TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

BULLETIN Nº 51 AUGUST 1987 THIRD QUARTER

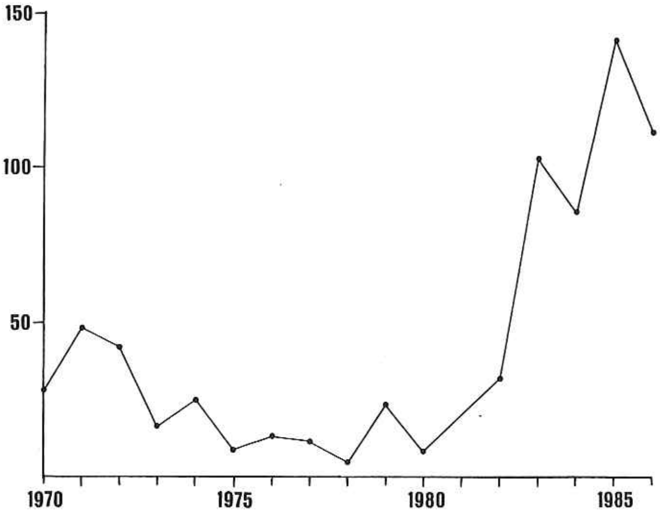
Tantalum usage in superalloys

In recent years, tantalum's fastest-growing market has been as an additive to superalloys. Almost 200 000 lb tantalum were shipped for this purpose last year, according to T.I.C. data; before 1982, a fraction of this quantity was being shipped.

The term "superalloys" describes those nickel, cobalt and iron-nickel based alloys used for components in gas turbines, primarily for aircraft jet engines, but also for marine and power applications. Around 75 % of superalloy production is accounted for by aircraft engines.

Historical demand for superalloys has been cyclical : following the peak period of 1979-80 when around 100 million lb per year were being shipped worldwide, demand fell to 60-65 million lb during 1982-84. The market is currently at around 90 million lb per year. Although the turbine market appears set to increase and will probably peak towards the end of this decade, superalloy demand will probably not rise proportionally, being off-set by the use of superplastic forging and net-shape casting. These techniques will reduce the high scrap rates prevalent in the superalloy industry. Hence the market has matured to some extent. The recent demand trend for tantalum alloy additive, however, bears little similarity to the overall trend for superalloys.

Tantalum alloy additive shipments (000 lb Ta; US data)



T.I.C. MEETING

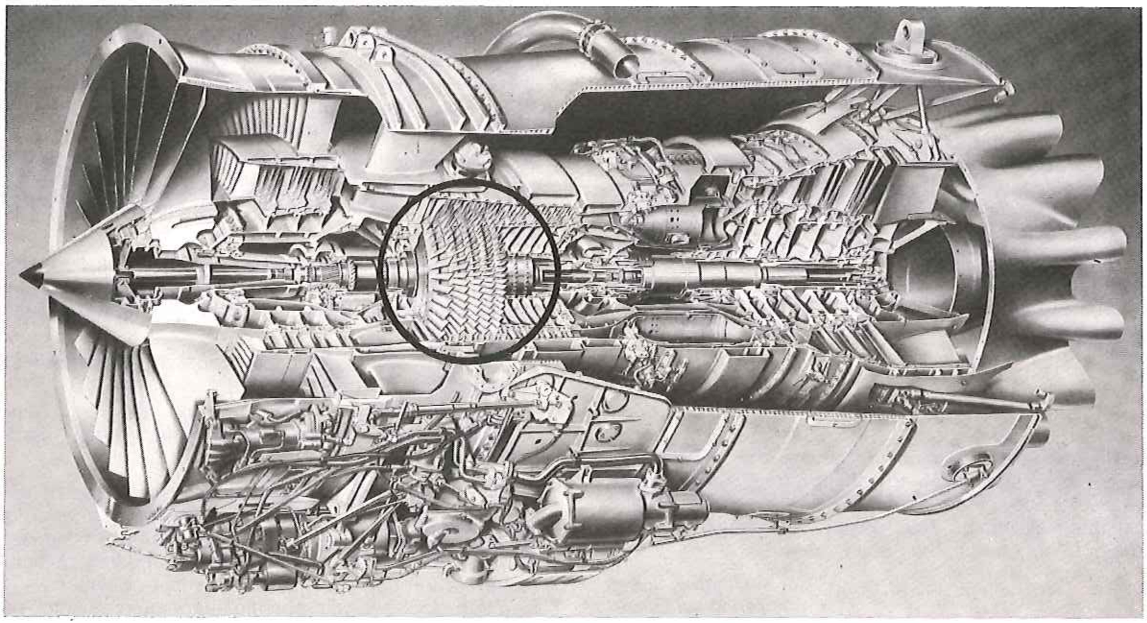
The Twenty-eighth General Assembly will be held at 40 rue Washington, 1050 Brussels, on October 20th 1987, and will be followed by a programme of technical presentations. Invitations will be sent to member companies; for non-member companies, those interested may obtain information from the Secretary General, T.I.C., 40 rue Washington, 1050 Brussels.

As amendments to the T.I.C. charter will be discussed at this meeting, it is hoped that members will make a special effort to be represented.

Tantalum had been accepted as an additive to superalloys by the early 1960's, but the first major user was alloy B 1900, containing 4.2 % Ta. This nickel-based, cast alloy was favoured by Pratt & Whitney during the early 1970's for their turbine blades which have to endure the jet engine's hottest and most corrosive environment. Tantalum was found to improve castability as well as increasing overall strength and oxidation resistance. Following the peak year of 1971, alloy B 1900 was superseded by an alloy containing no tantalum. Around this time, other alloys such as IN 738 (1.8 % Ta), IN 792 (4.2 % Ta), Mar-M 002 (2.5 % Ta), Mar-M 246 (1.5 % Ta) and Mar-M 247 (3.0 % Ta) were developed and commercialized, as were some cobalt-based alloys such as Mar-M 509 (3.5 % Ta). These alloys are still widely used today in both conventionally- and directionally-cast components. But since 1982, a new processing technique — single-crystal casting — has increased tantalum consumption significantly above previous levels.

