TANTALUM INTERNATIONAL STUDY CENTER

BULLETIN N° 45 JANUARY 1986 FIRST QUARTER

Editorial

Graham Brown, Editor of the T.I.C. Bulletin for the past ten years, has taken a well-deserved retirement from the post. Under his editorship, the Bulletin's circulation has increased many-fold and its readers now extend far outside the T.I.C. membership. In addition to companies actively involved in the exploration, production, consumption and trading of tantalum and niobium, the Bulletin is read in numerous government agencies and financial institutions. All these organizations have a common interest in tantalum and niobium and so an interest in obtaining current technical and market information on the two metals. The Bulletin is now recognized as the definitive source for this knowledge. Much of the credit for its success must go to Graham; yet many of our readers may be unaware of his identity as I have only been able to find his name in the pages of the Bulletin on a very few occasions since 1975. I'm sure that all Graham's many friends in the T.I.C. wish him further success in the future, as indeed I do. Graham, thank you from all of us — you will be hard act to follow.

From January 1986, the T.I.C. is starting a monthly abstracts service to its members based on the updates of Metadex — the data-base form of Metals Abstracts. The service will be prepared especially for the T.I.C. by Metals Information (a joint collaboration between The Institute of Metals and the American Society for Metals) and the literature abstracted will cover every aspect of tantalum and niobium from ore production to end-uses. Copies of the literature will be available directly from Metals Information in London at a normal cost of $10 per item. Initially, this service will be limited to T.I.C. members only, but it may be possible in the future to extend its circulation to non-members for a moderate charge. The purpose of this service is to effect free flow of information within the tantalum and niobium communities.

Please continue to send your company's literature and annual reports to the T.I.C. office, here in Brussels; they are much appreciated. In particular, we are short of material from companies involved in ore production and tin-smelting. By the way, this applies also to our many readers who are not T.I.C. members; we want to learn more about your activities in tantalum and niobium. Also, please send in any recent papers written by members of your company which you think may be suitable for publication in the Bulletin.

The past few years have been difficult ones for most T.I.C. members, producers, processors and capacitor manufacturers alike, and 1985 was no exception. Let us hope that 1986 sees a revival in our industry's fortunes.

Andrew Jones
Technical Officer

Twenty-fourth General Assembly

The T.I.C. held its Twenty-fourth General Assembly on October 22nd 1985 at the International Association Centre, Brussels.

Two companies were admitted to the T.I.C. :

- Coframines, a producer of tantalite in the Echassières region of France. They are a subsidiary of BRGM, the French Government Agency for mineral exploration and development worldwide.
- Talmina Trading, also a tantalite producer who operate in the Northern Territory of Australia.

Five resignations were accepted, bringing the total membership of the T.I.C. to seventy-four.

The transfer of membership from KBI Division of Cabot Corporation to Cabot Specialty Metals — Electronics was recognised by the T.I.C.

The General Assembly voted to increase the annual fees for membership from $750 to $1250, effective from July 1st 1986. This was the first ever such increase in fees since the T.I.C.'s foundation.

Dr Chikara Hayashi of Vacuum Metallurgical Co. was elected to be President for 1985/6. He succeeded Mr Carroll Killen of Tansitor Electronics, whose term as President had seen further progress being made in the work of the T.I.C. Available capacitor statistics now covered the three key geographical areas — the United States, Europe and Japan. Mr Andrew Jones, the T.I.C. Technical Officer, was investigating ways to make these data more useful to the members. He was being assisted in this task by a Statistical Committee comprised of representatives from the tantalum powder and capacitor industries.

Mr Herman Becker-Fluegel of National Resources Trading announced his retirement from the Executive Committee after this General Assembly. Mr Becker-Fluegel had served the T.I.C. in this capacity since the foundation of the association in 1974. The General Assembly thanked him for his tireless efforts in furthering the aims and interests of the T.I.C. for the past eleven years.

Dr Harry Stuart of Niobium Products Co. was elected to the Executive Committee.

The present composition of the Committee is as follows :

Mr Conrad Brown, Fansteel Inc.
Mr Robert Franklin, STC
Dr Chikara Hayashi, Vacuum Metallurgical Co.
Mr Carroll Killen, Tansitor Electronics
Dr George Korinek, NRC
Mr John Linden, Greenbushes
Dr Harry Stuart, Niobium Products
Mr Rod Tolley, Datuk Keramat Smelting
Mr René Van Achter, who serves as the member of Belgian nationality

On conclusion of the formal business of the T.I.C., presentations were given by Professor Tony De Ardo of Niobium Products Co, Professor Hugo Ortner of Metallwerk Plansee, Mr Hubert Hutton of Norore Corporation, Mr Michael Herzfeld of Sominki, Dr Edgar Manker of Niobec Inc. and Mr Andrew Jones of the T.I.C. A panel discussion which took as its theme 'How the T.I.C. can better serve its members' concluded an enjoyable and interesting meeting.

The Twenty-fifth General Assembly will take place from May 19th to 21st 1986 at Kobe, Japan. The Twenty-seventh General Assembly will be held in Brazil where the T.I.C. will be the guests of CBMM.

MEMBERSHIP

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

Coframines S.A.,
191 Rue de Vaugirard,
75737 Paris Cedex 15,
France.

Talmina Trading Pty. Ltd.,
c/o Transia Corporation,
19th Floor, 50 Bridge Street,
Sydney,
Australia.

This Assembly accepted the resignations of :

Hochmetals Africa
Sabemin
Somirwa
Thermo Electron
Zairetain

President's letter

In 1985, we were compelled to accept very dull trade in the tantalum market. Although our data only cover up to June or September in 1985, they show that the production of tantalum ore for the period from January to June amounted to 351 tonnes Ta_2O_5 — only 51 per cent of that for the whole of 1984. The sales in the above period were 216 tonnes Ta_2O_5 — only 34 per cent of those in 1984.

The U.S. sales of tantalum capacitors for the period from January to June were 466 million pieces; that was about 22 per cent lower than sales over the same period in 1984. In Japan, the production up to August increased by 5 per cent to 1470 million pieces; however, it has depressed since July. The decrease for this year over last year is estimated at about 5 per cent and the export of tantalum capacitors from January to August inclusive was reduced by 15 per cent; these figures are much lower than our conservative estimate made at the beginning of this year.

However, I never lose hope in this business. In the past, we experienced a severe decrease in demand and have not yet recovered perfectly. In production and shipment of ores particularly, we are still under the influence of this decrease in demand.

