and barium titanate dielectrics with X7R characteristics is close.



Effect on the dielectric constant of substituting tantalum for niobium in $Pb_{0.5}Ba_{0.5}Sr_{0.4}Nb_2O_6$ at atomic percentages indicated (US Patent 4 283 752)

CONCLUSION

The ceramic capacitor industry is breaking away from its forty-year dependence on barium titanate materials. Niobate-type perovskite dielectrics have already become established, and their future appears bright. Their foothold is in markets such as personal computers and consumer electronics, which are used essentially at room temperature. Other technical opportunities exist to introduce niobate-tantalate materials to service markets where end products must operate over wide temperature ranges, e.g. military and automotive. However, current tantalum pricing deters commercialization.