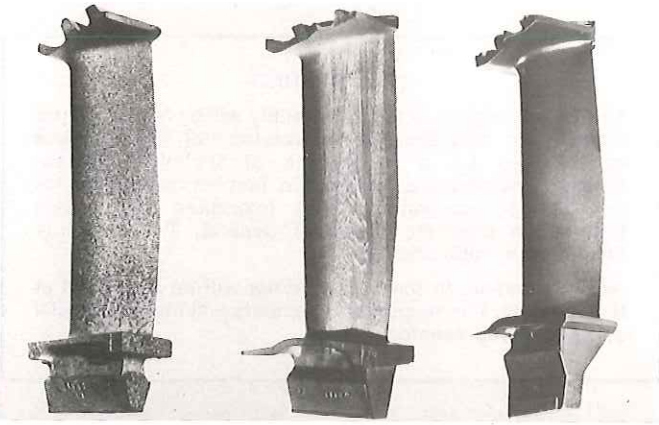
Over the last 20-30 years, jet engine design has increased temperature performance requirements of superalloy components, leading to progressive improvements in high-temperature properties, such as hot corrosion/oxidation resistance. Designers achieved this by changing alloy compositions and improving component manufacturing techniques. The emphasis in component design has shifted over the years from innovating alloy contents to innovating component processing technology : the major development of the 1980's has been single-crystal casting. By producing blades (rotating) and vanes (stationary) as single crystals, i.e. with no grain boundaries which are the major source of weakness in a metallic lattice, the need for grain boundary strengthening additives is eliminated. And so alloys can be constituted which take advantage of higher heat treatment temperatures. Single-crystal casting offers substantial improvements to a turbine component's creep strength, thermal

Jet engine (Rolls Royce RB 211) showing turbine blades (circled)



fatigue resistance and oxidation/corrosion resistance. This led to Pratt & Whitney introducing a nickel-based, single-crystal alloy — PWA 1480 — for the blades in their engine hot sections. This alloy contains 12 % Ta; its commercialization has driven the massive increase in tantalum consumption by superalloys over the past few years.

Blades conventionally cast (left), directionally solidified (centre) and cast as a single crystal (right)



Until recently, Pratt & Whitney held a dominant position in the patent coverage of this technology so other jet engine manufacturers, such as General Electric and Rolls Royce, were not free to take full advantage of single crystals. However, an important US patent held by Pratt & Whitney expired in March 1987. As a result, single crystals with tantalum-containing compositions should be introduced more widely in the turbine components field.

In the past, General Electric took the approach of improving engine design rather than materials, but the indications are that this approach is reaching its limits. They will almost certainly have to start using more single crystals in their engines, invariably containing tantalum. Rolls Royce use a single-crystal alloy, SRR 99 with 2.8 % Ta. Cannon-Muskegon Corporation, a manufacturer of turbine components, have developed and marketed single-crystal blades using alloys CMX 2 and CMX 3, containing 6 % Ta; these have been adopted by three turbine manufacturers : Allison, Garret and Turbomeca.

Tantalum benefits superalloy properties by increasing the overall strength of the alloy as well as improving the oxidation resistance. This latter benefit is demonstrated by the lower tendency of high-tantalum, low-tungsten alloys to form lines of small, equi-axed grains known as "freckles" within single-crystal components. A drawback in using tantalum at high levels is that the heat-treatment "window" (the temperature band within which heat treatments have to be performed) is greatly reduced, making reliable heat treatments difficult. This is why single-crystal alloys other than PWA 1480 contain significantly less tantalum, normally in the range of 2-6 %.

Over the last few years there has been a significant reduction in the quantity of tantalum scrap (such as that produced by capacitor manufacture) being used as alloy additive. Analytical specifications are becoming tighter, and this prohibits the use of scrap so that not many lots qualify. For example, tantalum added to PWA 1480 is allowed to contain only 0.12 % of Mn and Si, 0.02 % C and 0.15 % P and S; trace elements are also tightly controlled.

Extensive research has been performed on alternatives to single crystals which currently represent the state-of-the-art processing technology for turbine blades and vanes. Of these, none appear likely to become commercialized to the extent that single crystals are forecast to do. All have inherent obstacles to widespread acceptance. Orientated eutectics (some containing tantalum) are slow to produce; ceramics are too brittle; and powder-metallurgical techniques are too expensive. Turbine manufacturers are already in the process of developing second-generation single-crystal alloys containing tantalum.

SUMMARY

The fastest-growing market for tantalum in recent years has been as a superalloy additive; this seems likely to continue for the foreseeable future as single-crystal alloys other than PWA 1480 enter service and so achieve commercialization. This growth in demand will be sustained by the current upturn in the turbine market.

Andrew Jones
Technical Officer

President's letter

For many of those (including myself) attending the Twenty-seventh General Assembly in Brazil, it was a first visit to a fascinating and spectacular country. We are very grateful to CBMM and Metallurg for helping to contribute to our education, and to the success of the meeting itself.

Mr Fabiano Pegurier, speaking on behalf of the host companies at the dinner given by them on June 2nd, said that in the years to come we could well see the history of the T.I.C. in terms of "before- and after-Rio".

It certainly marked dramatically the full incorporation of niobium into our organisation's interests. We were in the country of the world's biggest pyrochlore producer, and earlier that day we had heard from Mr Egberto Silva details of the Pitinga deposit and Mamoré treatment plant which should make Paranapanema the largest producer of pure niobium oxide (and, incidentally, a significant producer of tantalum compounds).

We will also be collating the quarterly statistics on niobium production and consumption with effect from the beginning of 1987; I hope that, with the co-operation of all members, the figures we produce will quickly acquire equal international status with those that we publish for tantalum.

By October we should have a fair amount of statistical data to hand on niobium, and I hope you will be able to join us, at our Twenty-eighth General Assembly on October 20th in Brussels, to discuss the implications of the figures for our industry.

Yours sincerely,
R.J. Tolley
President

Twenty-seventh General Assembly

The venue for this meeting of the Tantalum-Niobium International Study Center was the Rio-Sheraton Hotel, Rio de Janeiro; it was held on June 2nd 1987. Mr Rod Tolley of Datuk Keramat Smelting, the current T.I.C. President, chaired the meeting.

Four new members were elected :

- Liarte Metalquimica, a Brazilian producer of niobium and tantalum oxides;
- Rohco Industria Quimica, a chemicals manufacturer in Brazil, investigating the possibilities of niobium and tantalum oxide production;
- Toho Titanium, a Japanese company researching the production of niobium metal and niobium-titanium alloy;
- West Coast Holdings, sponsoring a feasibility study of the Brockman mineral deposit at Kimberley, Western Australia, which contains defined reserves of niobium and tantalum.

Resignations accepted brought the total membership of the association to sixty-nine. The membership of Union Carbide Corporation was transferred to Kemet Electronics Corporation, and the denomination of Sandvik Hard Materials was changed to Sandvik Coromant.

