TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

BULLETIN No. 56 DECEMBER 1988 FOURTH QUARTER

Tanco restarts production of tantalite

The information for this article was obtained from "The return of Tanco" (Metal Bulletin Monthly, April 1988) and from company literature.

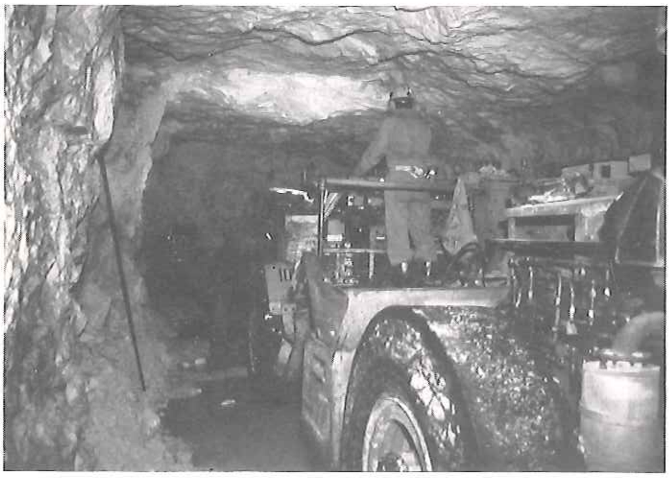
In August 1988, the Bernic Lake mine of Tantalum Mining Corporation of Canada Ltd. (normally abbreviated to "Tanco") restarted production of tantalite concentrates after a six-year suspension, enforced by the poor market conditions for tantalite. Tanco's pegmatite ore deposit is located underneath Bernic Lake, Manitoba province (Canada), 180 km north-east of Winnipeg.

The current operations at Bernic Lake date from 1967, although mining activity (not for tantalum) was recorded as early as 1930. The original interest in the Bernic Lake pegmatite was due to its lithium content. When demand for tantalum began to increase during the mid-1960's, earlier data collected from studies on the pegmatite were re-examined and development of the mine for its tantalum potential commenced in spring 1967. The corporation was formed in November of the same year. A full-scale gravity concentration plant began operating two years later.

Since 1978, Tanco has been owned by: Hudson Bay Mining & Smelting Co. Ltd. — 37.5 %; Cabot Corporation — 37.5 %; and the Manitoba government — 25 %.

Tantalite production was almost continuous during the 1970's. Adverse market conditions necessitated a closure for a period during 1973-74 and again in 1982. Annual production remained at around 350 000 lb Ta_2O_5 between 1974 and 1982 : lower grades of ore being mined were offset by increased tonnage throughput. Future capacity will be around 240 000 lb Ta_2O_5; immediate reserves are sufficient for eight years' tantalum production.

Underground workings at Bernic Lake

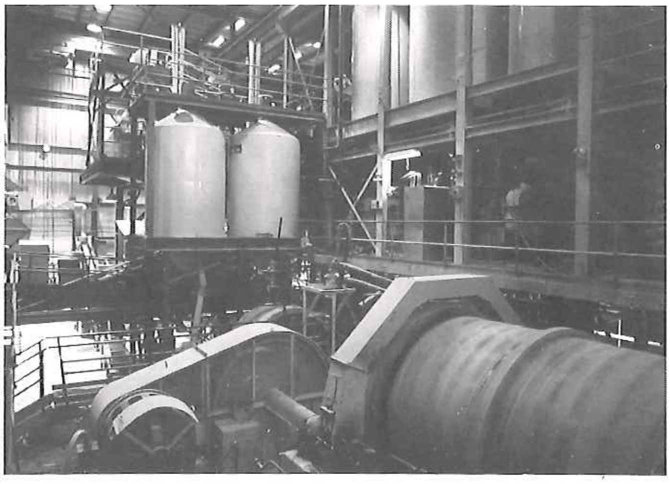


Since the last closure in 1982, the mine has become a significant producer of lithium ore (spodumene) concentrates. A pilot plant was installed in 1984 and produced a few hundred tonnes of spodumene in that year. Since then, output has been increased to some 15 000 tonnes a year. Milling of the ore has been taking place on equipment previously used for tantalum, so additional processing equipment was necessary so that the two circuits could run independently of each other. Spodumene reserves are adequate for production well into the next century.