I dare to remind you of this unhappy experience to make the best use of what we learned from this. That is to say that prices not balancing with those of other equipment cannot be effective.

Unfortunately, the present state of the market is very low for base metals, such as copper, lead or zinc, and for non-ferrous metals, such as molybdenum or tungsten. Therefore, both smelters and manufacturers are experiencing hard circumstances. In consideration of this, it is unreasonable to expect that tantalum alone can get out of such a recession.

However, the largest user of tantalum, the electronics industry, is expected to be the leading industry bringing a brilliant twenty-first century to the world. Although the electronics industry, including semi-conductors, descends to the bottom periodically, it is expected to come to the next ascent by the second half of this year at the latest.

This May, when all of you will be at Kobe in Japan for the Twenty-fifth General Assembly, the tantalum market will have a bright future, and we will be able to discuss an active tantalum market. The Twenty-fifth General Assembly will be held from May 19th to May 21st 1986.

At present, the Japanese Society of Newer Metals is co-operating with the T.I.C. so that the first General Assembly to be held in Japan will be enjoyable and significant. In Japan, we have the most beautiful days in May and we are looking forward to the participation of each member company of the T.I.C.

C. Hayashi
President

Niobium — Exotic applications

This paper was presented by Dr Edgar Manker, Niobec Inc., at the Twenty-fourth General Assembly in Brussels on October 22nd 1985.

Niobium has a multitude of properties and characteristics that have led to its use in a wide variety of special and exotic applications. A common theme of these applications seems to be that niobium is very good in "creating order". From the macroscopic properties of micro-alloyed steels to the subatomic properties of Josephson junctions and holographic filters, niobium contributes to an orderly and predictable result.

In what follows, applications of metallic niobium and of niobium (mainly oxide) compounds are discussed.

AIRCRAFT AND SPACE VEHICLES

The application of niobium-containing superalloys in the hot sections of commercial and military jet engines is well known. It is also generally acknowledged that superalloys for military jet engines contain significantly higher percentages of niobium. Because of its high-temperature properties and relatively low density, niobium has also been used in the nozzles of rocket motors, mainly the low thrust rockets used in the manœuvring of space vehicles.

These applications represent a very significant but variable use of niobium. The superalloys utilize high-purity ferroniobium and nickel-niobium, produced from commercial-purity niobium oxide. The rocket nozzles utilize niobium metal, or niobium alloys, which are also produced from commercial-purity niobium oxide. In total, these applications represent approximately five per cent of total niobium consumption.

URANIUM FUEL ELEMENT CLADDING

The uranium fuel elements in a conventional fission reactor must be clad with some other material to prevent oxidation of the uranium and consequent contamination of the reactor system with radioactive by-products of the fission reaction. This cladding material must have a low cross-section for the capture of thermal neutrons. For conventional low-temperature reactors (up to 400°C), the normal choice is zirconium.

After zirconium, niobium has the next lowest cross-section for thermal neutrons. It has many additional properties, such as strength at elevated temperatures, which are superior to those of zirconium and so niobium becomes the essential cladding material for nuclear reactors which are designed to operate above 400 °C.

The use of niobium cladding in experimental high-temperature reactors is relatively small, but published data suggests that nearly all land-based reactors in Russia and other Comecon countries have niobium cladding for their fuel elements. Other available information indicates that high-performance reactors used in some surface ships, virtually all modern submarines and a number of space satellites, all use niobium cladding.

Niobium used in this field is either commercially-pure metal, or alloyed, depending upon the particular operating conditions.

OPTICAL GLASSES

Optical glasses containing 10 to 30 per cent Nb_2O_5 have very high refractive indices, while maintaining densities similar to ordinary optical glasses. For a particular glass, the refractive index varies according to the wavelength of light passing through the lens and so color optics demand compound lenses to correct for variations in color refraction. These variations in color refraction are minimized by high refractive index, so that niobium oxide glasses can produce simpler and lighter compound lenses. These advantages have led to the widespread use of niobium glasses in lenses for cameras, copying machines and other demanding applications. Niobium optical glass is also used in eyeglass lenses, where the high refractive index allows lenses which are nearly as light as plastic lenses, but which retain the strength, abrasion resistance and "feel" of glass lenses.

The niobium oxide used for optical glass must be of a very high purity, and only a few ppm of color-forming impurities, such as chromium and manganese, can be tolerated. This special "optical grade" niobium oxide is normally produced by the further processing and purification of commercial-grade niobium oxide. The main producers of niobium oxide glass are optical companies in Japan, but niobium glass lens blanks for eyeglasses are also being produced in Brazil.

In total, it is believed that optical glass consumes around 50 000 kg of Nb_2O_5 each year. This is an interesting and beneficial application of niobium, but more than moderate growth is not anticipated.

PIEZO-ELECTRIC, ACOUSTIC AND ELECTRO-OPTIC DEVICES

Mixed oxides of niobium, such as lithium niobates, lead niobates, strontium barium niobates and others, have some very useful piezo-electric and electro-optic properties.

A piezo-electric material converts mechanical energy directly into electrical energy, or the reverse. Lithium niobate is very efficient as a piezo-electric transducer, and has found many applications because the crystals are relatively easy to fabricate. The piezo-electric transducer can produce an acoustic wave from a radio-frequency input, or the reverse and so a variety of filters, delay lines and other devices can be produced.

One interesting application involves an automated identification tag system. A lithium niobate crystal is masked or coated with a pattern of aluminium lines. A central "reader" transmits a radio-frequency signal, which excites the niobate crystal into producing a surface acoustic wave. This acoustic wave modifies the radio signal, which is reflected back to the "reader". The modified signal is processed by the reader to transform the analog signal to digital data or an identification number. A current masking system allows 250 million individual codes or identification numbers and so in a manufacturing application, up to 250 workpieces can be identified and monitored during the production operations.

In an electro-optic crystal, the index of refraction of the crystal varies according to the application of an electric field and thus a light beam can be modified directly by a suitable electrical input. Lithium niobate crystals have suitable properties, and most current applications seem to be military, such as laser range-finders and communications systems.

Experimental work has demonstrated the possibility of storing holographic images in potassium tantalate niobate. In theory, billions of holograms could be stored in, and retrieved from, a single crystal, but this potential is far beyond current technology.