It was announced that, in September/October 1988, the T.I.C. would be holding a major symposium on the applications, production and technology of tantalum and niobium. Participation will be open to all those interested : further details will be published when available. There will be no meeting of the T.I.C. in the spring of 1988. The Twenty-eighth General Assembly will take place on October 20th 1987 in Brussels.

Since the preceding General Assembly, the Executive Committee had co-opted two new members to fill vacancies, Mr Hans-Jürgen Heinrich (Gesellschaft für Elektrometallurgie) and Mr David E. Maguire (Kemet Electronics).

The collection of worldwide industry statistics on niobium was to be commenced by the T.I.C. Quarterly data received from producers will be compiled by the accountants Price Waterhouse and reported in several categories :

- Production (two categories) : niobium concentrates and occurring with tantalum (in tin slag, etc.).
- Product shipments (three categories) : compounds and alloy additive (vacuum-grade), metal and alloys, and HSLA-grade ferroniobium.

The T.I.C. Technical Officer then discussed some of his activities over the preceding few months. Market-oriented and technical information relevant to the niobium and tantalum industries had been collected from a wide range of sources and then communicated to the members through the "Bulletin" and newsletters. The T.I.C. had also corresponded with non-members such as small producers, thus fulfilling a vital role in bridging the communication gap. Some specific interests over the past year had been the impact of the tin crisis on tantalum production and the developing markets for high-purity niobium oxide. Several articles had also been prepared for metals journals on niobium and tantalum.

Following the General Assembly, presentations were made by Dr Simon Rodriguez (Ministry of Mines, Venezuela), Dr Michael Hörmann (W.C. Heraeus), Mr Hans-Jürgen Heinrich (GfE), Dr Harry Stuart (Niobium Products Co.) and Mr Andrew Jones (T.I.C.). The assembled participants then welcomed delegates representing the People's Republic of China : Mr Zhang Shou-Wu of the China National Nonferrous Metals Industry Corporation (Nanchang Company) introduced the activities of his corporation to the meeting. Mr Fabiano Pegurier (Cia. de Estanho Minas Brasil) and Mr Egberto Silva (Mamoré Mineração e Metalurgia) described the Brazilian tantalum industry; the development of the Pitinga deposit by the Paranapanema Group and the oxide plant currently being built were of particular interest.

On June 3rd, the mines of CBMM and Mibra were visited by participants from the meeting.

Mibra mine visit

MEMBERSHIP

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

Liarte Metalquimica Ltda.,
Rua Sete de Setembro 55 Grupo 2.401,
Rio de Janeiro, CEP 20050, Brazil.

Rohco Industria Quimica Ltda.,
C.P. 741,
CEP 09790 São Bernardo do Campo,
SP, Brazil.

Toho Titanium Co., Ltd.,
Shinagawa NSS Building,
2-13-31 Kohnan, Minato-Ku,
Tokyo, Japan.

West Coast Holdings Ltd.,
129 Edward Street,
East Perth, WA 6000, Australia.

The resignations of three members were accepted by the same Assembly :

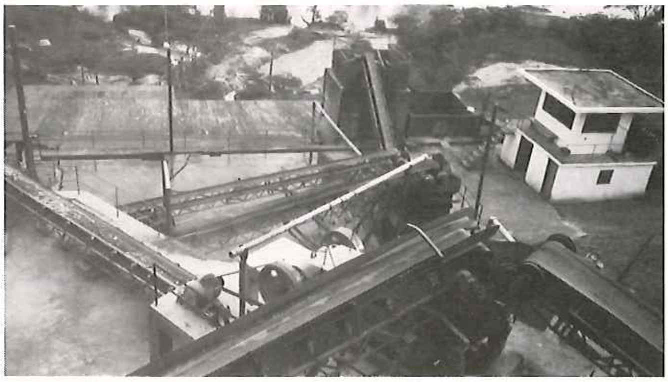
Intelligent Controls
Makeri Smelting Co. Ltd.
Metallurgical Industries Inc.

Brazilian producers "down-stream" into oxides

Later this year, a plant with the capacity to produce two million lb of niobium and tantalum oxides annually should be completed and operating near São Paulo. The Paranapanema Group, the world's largest tin miner, announced their plans to become a major oxide producer at the recent T.I.C. meeting in Rio de Janeiro.

Integration by mining companies into "down-stream" products is not uncommon in Brazil, demonstrated by CBMM's development of the Araxá pyrochlore deposit to become the world's major producer of HSLA-grade ferroniobium, as well as a significant source of oxide and vacuum-grade alloy additives (see Bulletin no. 50). The Mibra tantalite mine at São João del Rei, owned by the Metallurg Group, now ship all of their production as oxides (see also Bulletin no. 50). Despite the low prices for tantalite over the past few years, production has been maintained at a high level. The oxides produced at the Fluminense plant are used throughout the Metallurg Group.

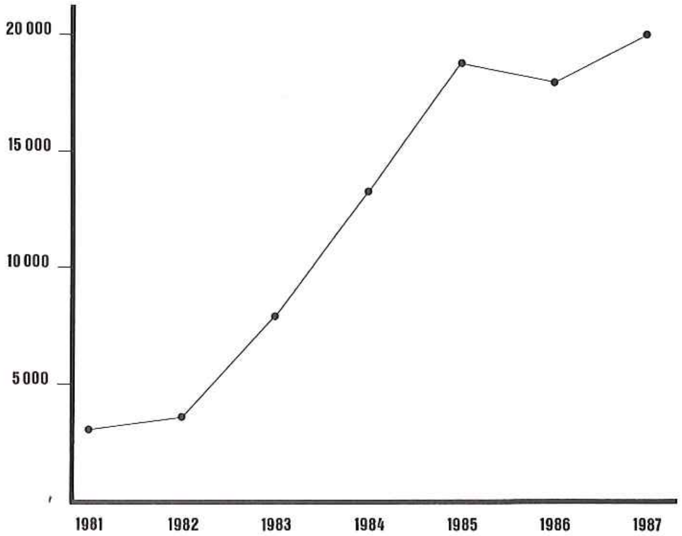
Ore classification and crushing at Mibra



Paranapanema have achieved their position as the largest and lowest-cost producer of tin in a comparatively short period of time, now holding 12 % of the world's market. Until this year, the only niobium and tantalum which they produced was contained in the by-product slag from their Mamoré smelter near São Paulo. This material has a very low grade — 2 % Ta_2O_5 and 4-5 % Nb_2O_5 — and so has been stockpiled since tantalite prices were not high enough to make tantalum recovery economic.