A total of C$ 4.7 million (about US$ 3.9 million) has been spent on refurbishing the mine and mill infrastructure, including : an overhaul of the sand plant and slime plant; changing the shaft to mine two different ores at the same time; completion of the spodumene mill at the site (including a primary grinding circuit); and upgrading power and water services.

Mining is by a "room and pillar" plan with 15 metre wide rooms and 7.7 metre square pillars. The average room heights are 15-20 metres with some as high as 45 metres. This mining method allows for up to 89 % extraction.

Ore grinding



Concentration on shaking tables

Before 1982, Tanco's concentration plant processed about 175 000 tonnes of fresh ore per year, plus another 75 000 tonnes of tailings during the summer months. After the ore is ground in a ball mill, it is separated into different particle sizes by cyclones and vibrating screens. Concentration takes place on spirals, shaking tables and other fine gravity concentration equipment. Flotation of tantalite was attempted prior to the 1982 closure, but the plant will return to an all-gravity system upon restart. The grade of the final tantalite concentrate exceeds 35 % Ta_2O_5.

The decision to restart tantalite production was made in October 1987 following a number of new long-term contracts with deliveries due to start late this year.

T.I.C. statistics

QUARTERLY PRODUCTION ESTIMATES

(quoted in lb Ta_2O_5 contained)

MB quotation :	*US $ 30*	*US $ 40*	*US $ 50*
3rd quarter 1988	240 300	335 800	396 800
4th quarter 1988	237 300	353 800	401 800
1st quarter 1989	237 300	366 800	401 800
2nd quarter 1989	240 300	368 800	416 800
3rd quarter 1989	240 300	368 800	416 800

Note : The quarterly production estimates are based on information available, and do not necessarily reflect total world production.

PRODUCTION AND SHIPMENTS

(quoted in lb Ta_2O_5 contained)

2nd quarter 1988

Material grade	*Production*	*Shipments*
Tin slag (over 2 % Ta_2O_5)	224 010	330 231
Tantalite, other materials	400 530	169 273
Total	624 540	499 504

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

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

PROCESSORS' SHIPMENTS

2nd quarter 1988

Product category	*lb Ta contained*	*lb Ta_2O_5 equivalent*
Tantalum oxide, K-salt	27 442	37 047
Alloy additive	37 811	51 045
Carbide	167 768	226 487
Powder, anodes	269 567	363 915
Mill products	102 001	137 701
Scrap	4 334	5 851
Ingot, unworked metal, other	9 791	13 218
Total	618 714	835 264

Notes :

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

Capacitor statistics

EUROPEAN TANTALUM CAPACITOR SHIPMENTS

(thousands of units)

2nd quarter 1988	186 699

(Data from ECTSP)

JAPANESE TANTALUM CAPACITOR PRODUCTION AND EXPORTS

(thousands of units)

	Production	*Of this, exports*
2nd quarter 1988	862 271	254 730

(Data from JEIDA)

U.S. TANTALUM CAPACITOR SALES

(thousands of units)

2nd quarter 1988	*U.S. shipments*	*Exports*	*Total*
Foil	268	11	279
Metal-cased	31 692	9 850	41 542
Molded	104 856	16 864	121 720
Dipped	94 915	26 577	121 492
Chips	37 878	10 176	48 054
Wet slug	2 450	259	2 709
Total	272 059	63 737	335 796

(Data from EIA)

WORLD TANTALUM CAPACITOR SHIPMENTS

(millions of units)

1st quarter 1988	1317.8
2nd quarter 1988	1351.2

(Data compiled by combining regional and export data)

President's letter

As a major event for everybody involved in tantalum and niobium, the second international conference on these elements, the "International Symposium on Tantalum and Niobium", will take place a few days after this Bulletin is printed. At this stage I can say that the programme looks excellent and as informative as all of us expect it to be.