Recently, scientists have described an iron-doped lithium niobate audio filter. By directing two argon-lasers at a crystal, a holographic grating is created within the niobate crystal, where different regions in the crystal have varying densities. The variations in density affect the speed of sound waves, so that crystals can be made to reflect, and so filter or eliminate specific audio frequencies. It is thought that these holographic filters are ideally suited to many communications applications as they are simple, compact and can be mass-produced.

OTHER APPLICATIONS

The attractive properties of niobium have led to a host of other special uses which include :

- Corrosion protection devices
- Particle accelerator cavities
- Catalysts
- Prosthetic implants
- Commemorative coins
- Jewellery

These applications are either under development or account for relatively insignificant quantities annually.

There are many unpublicized applications about which we can only speculate. Major repair work on U.S. nuclear submarines usually results in the disappearance of significant quantities of niobium. Many facets of the Strategic Defense Initiative (Star Wars) program necessarily involve niobium and niobium alloys. There is significant niobium production in Russia which does not seem to be going into steel plate and line pipe. In total, these applications may account for a few per cent of niobium production.

SUMMARY

Thirty years ago, niobium was used in some high-temperature alloys and as a stabilizing element in a few stainless steels. Elsewhere it was little more than a curiosity in the chart of elements.

Today niobium is present in many facets of everyday life, and science and technology are still only beginning to utilize the many properties of niobium and its compounds. There are some ninety-odd elements to work with, but it is doubtful if any of them will fill so many roles in our future as niobium.

Tantalum supply and demand

This article is based on a presentation made by Mr John Linden of Greenbushes Ltd. at the October meeting of the T.I.C. in Brussels.

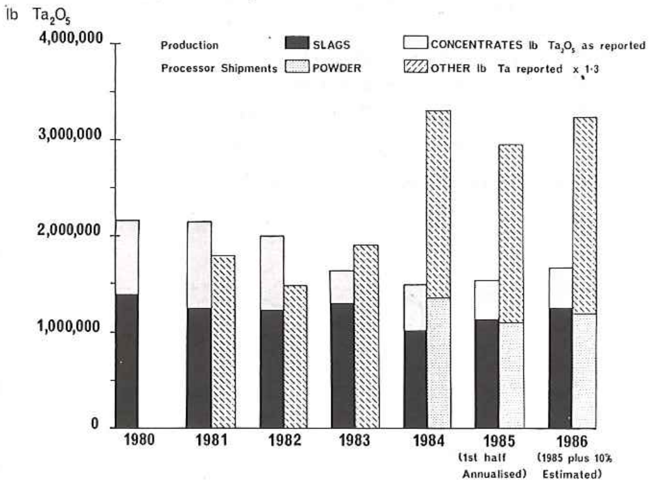
The market for tantalum raw materials, both historical and forecast, is summarised below from 1980 to 1989. The supply figures up to 1984 are based on T.I.C. statistics; those from 1985 onwards presume the prices quoted.

Supply is rationalised into four raw material types :

- tin slags less than 10 % Ta_2O_5 (need upgrading prior to processing into tantalum products with a resultant yield loss);
- tin slags greater than 10 % Ta_2O_5;
- ore concentrates (tantalites, columbites and struverites);
- tantalum scrap (estimated as 20 % of the two years' prior processor shipments).

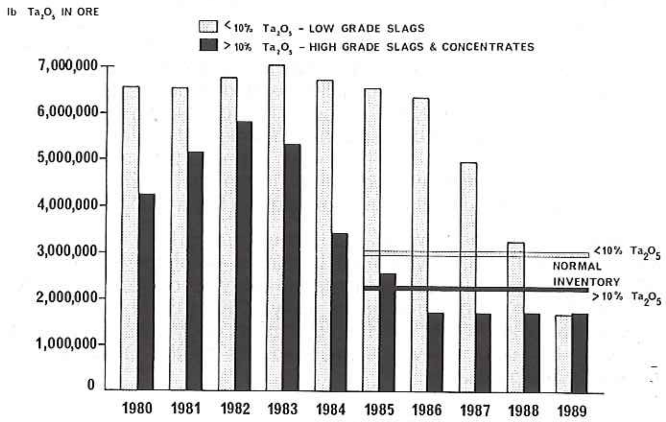
Some of this supply is shipped to Eastern Bloc countries; some is purchased by the GSA for the U.S. National Stockpile. This material is effectively eliminated from the supply and demand equation.

Processor shipments in terms of "lb Ta" are converted to "lb Ta_2O_5" by a factor of 1.3 which accounts for unrecoverable material losses occurring during processing.



By comparing raw material shipments and processor shipments converted to lb Ta_2O_5, it can be seen that, for the years 1984 and 1985, there was a supply shortfall which was met by processors' inventories of low-grade slags and normal materials (slags greater than 10 % Ta_2O_5 and concentrates). In 1986, this shortfall is anticipated to occur again.

Inventories of high-grade slags and concentrates are forecast to fall below "normal" levels (assumed to be 2 250 000 lb Ta_2O_5) by the end of 1986. Low-grade slag inventories are forecast to fall below the "normal" level of 3 000 000 lb Ta_2O_5 by the end of 1989.



Inventory positions, both historical and forecast, can be summarised thus (all figures in 000's lb Ta_2O_5) :

	Low-grade slags	*Other (high-grade slags, concentrates)*
Opening inventory 1980	6 560	4 919
Estimate at December 1985	6 549	2 560
Closing inventory 1989	1 689	1 722
Normal inventory (nine months)	3 000	2 250

TANTALUM SUPPLY AND DEMAND 000's lb Ta_2O_5

Year	Price US$/lb	Tin Slags -10%	Tin Slags +10%	Concentrates	Scrap Recycle 20%	Total Supply	Less Exports and GSA	Avail to W W Processors	Processor Shipments (Demand)	Inventory Change - 10% Slags	Inventory Change All Other
1980	100	300	1083	792	565	2740	200	2540	3208		(668)
1981	60	228	1000	926	695	2849	200	2649	1755		894
1982	25	209	1000	685	641	2535	200	2335	1460	209	666
1983	30	280	1000	368	357	2005	300	1705	1912	280	(487)
1984	30	200	801	473	292	1766	600	1166	3312	(300)	(1846)
		1217	4884	3244	2550	11895	1500	10395	11647	189	(1441)
1985	30	200	800	400	382	1782	300	1482	2600	(200)	(918)
1986	35	200	800	500	662	2162	300	1862	2900	(200)	(838)
1987	40	200	800	600	520	2120	300	1820	3200	(1380)	
1988	50	200	800	600	580	2180	600	1580	3300	(1720)	
1989	65	200	800	600	640	2240	300	1940	3500	(1560)	
		1000	4000	2700	2784	10484	1800	8684	15500	(4871)	(3197)

Tantalite production in Zaire and Rwanda

This paper was presented by Mr Michael Herzfeld of Sominki at the T.I.C. General Assembly in Brussels on October 22nd 1985. Tantalite has been a major field of interest for Mr Herzfeld since 1956, and so he has maybe a unique experience of the development of this business.