At present, around 70 % of Paranapanema's tin concentrates originate from the Pitinga district, 320 km north-east of Manaus in

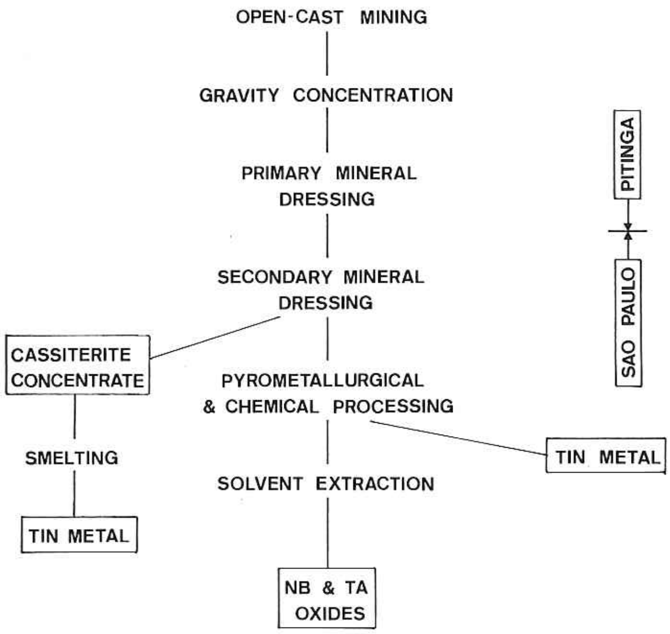
Tin metal production at Mamoré (tonnes Sn)



Amazonas state. The remainder comes from three mines in Rondonia, but these sources are declining. The Pitinga deposit was discovered in 1980 and production commenced in 1982. Two mines are in operation : Madeira and Queixada. Previously, mining was by dredging of alluvial deposits, the ore then being concentrated by gravity separation. This concentrate is shipped to Mamoré for further upgrading and smelting. From 1987, however, the main ore body at Madeira will be mined. This body is approximately 2 km diameter and has a weathered layer, 40 metres deep. This weathered layer contains : 300 000 t Sn, 300 000 t Nb_2O_5 and 30 000 t Ta_2O_5 (approximate quantities only), as well as reserves of hafnium, yttrium and zirconium. Open-cast mining will be employed to extract the ore at a very low cost. A concentration facility, described as a "pilot plant" by Paranapanema, was operational in June and will be able to process 20 000 cubic metres of ore per month. The hard rock underneath the weathered layer also contains significant values of tin, niobium and tantalum, but the 40 metre layer is sufficient for 20 years' production.

A new processing route has been developed by Paranapanema for the ore from this site. The products will be tin metal and oxides of niobium and tantalum.

Processing route for Pitinga ore



After gravity concentration of the ore, a primary mineral dressing operation will remove zirconium, yttrium and hafnium (as yet, no plans exist to extract these metals). The resulting concentrate containing tin, niobium and tantalum will then be transported to the Mamoré site near São Paulo where a secondary mineral dressing operation will produce a cassiterite concentrate and a mixed concentrate of tin, niobium and tantalum. The cassiterite concentrate will be smelted by the existing facility; the mixed concentrate will undergo a pyrometallurgical and chemical process developed by Paranapanema which will produce tin metal and niobium and tantalum oxides. These will be extracted using MIBK as the solvent.

The exact details of the pyrometallurgical and chemical process are maintained as proprietary by Paranapanema. The plant is expected to be running by the end of August 1987 and will have an annual capacity of two million lb of oxides. As the ratio of Nb_2O_5/Ta_2O_5 in the concentrate is 10/1, no more than 200 000 lb Ta_2O_5 will be able to be produced. So far, no marketing plan exists for these products.

Another Brazilian company, Liarte Metalquimica, began producing niobium and tantalum oxides in 1985 at their plant near São João del Rei. Hydrofluoric acid treatment, followed by MIBK solvent extraction, is used by Liarte to convert locally-produced tantalite into oxides for the domestic cemented carbide industry. Brazilian demand is around 25 000 lb oxide per year. Now Liarte are interested in exporting oxides so production is being increased. In 1986, they produced 11 000 lb Nb_2O_5 and 15 000 lb Ta_2O_5; this year's output is expected to be around 44 000 lb Nb_2O_5 and 48 000 lb Ta_2O_5.

In 1987, Liarte began utilising a new process to upgrade "lean" concentrates, containing less than 25 % combined oxides, into higher grade material at a very low cost. The process has two steps : a fusion stage, followed by filtering with sulphuric acid. The plant also uses columbite concentrates produced by a major tin miner as a by-product; a chemicals company in São Paulo, Rohco Indústria Química, is also planning to convert this columbite into refined products — oxides in the first instance. But Liarte want to use raw material richer in tantalum rather than niobium in the future.

Most of Liarte's raw material originates from so-called "garimpeiro" production — groups of prospectors working small deposits by comparatively primitive methods. The area around São João del Rei is a major centre for this activity, but over half of Brazil's tantalite produced by garimpeiros originates from the north-east of the country, near to the port of Recife. The third important area is in Goiás state, north-west of Brasilia.

Brazilian production centres

This material is collected by large trading companies and accumulated into quantities sufficient for export. Brazil exported around 150 000 lb Ta_2O_5 in 1985 but less than 100 000 lb Ta_2O_5 last year; this year's total will be significantly lower again as many of the exporters have reduced and in some cases terminated their activities in tantalite. In the future, Brazil will probably be a major exporter of oxides rather than tantalite concentrates.

Production of NbTi superconducting materials by using NbTi powders and subsequent arc melting

This paper was presented at the T.I.C. meeting in Rio de Janeiro, June 2nd 1987, by Mr Hans-Jürgen Heinrich, Gesellschaft für Elektrometallurgie (GfE). The author is Dr Reinhard Hähn, also of GfE.

Because of their favourable superconducting characteristics and optimum workability, NbTi superconductors are preferred for magnetic fields up to 10 tesla. These superconductors are obtained by melting the pure metals in vacuum arc or electron-beam furnaces. As a result of the high vapor pressure of titanium during melting and the wide crystallization range in the niobium-titanium phase diagram, marked differences in concentration may occur along the length and across the diameter of the ingots. To produce homogeneous NbTi ingots it is necessary to have a special technique, where several melting and deforming processes take place one after the other.