I think it is also the right time to review the T.I.C.'s performance in distributing information, collecting statistics, organizing our meetings and answering all sorts of questions from all over the world. A survey of producers and processors has been prepared and published and will be updated once a year. Our staff in Brussels has put a great deal of effort and time into the preparation of the Symposium, in addition to maintaining the routine work, and there will still be a lot to do after the meeting to publish the Proceedings and complete the work thoroughly.

But I should like to ask all of you to think how the T.I.C. can improve its services to the members and how it can promote tantalum and niobium even more efficiently.

Your suggestions are highly appreciated and will be discussed in Orlando, as well as during the following weeks.

H-J. Heinrich
President

An update of tantalum raw materials supply and availability

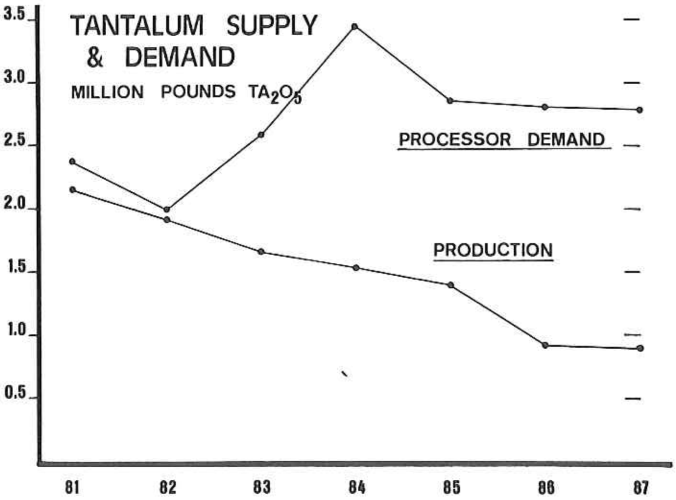
Prices for tantalum ore concentrates have risen significantly in recent months and are now almost double the level of one year ago, according to the *Metal Bulletin* tantalite quotation. A positive effect of these price rises has been to encourage tantalite miners to increase or even to re-start their production.

"Metal Bulletin" tantalite prices (25/40 % basis), U.S. dollars per lb Ta_2O_5 : annual ranges since 1982 and this year's increases

1982	20.00-38.00
1983	20.00-35.00
1984	25.00-33.00
1985	20.00-33.00
1986	17.00-26.00
1987	18.00-28.00
March 17 1988	28.00-30.00
March 28 1988	30.00-34.00
May 9 1988	32.00-36.00
June 20 1988	34.00-38.00
July 7 1988	37.00-42.00
August 1 1988	38.00-43.00
August 4 1988	40.00-45.00
September 8 1988	43.00-45.00
October 13 1988	47.00-50.00
November 17 1988	47.00-51.00

THE IMBALANCE IN SUPPLY AND DEMAND

Raw materials supply and demand have been out of balance since 1982. Around the time of the price increases of 1979-80, when the *Metal Bulletin* quote peaked at $ 120.00 per lb Ta_2O_5 in mid-1980, the tantalum processors accumulated large inventories of raw material as a defensive measure against perceived shortages. These processor inventories depressed tantalite demand and prices for some years afterwards, but now appear to have been run down to more usual levels, judging by the increased activity in the market this year.



Tantalum supply has several components, but overall has a strong tin association : first, tantalite concentrates, often but not always co-produced with tin concentrates; second, by-product slag from tin smelters, containing significant grades of tantalum; finally, metal and carbide scraps, which are re-introduced into the raw materials stream to displace between 10 % and 20 % of processor requirements (not included in the supply data).