HISTORICAL SUMMARY

Before Zaire and Rwanda became independent in 1960 and 1962 respectively, the main production of tantalite was under the control of these groups :

— *Geomines* in the Manono area of Northern Katanga (now Northern Shaba).
— *Sermikat*, also in Northern Katanga.
— The *Empain Group* of companies, operating mainly in the Maniema and Kivu areas.
— The *Comité National du Kivu*, operating in the Kivu Province.
— *Minetain* in Rwanda.

Of these companies, Geomines were by far the largest producers. All were privately-owned.

Their operations were widely dispersed, but they had access to a good, although primitive, system of trails, which were maintained by the native population under the broad supervision of a thinly-staffed colonial administration. There was also access to a system of waterway transport, linked occasionally by rail segments.

The production of Geomines was marketed by their Brussels headquarters and consisted of tantalite concentrates and tantalum-containing slags from their own tin smelter in Manono. The tantalite was in the range of 30-40 per cent each Ta_2O_5/Nb_2O_5, with a ratio of approximately 1:1. The slags usually assayed about 12-13 per cent Ta_2O_5 and 7-8 per cent Nb_2O_5. Most of the production of the other companies was then sold by a special department of Société Générale des Minerais in Brussels, which was an extension of their tin department. The assays were generally in the 25-40 per cent Ta_2O_5 range, being high in combined pentoxides and low in TiO_2 and SnO_2.

Production in Zaire and Rwanda had started during the Second World War, when the U.S. government began to purchase tantalite for military purposes, but the main increase in activity occurred during the GSA stockpiling programme of the early 1950's, at the time of the Korean war. By the early 1960's, many operations had been drastically curtailed or even suspended due to the GSA tantalite purchases being halted.

POST-COLONIAL RESTRUCTURING

After Zaire and Rwanda became independent countries, a number of reorganisations occurred over a substantial period of time.

Comité National du Kivu became Kivumines, later to be merged with the Empain Group. This combined new entity (after various other mergers and consolidations) is now Sominki which also includes the former Symetain group of tin mines. Sominki is owned 72 per cent by the Empain Group and 28 per cent by the Zairean government.

Geomines (Manono) became Zairetain with 50 per cent of the shares being held by Geomines (Brussels) and 50 per cent by the Zairean government.

Sermikat eventually closed down, some of its operations being taken over by Somika (Coframines), which is controlled by the BRGM (the French government mining and prospecting organisation).

Minetain was ultimately bought by Somirwa, which ended up with practically all of the Rwanda mines and is now owned 51 per cent by Geomines (Brussels) and 49 per cent by the Rwanda government.

Since its independence, Zaire's production of tantalite has declined dramatically, the main reasons for this being :

— The head grades have declined in many cases. In other cases old deposits have been effectively exhausted.
— During the years of depressed tantalite prices, finance for new investment was directed toward cassiterite deposits with good tin values and no significant by-product values.
— It became difficult to get adequate expatriate staff in sufficient numbers.
— The internal road system deteriorated due to the native population no longer performing their regular maintenance, as there were no Belgian civil authorities to make them do it. The inland waterways system was nationalised and became increasingly less efficient. Many of the mining companies had to send their shipments by air within the country, and even for exports as well.
— There were sporadic rebellions and local conflicts.

Much of this appears very discouraging. However, these problems are slowly starting to disappear. In both Zaire and Rwanda the local population is taking over the basic mining tasks on an artisanal basis, that is, by smaller-scale and simpler mining methods. The work is often done cooperatively on a familial/tribal basis. In many cases these families had been eking out a bare living from an agricultural subsistence economy. Thus, anything that they receive for their artisanal work enables them to buy goods that were previously considered luxury items. This is still enough of an incentive for working very long hours for what they perceive as a reasonable price for their "pre-concentrates".

What does this all mean at this time and in the long-term ?

Where some companies have pulled out of areas that they considered as being uneconomic to mine, there are now a large number of local workers producing these "pre-concentrates". So that the same mining company can now ship out "normal" concentrates at a profit by maintaining strategically-located buying offices and concentrating plants.

The workers are also motivated because their real net income has improved dramatically and to some extent they are finding new reserves in old areas that were judged to have been exhausted.

If there are no large scale expenditures by the major mining companies in the affected areas, this artisanal work may gradually decline, as old reserves are exhausted and not fully replaced by new discoveries. In the medium-term this should not happen, because the overall undeveloped areas, many of which were not developed in the boom period of the early 1950's, are considerable. However, over the longer term (25-30 years) these remaining reserves will almost certainly be exhausted.

CURRENT PRODUCTION LEVELS

Meaningful figures concerning the artisanal production are difficult to obtain, for the following reasons :

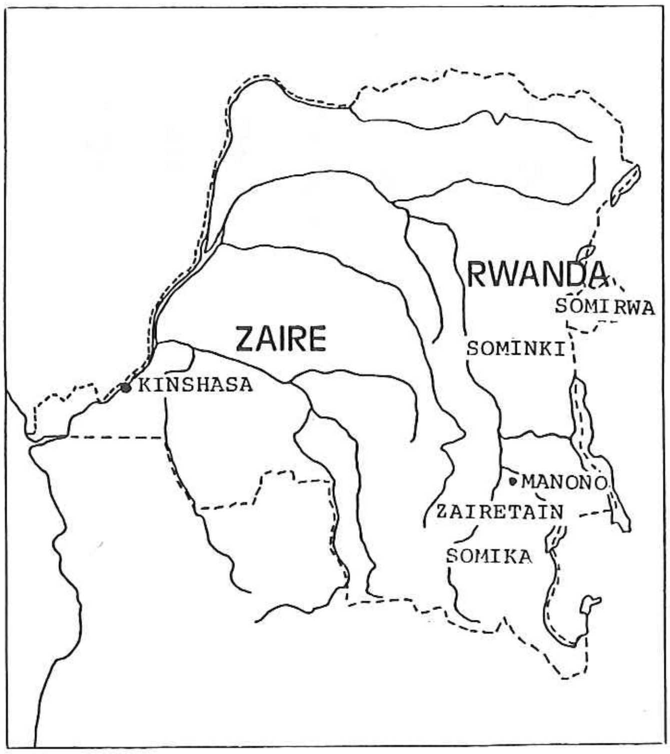
— The quantities and grades vary considerably from month to month due to worker movements.
— Normally the tantalite occurs as a by-product of tin concentrates, and the amount of tantalite in these cassiterites is extremely variable, as is the actual grade of tantalite (in terms of Ta_2O_5 content), that is finally produced in the concentrating plants out of these intakes.