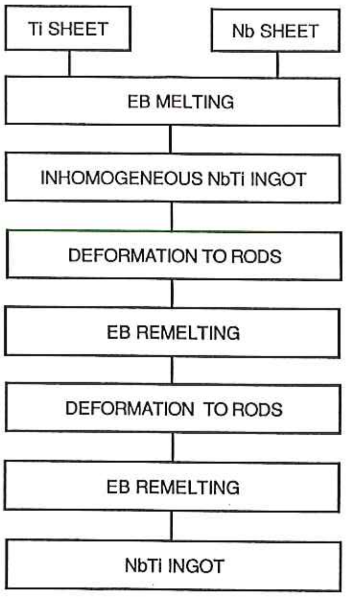
Because these types of procedures are quite cost-intensive, Gesellschaft für Elektrometallurgie (GfE) studied the possibilities of producing homogeneous NbTi ingots by a combination of melting and powder-metallurgical steps.

CONVENTIONAL PRODUCTION METHOD

NbTi alloys for superconductors are produced from high-purity, electron-beam-melted (EBM) niobium and pure titanium. Because of a high critical field strength, the NbTi alloy containing 48 wt% titanium is preferred. Usually niobium and titanium metal strips are bundled and melted several times in either the arc furnace or the electron-beam furnace, the advantage of electron-beam melting being that the final ingot has a lower oxygen content. So, for instance, when base electrodes with the same oxygen content were melted by the two alternative methods, the content of the VAR ingot was 700 ppm, whereas EB melting produced an oxygen content of only 350 ppm.

EB melting of NbTi ingots has the disadvantage that the necessary tolerance in titanium content of 2 wt% between ingot top and bottom, and a titanium content between 46 and 48.5 wt% are quite difficult to maintain and ensure.

Production of NbTi ingots by EB melting



During the first melt there is a risk with both electron-beam and vacuum arc melting that unmelted niobium particles may drop from the electrode into the melting bath. Because the melting temperature is approximately 500 °C lower than the melting temperature of niobium, it is possible that these particles will not be dissolved. Therefore, in the industrial production of NbTi superconductors, EBM ingots are deformed and remelted. The deformation of the ingot from the first melting stage produces fine filaments from the undissolved niobium particles which should then dissolve during the next melt.

PRODUCTION OF NbTi INGOTS BY GfE

The conventional production of NbTi ingots is expensive because of the homogeneity required for the material; to simplify the technology, GfE tested a different production process. This method comprises the production of high-purity NbTi alloys of different titanium contents by electron-beam melting. These alloys are then hydrided, crushed and dehydrided (HDH process). Subsequently, the desired titanium content is obtained from the various NbTi powders by simple mixing. The powder mix is isostatically pressed into electrodes which are then VAR melted to produce a homogeneous NbTi ingot.

1. Base materials and electron-beam melting

Both the superconducting properties and workability of NbTi alloys are greatly influenced by the interstitial impurities O, N and C. The content of these elements should be as low as possible so the first melt was performed in the electron-beam furnace. The required alloy compositions were NbTi 40, NbTi 50 and NbTi 60. The adjustment of a defined composition was not necessary, as the exact contents of the final alloy were adjusted by mixing the various granulate materials together. The starting materials were niobium granulate, obtained from pure ingot via the HDH process, and titanium sponge. Both these materials were available in grain sizes from 1-5 mm.

Analysis of starting materials

ELEMENT	Ti SPONGE [ppm]	Nb GRANULES [ppm]
OXYGEN	700	50
NITROGEN	< 10	< 10
HYDROGEN	100	10
CARBON	< 10	40
IRON	70	30
MAGNESIUM	< 10	< 10
SODIUM	700	< 10
CHLORINE	800	< 10

The granulate mixture was pressed into electrodes having the dimensions 80 × 80 × 800 mm. Because vaporization and spatter losses were expected during melting, a titanium surplus was added. Drip melting was used to produce an ingot with 100 mm diameter. The melting energy was between 3.6 and 4.8 kWh/kg, the melting speed between 9 and 18 kg/h. Depending on the alloy composition and thus on the melting temperature and speed, the vaporization of titanium, including spatter losses, was between 10 and 16.8 wt% titanium.

Results of EB melting

		MELTING RATE [kg/h]	MELTING TEMP. (LIQUIDUS) [°C]	CHEMICAL COMPOSITION			REL. INCREASE IN OXYGEN [%]	Ti LOSSES [%]
				Nb [wt %]	Ti [wt %]	O [wt %]		
ALLOY I	ELECTRODE	–	–	36	64	0,045	–	–
	INGOT	18	≈2100	43,2	56,7	0,058	29	10,9
ALLOY II	ELECTRODE	–	–	47	53	0,039	–	–
	INGOT	9	≈2180	55,8	44,1	0,045	15	16,8
ALLOY III	ELECTRODE	–	–	57,6	42,4	0,033	–	–
	INGOT	13	≈ 2240	64	36	0,040	21	15,1

The oxygen content of the alloys increased as the titanium content increased; this was mainly due to the higher input of titanium sponge. While melting the material in the electron-beam furnace, an increase of oxygen occurred under these conditions. The highest increase in oxygen (29 %) was observed at the highest melting speed, the lowest increase in oxygen (15 %) at the lowest melting speed; this was explained by an increased vaporization loss of titanium oxide.

After the material had been melted once in the electron-beam furnace, there were differences in concentration of up to 5.65 wt% titanium over the cross-section and along the length of the ingot.

Analysis of EBM ingot (first melt)

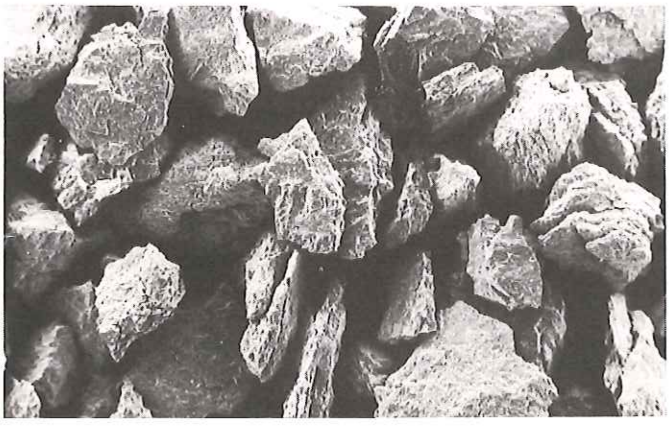
LOCATION OF SAMPLE		Nb [wt %]	Ti [wt %]	O [wt %]	N [wt %]
	○	51,6	48,2	0,030	0,002
	⊙	57,15	42,55	0,040	0,002
	○	55,9	43,7	0,046	0,002
	○	52,15	47,4	0,032	0,002
	⊙	52,85	46,8	0,032	0,002

2. Production of NbTi granulate

The NbTi granulate was obtained via the HDH process. The ingot was scarfed and etched in a $HF/HNO_3/H_2O$ mixture for 10 minutes, then hydrided in a steel vessel (Thermax) using purified hydrogen at a constant pressure of 1500 mbar and a temperature of 650 °C. The material was cooled down under H_2. Between 500 and 550 °C, heavy absorption of hydrogen took place which, depending on the material composition, was 1.5-3 wt%. The very brittle hydride was crushed under argon to less than 2 mm. The degassing was carried out at 700 °C and 10^{-3} mbar.

An SEM photograph of resulting NbTi granulate shows the grain configuration typical for HDH granules.

SEM photograph of NbTi granules (0.5-2 mm)



Analysis of NbTi granules

	Nb [wt %]	Ti [wt %]	O [wt %]	N [wt %]
GRANULES ALLOY I	43,2	56,7	0,061	0,002
GRANULES ALLOY II	55,8	44,1	0,052	0,001

3. Production of the NbTi 48 alloy in the vacuum arc furnace

As a titanium loss of 0.5-1 % occurs during melting, the granules of alloys I and II were mixed so that the titanium content of the electrode was 49 wt%.

Subsequently, the granulate mixture was pressed into electrodes of 60 mm diameter and 500 mm length. Two electrodes were welded together and melted in the vacuum arc furnace into ingots of 80 mm diameter. The melting energy was 5.0 kWh/kg, the melting pressure approximately 100 mbar.

During vacuum arc melting, the applied pressure is between 10^{-2} and 200 mbar, depending on the material used. The pressure values which have to be used for electron-beam melting are much lower, usually less then 10^{-4} mbar. When melting the material in the vacuum arc furnace, the vaporization loss of titanium is considerably reduced.

Analysis of final NbTi ingot produced by vacuum arc melting

LOCATION OF SAMPLE		Nb [wt %]	Ti [wt %]	O [wt %]	N [wt %]	HARDNESS [VHN 10]
		51,65	47,7	0,075	0,006	n.d.
		51,1	48,5	0,075	0,006	154
		51,4	48,15	0,075	0,006	156
		51,3	48,0	0,070	0,006	n.d.
		51,2	48,5	0,075	0,006	160

The titanium content of the NbTi ingot melted in the vacuum arc furnace varied only by 0.6 wt% over the 400 mm length of the ingot, and the cross-section values by approximately 0.8 wt%. The oxygen content was between 0.070 and 0.075 wt%; the content in the feed electrode was 0.055 wt%. The nitrogen content increased during the vacuum arc melting process from 20 to 60 ppm. The vaporization loss of titanium amounted to approximately 0.8 %. Consequently the produced ingot complied with the commercial requirements for NbTi superconductor materials.

DISCUSSION

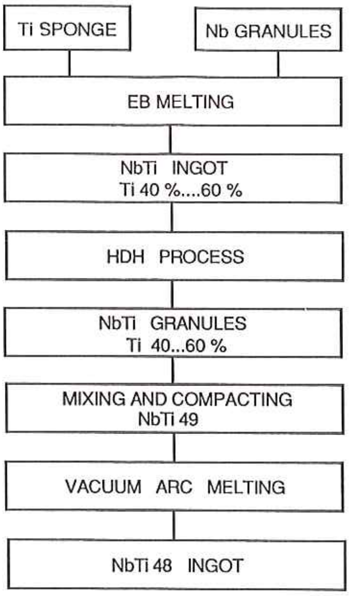
The results obtained show that the production of NbTi ingots via powder-metallurgical process steps in conjunction with EB and VAR melting offers a number of advantages.

Compared to the conventional procedure, the adjustment of a defined titanium content in the first melt is not of critical importance. This allows the use of the least expensive base materials, such as titanium sponge and niobium granulate, and it is also possible to recycle NbTi, Nb and Ti scraps to a certain extent.

As a result of electron-beam refining, the required NbTi alloys are produced with sufficiently low contents of interstitial impurities. Losses due to spattering and vaporization can be accepted in view of the low cost of the raw materials.

When homogeneous NbTi ingots are to be produced in an electron-beam furnace, the melting parameters, such as the illumination of the molten bath and the monitoring and control of the declining rate, must meet critical requirements. These parameters do not influence or affect the homogeneity of the ingots produced by GfE's process.

Production of NbTi ingots by GfE's process



In order to achieve the required homogeneity, the HDH process is being introduced in the proposed method. The process technology is state-of-the-art and can be operated without any problems. The degassed granulate can easily be pressed into electrodes.

Melting in the arc furnace is also state-of-the-art. The homogeneity of the produced ingots is comparable to that achieved by conventional processes.

Working with tantalum and columbium

This article first appeared in the 1985 Welding Issue of "The Fabricator" and was prepared from information provided by Mr Sherwood Goldstein and Mr Louis E. Huber, both of Cabot Corporation.

Equipment made from tantalum, columbium and other refractory metals probably will never be commodity items. These metals are, however, becoming increasingly common as the process industries seek greater efficiency, often going to much higher temperatures and harsher, more corrosive conditions as they do so. In many instances, only the refractory metals can provide the necessary temperature and corrosion resistance and, usually, the choice will be tantalum or columbium.

Is it worthwhile for the typical welding shop and fabricator to become familiar with tantalum and columbium ? Often, the answer is yes.

Certainly the size of the shop is not a problem : with large orders a rarity, virtually all this business is handled by custom welders/fabricators; normally, little or no expensive, special equipment is required.

It is true that making a good weld requires skill and experience with the metals. For example, the melting points are quite high : 2415 °C for columbium; 2996 °C for tantalum. Thermal conductivities are also high, so the total heat input needed for a weld can be large. These metals are extremely reactive and relatively sensitive to impurities, and so both cleanliness and an inert welding atmosphere are essential. Moreover, the thin sheets in which tantalum and columbium are often used introduce other complications.