These are rough estimates for the mining groups (for 1985 only) :

— *Zairetain* (Manono) — 12 mt of concentrates (28/32 % Ta_2O_5) and about 30-50 mt of tin slags (10/12 % Ta_2O_5).
— *Somika* — 24 mt of concentrates (25/26 % Ta_2O_5).
— *Sominki* — 50-60 mt of concentrates (30/40 % Ta_2O_5).
— *Somirwa* — 40-50 mt of tantalite concentrates (25/28 % Ta_2O_5).

All figures given above are approximate only.

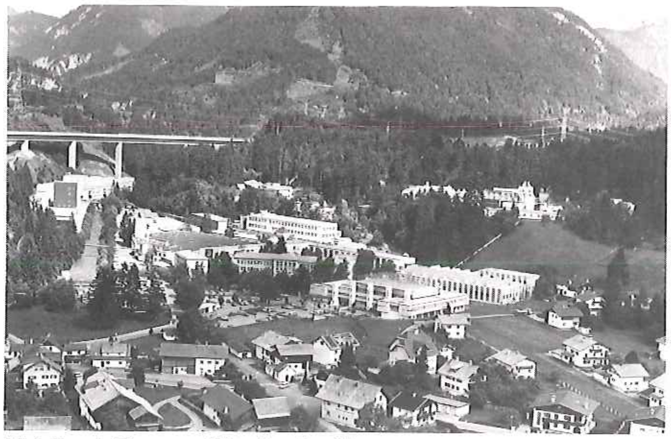
Areas of tantalite production in Zaire and Rwanda



MINING COSTS VERSUS SALES PRICES

There is some difficulty in talking about real mining costs, because of the mixture of artisanal intake and industrial intake at the concentrating mills. Hence it is difficult to know where to allot the costs. Also, because much of the production is associated with tin-mining, it is not certain whether costs should be allotted against tin only or proportionally between tin and tantalite.

What is needed in this market is stability of prices and indeed stability of sales. Also long-term arrangements with reliable consumers would avoid the "feast and famine" syndrome which has affected this business for much too long a time. Without such long-term arrangements, the mining companies cannot continue indefinitely to give the needed financial and technical support to their own mines and to the artisanal production.



Metallwerk Plansee at Reutte, Austria.

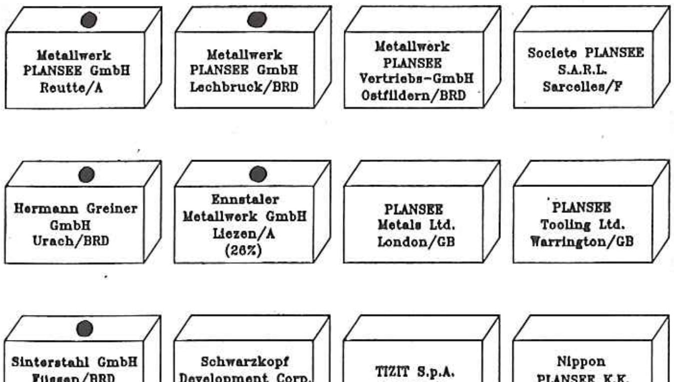
Plansee and powder metallurgy - Special activities in tantalum and niobium

This paper was presented by Prof. Hugo M. Ortner of Metallwerk Plansee at the T.I.C. meeting in Brussels on October 22nd 1985.

To tell about the development of Metallwerk Plansee is to tell a major part of the history of powder metallurgy itself. The Reutte company was founded in 1921 by Prof. Dr Paul Schwarzkopf who, with a team of twenty workers, started to produce molybdenum and tungsten wires. From the beginning, great emphasis was placed on research and development as a foundation of the company.

Many pioneering developments have come out of Plansee since that time. In 1929, the first mixed-carbide tools, containing TiC and Ta (Nb) C besides WC and Co, brought a new era in steel machining. At the end of the 1930's, Plansee played a leading part in sintered iron and steel technology. From 1932 onwards, W-Cu and W-Ag pseudo-alloys were produced for electrical contacts and high tension switches. Permanent magnets were also produced at Plansee in the 1930's. In 1940, a central research and development institute was installed. The company employed 500 people at this time. In 1952, the first Plansee Seminar was held at Reutte on the initiative of Prof. Schwarzkopf. This conference has become a major event in the field of powder metallurgy and the 11th Plansee Seminar, which took place in May 1985, was attended by over 600 participants from thirty-one nations — a unique opportunity to discuss the latest findings in technology, new applications and recycling of refractory and hard metals.

In 1967, Prof. Schwarzkopf retired as Chairman of the Executive Committee and his son, Walter M. Schwarzkopf, succeeded him. Under his leadership, the specialist powder metallurgy firm developed into a modern industrial undertaking.



Present structure of Metallwerk Plansee (five production works marked)

The present Executive Board, under the chairmanship of Dr Rudolf Machenschalk since 1979, sees its principal task in the development of Plansee as an international company responsive to ever-changing technology. Today, the parent firm in Reutte employs some 2000 people, and the world-wide figure is approaching 2800. The four product groups are :

— the refractory metals, namely Mo, W, Ta, Nb and their alloys;

— hard metals : WC-Co, WC-Co-TiC, Ta (Nb) C and TiC based, coated with Ti (C, N) or Al_2O_3-TiC multilayers;

— composite tungsten materials;

— sintered iron and steel.

Plansee is presently the largest firm in Europe specialising in powder metallurgy and is a world leader in the field. The total turnover in 1984-1985 was approximately US$100 million.

TANTALUM AND NIOBIUM AS MATERIALS FOR PROSTHETIC DEVICES

The stainless steels and cobalt-based alloys that have been used in the past for load-bearing implants exhibited the necessary strength and biocompatibility as long as a smooth shape in a metallurgically perfect state was obtained. A decisive improvement in biocompatibility was brought about by the introduction of titanium as an implant material, but its hexagonal crystal structure made it liable to cracks and fractures. Because of the limitations of the materials, tantalum and niobium were introduced by Plansee for implants. Until then, tantalum had only been used for the manufacture of surgical nets and wires, vascular and other clips, pacemaker electrodes and dental implants.

Both niobium and tantalum belong to the most corrosion-resistant group of metals which act neutrally in living tissue. Besides their biocompatibility, their stability against crevice corrosion is an important property. Allergic reactions, carcinogenic properties and general reactions of resistance, well-known for cobalt, nickel, chromium and others, have not been observed with these two metals. Electrochemical reactions and their results — corrosion or metallosis — do not occur in the bio-inert pure metals, niobium and tantalum. Their excellent biocompatibility was also proved in animal tests over a period of five years in studies at clinics. It could be demonstrated that even deformed wear particles, removed by abrasion, did not show any reaction in histological examinations of the tissue.

The mechanical properties of tantalum and niobium can be adapted to satisfy particular circumstances by the manner in which they are worked. This does not result in a reduction of corrosion resistance and thus of tissue compatibility, as is the case when, for example, stainless steel is cold-worked. In addition, the two metals have a modulus of elasticity closer to that of bone than have other high-strength materials; this fact may contribute to the favourable bone reaction.

Based on a fluted profile, Plansee have developed niobium intramedullary nails for femurs, tibias and humeri which have a higher torsional stability over other such nails. Also, the favourable properties of niobium enable the adaptation of the intramedullary nail to the curves of long bones.

NIOBIUM AND TANTALUM AS MINT METALS

Coins and religious objects made of precious metals were produced powder-metallurgically in ancient times. Later, metals were fabricated almost exclusively by melting. Only in 1830, did the Russian metallurgist, Sobolewskoy, develop a powder-metallurgical procedure for producing platinum roubles. The procedure was further developed by Wollaston whose name the procedure still carries. The technology developed for this purpose still forms the basis of modern powder metallurgy. After an interval of 150 years, efforts are again being made to use the PM-method for coin production because of the following reasons :

— No scrapping of coinage metal due to pressing and sintering of final shapes.

— Possible to produce a counterfeit-proof article.

Coins made out of either tantalum or niobium have the additional advantages of corrosion-resistance and good workability. For special medals, anodic oxidation yields appealing colours. By inserting small plates or rods of, for example, magnesium oxide, they can be made counterfeit-proof as these inclusions can be detected by X-ray inspection.

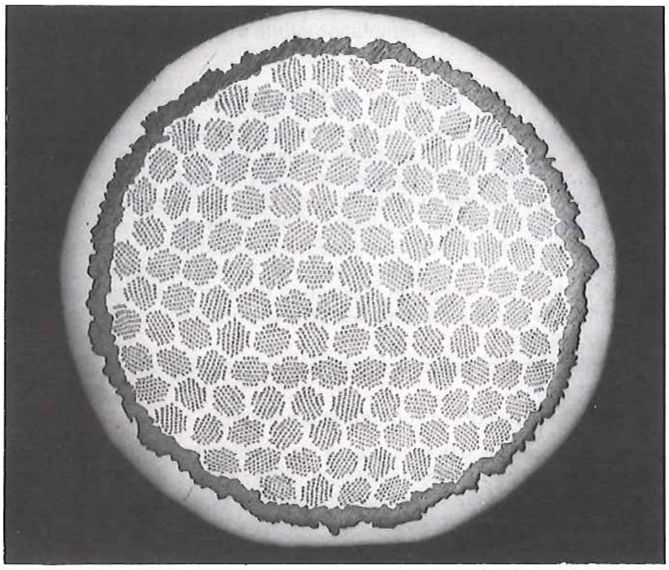
Nb_3Sn - SUPERCONDUCTORS

An application of niobium of rising interest is for Nb_3Sn-superconductors. It has been found that superconductivity disappears, not only above a critical temperature, T_c, but also above a certain electric current, I_c, and under the influence of a critical magnetic field, H_c. These three critical values are interdependent and are the basic characteristics of a superconducting material. For most pure metals, the critical magnetic field is small which prohibits their use as technical superconductors. Only the discovery and development of new materials — alloys, intermetallic compounds and ternary molybdenum sulfides — has opened the way to the practical application of superconductivity. Some of these materials are listed below :

Superconductor	T_c (Kelvin)	$\mu_o H_{c2}$ (T = OK) (Tesla)
W - Type		
Nb Ti	9,0	14,1
Cr_3Si - Type		
V_3Ga	14,8	25
Nb_3Sn	18,0	28
Nb_3Al	18,7	33
Nb_3Ga	20,2	34
Nb_3Ge	23,0	38
$Nb_3(Al_{0,7}Ge_{0,3})$	20,7	43,5
NaCl - Type		
NbN	15,7	15,3
$Nb(C_{0,3}\ N_{0,7})$	17,4	11
$MgCu_2$ - Type		
HfV_2	9,2	26,8
$Hf_{0,5}Zr_{0,5}V_2$	10,1	26,9
$PbMo_6S_8$ - Type		
$PbMo_6S_8$	15	60
$SnMo_6S_8$	14	34
$LaMo_6Se_8$	10,8	44,5

Critical temperature T_c and upper critical magnetic field H_{c2} (at T = 0 K) for the most important high field superconductors.

The relevant phases (known as Chevrel phases) are extremely brittle and the production of relevant superconductors is, at present, problematic.



Transverse section (metallographic preparation) of a Nb_3Sn-multifilament superconductor produced at Plansee (diameter : 0.60 mm).
Outside : copper mantle.
Intermediate ring : tantalum diffusion barrier.
Inside : Nb filaments in CuSn bronze matrix.

Plansee, in collaboration with several research institutes, is developing Nb_3Sn-superconductors which have much better characteristics than the conventional NbTi materials. A powder-metallurgical route for producing Nb_3Sn-superconductors has already been developed. Since Nb_3Sn is also a very brittle substance, the annealing is carried out in the final wire at temperatures between 650 °C and 750 °C under argon lasting up to five days. This annealing leads to the formation of Nb_3Sn by Sn diffusion to the Nb-filaments.

NIOBIUM, TANTALUM AND SOME ALLOYS AS ULTRAPURE SPUTTER TARGETS FOR THE ELECTRONICS INDUSTRY

Physical Vapour Deposition (PVD) methods are commonly used for the deposition of thin layers on a variety of substrates and for a wide range of applications.