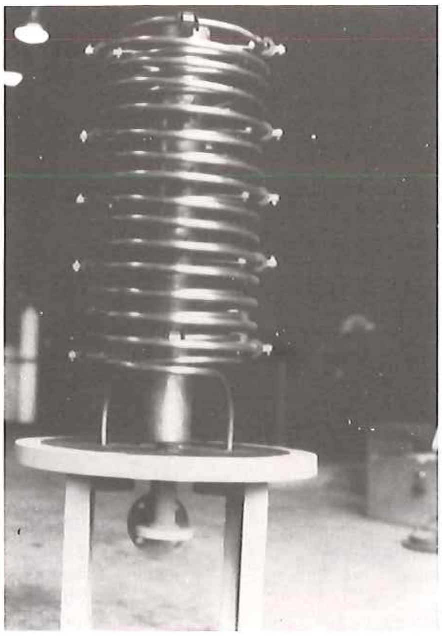
Yet, for the welder, these properties imply techniques to be learned and skills to be developed, not insuperable difficulties. Anyone who wants to learn how to weld tantalum and columbium, and get a share of the available business, can certainly do so.

GAS TUNGSTEN ARC WELDING

There are three standard methods for welding tantalum and columbium : gas tungsten arc welding (GTAW), resistance welding and electron-beam welding. Of the three methods, GTAW (also known as TIG — tungsten inert gas) is by far the most common.

Successful GTAW of tantalum and columbium rests on a single foundation : the weld must be clean. This not only means that all surface contamination must be removed before welding, but that air, which reacts readily with the molten metal, must be strictly excluded from the weld area.

Tantalum coil heat exchanger. Tantalum's high heat conduction and resistance to corrosion and biofouling make it an attractive choice for heat exchangers.



A new metal surface can be adequately cleaned with any of a variety of solvents that leave no residue. For example, acetone would be ideal if its vapors did not form explosive mixtures with air, as Bill Maguire of Special Metals, Houston, Texas, points out. But since it does, the most common choices include trichloroethane, methyl alcohol, methyl ethyl ketone and various proprietary "safety solvents". Each of these has its own drawbacks, and so the best choice for each shop is a matter of judgement. Weld repairs, or any weld on a piece that has seen service, pose a more difficult cleaning problem; precisely what is needed will depend on the condition of the individual piece. In general, cleaning begins with a thorough wire brushing. The next step is usually etching to remove accumulated oxides; Maguire recommends an etching mixture that is one-third water, slightly over a half sulfuric acid, and the remainder nitric and hydrofluoric acids, but he notes, however, that each welding contractor usually develops his own etching solution. Any remaining visible contamination is then removed with a plastic scouring pad. Finally, the piece is degreased with the same non-residue solvent used for new metal. It is then ready for welding.

As a rule, GTA Welding of tantalum or columbium requires that the workpiece be totally enclosed in an inert atmosphere, usually argon. A simple inert-gas purge provided by trailing cup shields and backing bars, such as is often used for titanium and nickel-base alloys, is not recommended for the refractory metals. Purges sometimes can be used for small (one-half inch) welds, according to Maguire. But when even the slightest intrusion of air can ruin the weld, the risk that the entire weld will have to be ripped out and done again is too great for longer seams. Totally enclosing the workpiece, however, does not require a permanent, dedicated installation as many shops find that inflatable vinyl enclosures are adequate. These enclosures come in many sizes ranging from three-foot glove boxes to tents several feet square. Whether an inflatable or a permanent enclosure is used, it is customary first to evacuate all the air. The enclosure can then be backfilled with inert gas without extensive and expensive purging.

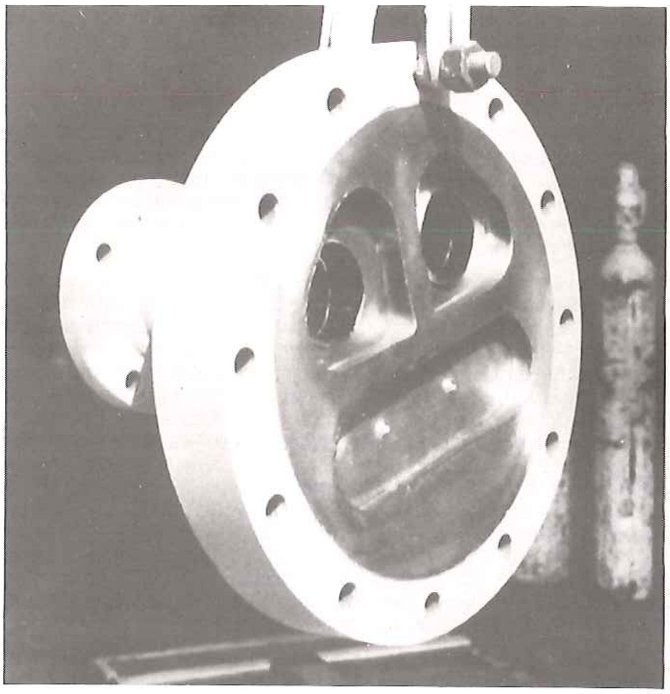
GOOD FIT ESSENTIAL

Some of the difficulties in welding tantalum and columbium arise not from their reactivity, but from the fact that they are commonly used as very thin (0.010 to 0.016 inch) sheets. Such thin pieces require an exceptionally good fit if they are to be welded successfully as even a slight gap (one that might be acceptable when welding thicker pieces) will make it impossible to heat one piece adequately without vaporizing the other. As a result, the gap will grow wider, and welding will become hopeless.

Use of thin sheets also makes it both possible and desirable to fabricate using end welds rather than butt or fillet welds. For example, shell-and-tube heat exchangers are normally fabricated by drawing out the shell flanges at least one-quarter inch over the tubes. These flanges can be welded to the tubes without fear of melting the shell.

Welding thick-section pieces of tantalum or columbium, such as spray nozzles, requires a great deal of heat. Since these metals also exhibit outstanding thermal conductivity, areas many inches from the weld zone can become quite hot. Inexperienced welders have burned themselves badly because they failed to appreciate this fact.