In electronic applications, layers serve as diffusion barriers, coatings for masks or displays and resistance layers. The quality of surface coatings deposited by PVD depends to a high degree on the properties of the target. For applications in micro-electronics, materials with low contents of "mobile ions" are mandatory. Mobile ions are essentially the alkali metal ions, namely Li^+, Na^+, and K^+, and the lighter and more abundant alkaline earth metal ions, Mg^{2+} and Ca^{2+}. For certain types of electronic elements, intrinsic radioactivity can also have harmful effects and so target materials should be free of uranium and thorium traces. Non-metals (O, N, H and C) are also detrimental as are magnetic impurities (Fe, Co and Ni) for certain applications. In some instances, concentrations as low as < 0.001 ppm (< 1 ppb) may have an effect.

The purity of ultrapure refractory metals is in the order of 4-N (99.99 per cent). Not only are the procedures for the production of these metals costly, but also their analytical characterisation at the sub-ppm level presents many problems. For niobium and tantalum, the 4-N purity, with a sum of impurities of 100 ppm, can be regarded as the best achievable if non-metals are also considered. These are very reactive metals with respect to O, N, H and C and, therefore, their non-metal free production is, in practice, difficult under large-scale conditions.

As for alkali and alkaline earth metals and U and Th, the first problem to be solved is the analytical one. The chart (given below) summarises present possibilities for the analytical characterisation of niobium and tantalum.

Traces	Nb	Ta
Li	0,0013 CPAA (p,d) 0,006 NAA	0,003 CPAA (d)
Na	5.10^{-5} NAA	10^{-4} SIMS 0,01 GFAAS (after sep.)
K	5.10^{-6} NAA	3.10^{-5} SIMS
Mg	0,02 NAA 0,2 ICP-OES	0,4 ICP-OES
Ca	0,5 ICP-OES	2.10^{-4} SIMS 0,5 ICP-OES
Th	3.10^{-4} NAA 0,01 Voltammetry	
U	14 ICP-OES 5.10^{-6} NAA	15 ICP-OES

Detection limits for Nb and Ta of critical elements (all values in µg/g).
Explanation of abbreviations used :

CPAA	*charged particle activation analysis.*
d	*deuterons.*
FAAS	*flame atomic absorption spectrometry.*
GFAAS	*graphite furnace atomic absorption spectrometry.*
ICP-OES	*inductively coupled plasma - optical emission spectrometry.*
NAA	*neutron activation analysis.*
p	*protons.*
SIMS	*secondary ion mass spectrometry.*

For niobium, the situation is best since all the elements in question (except Ca) can be determined by neutron activation analysis down to ppb-level or even better. For tantalum this is not possible due to a pronounced activation of the matrix itself. It is hoped that SIMS will be applicable to all listed elements which are presently investigated. Methods like NAA or SIMS are not usually available to industrial laboratories so that a new strategy will be necessary in the future for the selection, purification and characterisation of ultrapure refractory metals :

- Sorting out of high-purity material from normal production by analytical methods applicable to routine industrial control like GFAAS, FAAS, ICP-OES;
- Possibly purification procedures like multi-cycle electron beam melting have to be carried out at this stage;
- Putting these pre-characterised and/or purified materials on stock for special applications. Final external analytical characterisation has to be undertaken now by NAA, CPAA, SIMS, etc.

Similar problems occur also for the application of Nb, NbZr or NbTi as superconducting materials for the construction of, for example, large electron-positron colliders such as the LEP-project, CERN, Geneva. The need for ultrapure Nb for this project could amount to approximately 50 tons until 1990.

From this it should be clear that for many advanced applications of refractory metals, the production of high purity or even ultrapure materials becomes a fascinating challenge. The higher the purity level, the more complicated and costly becomes the relevant analytical characterisation which to a rising degree also contributes to material costs.

ULTRA-TRACE ANALYSIS OF GRAIN-STABILISED TANTALUM FOR YTTRIUM

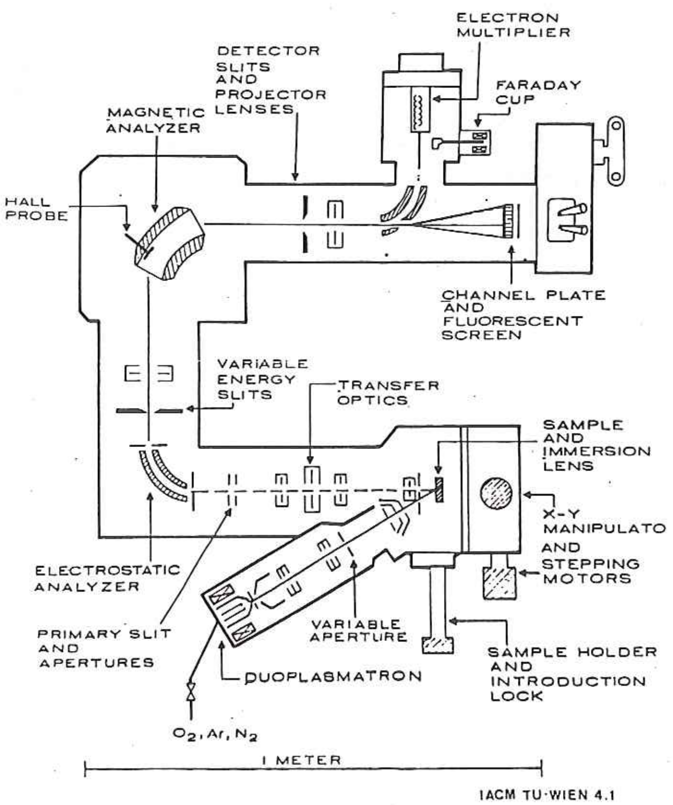
Since tantalum capacitors will eventually replace miniature aluminium electrolytics, the trace levels of yttrium leading to grain-stabilisation in tantalum capacitor wire are of interest.

Plansee tantalum wire remains fine-grained even after thirty minutes of annealing at 2100 °C. This is achieved by doping the tantalum starting powder with Y_2O_3 using concentrations in the order of 50 μg/g which can still be checked by X-ray spectrometry. However, the remaining Y-content after sintering lies below the detection limit of XRS and other modern methods of bulk trace analysis available in industrial laboratories. Since varying resistance against recrystallisation was observed for different production charges of tantalum, the question of sufficient Y-contents in this material for grain-stabilisation gained interest. It was possible to solve this problem with SIMS.

Shown below is a schematic diagram of the IMS 3f-SIMS instrument used for this investigation.

CAMECA ION MICROANALYZER

IMS – 3F



In a series of analyses of recrystallised tantalum wires, which were doped with varying amounts of Y_2O_3, it was found that the first detectable grain-stabilising effects appeared at a Y-concentration of 0.03 ppm (30 ppb). At Y-contents between 0.30 ppm and several ppm, the best structure was observed, with a homogeneous grain size ranging from 5 to 7 of the ASTM grain size numbers.

Analysis of tantalum raw materials

During the recent T.I.C. meeting, there was an interesting discussion concerning the assaying of tantalum-containing raw materials — namely tin slags and tantalites. Alfred H. Knight International, the well-known samplers and assayers, have made available their analytical methods for these raw materials which form the basis of this article. The T.I.C. invites any Bulletin reader to express views on this subject by writing to us; it may be possible to publish any letters received in a future edition of the Bulletin.

The routine analysis of Ta_2O_5, Nb_2O_5, TiO_2 and SnO_2 in tantalum-containing tin slags and tantalites is performed using an XRF fused bead technique. Linear calibrations are obtained using synthetic standards made from pure oxides, which are listed below :

	Tin slags	*Tantalites*
Ta_2O_5	NiO	WO_3
Nb_2O_5	MoO_3	MoO_3
TiO_2	$Ba(NO_3)_2$	—

($Ba(NO_3)_2$ also acts as an oxidant during the fusion process and as a heavy absorber.)

Trace amounts of internal standard elements may be present in the natural state sample. Therefore, analysis of these is undertaken prior to the fusion procedure and the weight of the internal standard is adjusted accordingly.

METHOD

An accurately-weighed quantity, 0.5 g, of the sample and the fusion mixture is put into a Pt/Au crucible which is then, after mixing, placed in a silicon carbide rod furnace preheated to 1250 °C. A homogeneous melt is achieved in fifteen minutes, swirled within the furnace and poured quickly on to an aluminium mould preheated to 300 °C. After ten minutes annealing, the bead is removed and presented to the spectrometer.

Fusion mixtures used :

Tin slags	*Tantalites*
12 g Borax	12 g Borax
4 g Boric Acid	4 g Boric Acid
2 g Barium Nitrate	1 g Lanthanum Oxide (heavy absorber)
0.05 g Nickel Oxide	0.3 g Tungsten Trioxide (calcined)
0.04 g Molybdenum Oxide	0.15 g Molybdenum Oxide

Calibration ranges :

	Tin slags	*Tantalites*
Ta_2O_5	0-30 %	30-70 %
Nb_2O_5	0-30 %	3-35 %
TiO_2	0-60 %	0-5 %
SnO_2	0-10 %	0-5 %

Instrumental conditions (applicable to both tin slags and tantalites) :

- PW 1450 Spectrometer
- Cr target X-ray tube
- 60 KV, 45 mA
- LiF 200 crystal
- Fine collimator (except for Sn and Sn background - coarse)

Other conditions vary with the element in question and are given below :

Element	*Line*	*Detector*
Mo	Kα'	S
Nb	Kα'	S
Ta	Lα'	F + S
Ti	Kα'	F
Sn	Lα'	F
Sn background		F

These elements are analysed in both tin slags and tantalites. In addition, Ni (Kα', F + S) and Ba (Lα', F) are analysed in tin slags and W (Lα', F + S) is analysed in tantalites.

CALCULATION

Tin slags :

$\frac{\text{Nb count}}{\text{Mo count}}$ interpolated against % Nb

$\frac{\text{Ta count}}{\text{Ni count}}$ interpolated against % Ta

$\frac{\text{Ti count}}{\text{Ba count}}$ interpolated against % Ti

Sn (peak-background) against % Sn

Tantalites :

$\frac{\text{Nb count}}{\text{Mo count}}$ interpolated against % Nb

$\frac{\text{Ta count}}{\text{W count}}$ interpolated against % Ta

Ti count against external monitor

Sn (peak-background) against % Sn

T.I.C. Statistics

Price Waterhouse report the following collected statistics :

PRODUCTION AND SHIPMENTS

3rd quarter 1985
(quoted in lb Ta_2O_5 contained)

Category	*Material grade*	*Production*	*Shipments*
A/B	Tin slag	259 799	31 400
C/D/F	Tantalite and Other materials	54 257	61 281
	Total	314 056	92 681

Notes :

1. In accordance with the rules of confidentiality, categories A and B, and C, D and F, have been combined, as shown, because certain individual returns accounted for more than 65 per cent of the total of the category concerned.
2. The response from the companies asked to report was 18/23; the statistics given above include reports from these producers :
   Datuk Keramat Smelting
   Greenbushes Tin
   Malaysia Smelting
   Metallurg Group
   Tantalum Mining Corporation of Canada
   Thailand Smelting and Refining
3. Taking into account unrecoverable processing losses, it can be estimated that the above raw material shipments are equivalent to 68 652 lb tantalum (after processing).

PROCESSORS' SHIPMENTS

3rd quarter 1985
(quoted in lb tantalum contained)

Product category	*Shipments*
Tantalum oxide /K_2TaF_7	23 464
Alloy additive	46 488
Carbide	132 621
Powder/anodes	160 544
Mill products	62 852
Scrap, ingot, unworked metal and other	54 416
Total	480 385

Notes :

1. In accordance with the rules of confidentiality, the categories of "Scrap" and "Ingot, unworked metal and other" have been combined, because in each category one individual return exceeded 65 per cent of the total of the category concerned.
2. The response from the companies asked to report was 17/18; the statistics given above include reports from 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

QUARTERLY PRODUCTION ESTIMATES

(quoted in lb Ta_2O_5 contained)

LMB quotation :	*US $ 30*	*US $ 40*	*US $ 50*
4th quarter 1985	409 165	488 115	613 815
1st quarter 1986	415 765	494 715	620 815
2nd quarter 1986	425 965	504 915	643 015
3rd quarter 1986	425 965	516 915	673 015
4th quarter 1986	430 965	526 915	678 015

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

Capacitor Statistics

Japanese tantalum capacitor production and exports

(thousands of units)

	Production	*Of this, exports*
2nd quarter 1985	552 722	90 126
Total for year up to August 1985	1 473 631	263 612

(Data from JEIDA)

Address

Is your Bulletin correctly addressed ? If there are changes to be made, please let us know.

PRINTED BY PUVREZ 59, av. Fonsny, Brussels