Head for a heat exchanger lined with tantalum



RESISTANCE WELDING

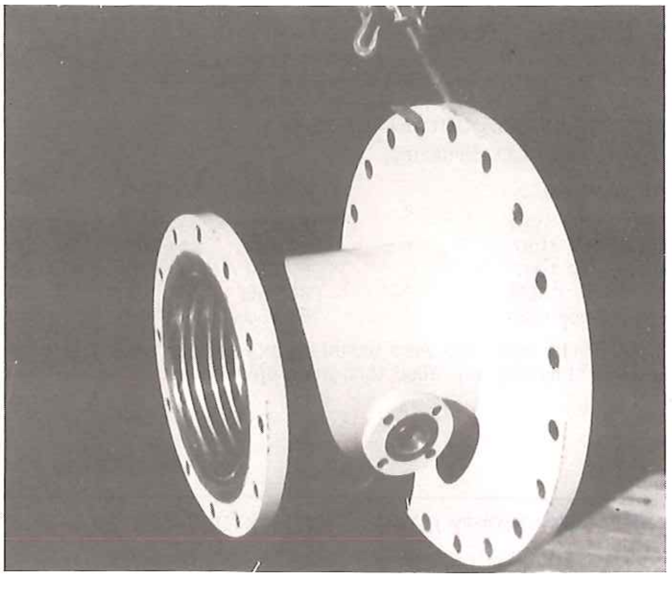
Despite their high melting temperatures, tantalum and columbium can be successfully resistance welded. Factors requiring careful attention include cleanliness protection from the air and current density. Most of the required techniques are considered proprietary by the relatively few shops that do resistance welding.

ELECTRON-BEAM WELDING

In electron-beam welding, the workpiece may be either in a vacuum chamber with the electron gun or outside the chamber in a suitable protective atmosphere. Atmospheric welding allows welding of larger pieces, but scattering of the beam renders the weld broader and shallower than would be the case with vacuum welding. Even so, such welds are narrower and deeper (up to three-quarter inch) than those obtained with other methods. Vacuum electron-beam welds can be up to five inches deep.

Other welding methods pose certain difficulties with deep welds of high-melting-point metals such as tantalum and columbium. Electron-beam welding is therefore commonly used for thick sections of these metals. It also offers some advantage with very thin sections,

Tantalum-lined spool piece (two foot by four foot)



where the narrow weld zone reduces the chance of distorting the workpiece.

Electron-beam welding of tantalum and columbium does not normally introduce major complications.

WELDING AND FABRICATING CLAD MATERIALS

An attractive way to get around the high cost and relatively low strength of tantalum and columbium is to use them as cladding materials for lower-cost, higher-strength materials such as steel. Their high melting temperatures render traditional weld overlays impossible; fortunately, their ductility makes an alternative process possible : explosion bonding.

In the best-known process of this type, Du Pont's "Detaclad" process, a sheet of tantalum is positioned above a thin copper sheet which, in turn, lies above a steel backer plate. All three are slightly separated. A specially-formulated explosive is then placed on the outer surface of the tantalum sheet. On ignition, the explosion propagates across the surface of the upper sheet, and the force it generates bends the sheet under the instantaneous reaction area. The tantalum travels across the "stand-off" space and collides with the copper sheet, where the force of the impact is sufficient to form a true metallurgical bond between the metal surfaces. Transmittal of the impact force to the copper similarly drives it across the second stand-off space to form a metallurgical bond with the steel backer plate. Since the surfaces have been scoured clean by a mist of metal particles emitting from the point of impact, and since bonding is accomplished too quickly for brittle intermetallic compounds to form, the resulting bond is clean, ductile and defect-free.

Forming of the explosion-bonded plates is carried out by conventional methods. However, since tantalum flows more readily than steel, press-forming is usually preferred to rolling. In any operation, special care should be taken to avoid marring the relatively soft tantalum surface.

When plates are to be heat-cut, the tantalum and copper first must be removed from the cutting area. This prevents formation of brittle tantalum-iron intermetallic compounds with poor corrosion resistance.

Plates are joined by a "batten-strip" method, patented by Nooter Corporation, which also governs the tantalum-copper thickness relationship. This method starts by removing the tantalum and copper from the area immediately adjacent to the joint. The steel is then welded by any usual method. Next, a copper inlay is used to build up the area from which the cladding has been removed. Finally, a tantalum batten strip is placed over the inlay and adjacent clad areas and welded to the cladding with a fillet weld. The copper sheet is essential to the success of this tantalum-tantalum weld. Without it, the heat required to weld tantalum would be more than enough to melt also the underlying steel. Even if the tantalum were thick enough to prevent liquid steel from erupting through the weld zone, brittle intermetallic compounds at the tantalum-steel boundary would still cause the material to fail common bend tests. The high thermal conductivity of copper, however, carries excess heat rapidly away from the weld zone. The tantalum batten strip thus can be welded to the cladding by any standard tantalum-tantalum welding method, and fabrication of complex equipment from explosively-bonded material becomes relatively straightforward.

To be completed in bulletin nº 52.

T.I.C. statistics

Price Waterhouse report the following statistics :

QUARTERLY PRODUCTION ESTIMATES

(quoted in lb Ta_2O_5 contained)

MB quotation :	*US $30*	*US $40*	*US $50*
2nd quarter 1987	257 750	334 700	462 800
3rd quarter 1987	257 750	344 700	462 800
4th quarter 1987	257 750	344 700	492 800
1st quarter 1988	285 750	372 700	520 800
2nd quarter 1988	285 750	392 700	540 800

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 1987

Material grade	*Production*	*Shipments*
Tin slag (over 2 % Ta_2O_5)	116 797	58 593
Tantalite (all grades)	42 223	29 404
Other materials	0	0
Total	159 020	87 997

Note : The response from the companies asked to report was 15/16 and included these producers :

Datuk Keramat Smelting
Greenbushes
Malaysia Smelting
Metallurg Group
Tantalum Mining Corporation of Canada
Thailand Smelting and Refining

PROCESSORS' SHIPMENTS

1st quarter 1987

Product category	*lb Ta contained*	*lb Ta_2O_5 equivalent*
Tantalum oxide/K_2TaF_7	24 436	32 988
Alloy additive	49 441	66 745
Carbide	105 579	142 532
Powder/anodes	211 908	286 076
Mill products	74 082	100 011
Scrap, ingot, unworked metal and other	11 503	15 529
Total	476 949	643 881

Notes :

1. The response from the companies asked to report was 15/17 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
2. Reports were made in lb tantalum contained.

Capacitor statistics

EUROPEAN TANTALUM CAPACITOR SHIPMENTS

(thousands of units)

1st quarter 1987 139 947

(Data from ECTSP — shipments from European manufacturers to European-located consumers only.)

JAPANESE TANTALUM CAPACITOR PRODUCTION AND EXPORTS

(thousands of units)

	Production	*Of this, exports*
1st quarter 1987	652 861	159 468

(Data from JEIDA)

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PRINTED BY PUVREZ, avenue Fonsny 59, 1060 Brussels.