Tantalum supply from slag and concentrates, thousand lb Ta_2O_5

	Slag	*Concentrates*	*Total*
1981	1228.2	926.2	2154.4
1982	1210.1	685.8	1895.9
1983	1280.3	368.8	1649.1
1984	1010.4	509.9	1520.3
1985	1071.0	323.4	1394.4
1986	760.5	135.4	895.9
1987	662.8	222.8	885.6

Demand for raw materials, equivalent to processor shipments of refined products, increased by over 30 % a year from 1982 to 1984. Tantalite production was also up in 1984 due to slightly higher prices. This "boom" period for the industry was short-lived, however : processor demand was down by 17 % in 1985, causing tantalite prices to fall. Production was cut back again in 1985 due to the downturn in the tantalite market. Total output, according to T.I.C. data, was less than one million lb Ta_2O_5 a year in 1986 and 1987. But the production data for this year should show a significant increase.

EFFECT OF THE TIN MARKET

Apart from raw material inventories, the major factor to influence tantalum supply in the 1980's has been the tin market : tantalum comes extensively as a co- or by-product of tin production. Before October 1985, the tin price was sustained at an artificially high level by the International Tin Council (ITC), an organisation founded by the governments of most tin-producing and tin-consuming countries. The ITC supported the tin price by export controls on producer countries and buying tin on the London Metal Exchange. These purchases were halted on October 24th 1985 by the onset of the "tin crisis". The price began to fall, curtailing tin mining and smelting almost universally. Western world production of tin concentrates fell from 157 840 tonnes Sn in 1985 to 138 850 tonnes in 1986 and 134 000 tonnes (estimated) last year. Outputs have been declining since at least 1981; the "tin crisis" just accelerated this decline.

Tin-in-concentrate production, tonnes

	1981	*1985*	*1986*	*1987 (est.)*
African countries	7 573	5 168	4 016	4 160
Australia	12 925	6 934	8 470	7 640
Bolivia	29 830	16 136	10 479	4 100
Brazil	8 297	26 514	25 449	26 000
Indonesia	35 268	21 758	24 634	27 405
Malaysia	59 938	36 884	29 134	30 545
Thailand	31 474	16 593	16 792	13 500
Other	19 280	27 853	19 876	20 650
Total	204 585	157 840	138 850	134 000

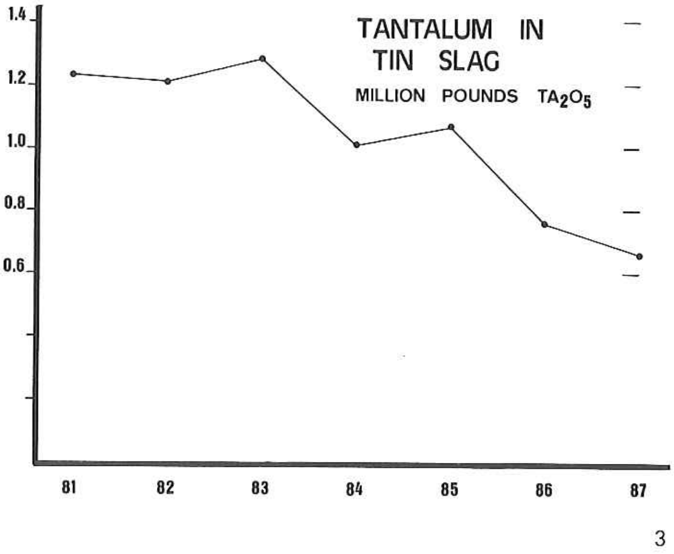
It is important to note that not all tin production has an associated tantalum output, although the regional data can often indicate the local trend for tantalum production. Tin ore in Bolivia, Indonesia and the "other" countries has no significant tantalum content.

As a result of the lower prices for tin, tantalum production in slag fell from 1.07 million lb Ta_2O_5 in 1985 to 0.76 million lb in 1986 and 0.66 million lb last year. From 1981 to 1985, this production always exceeded one million lb Ta_2O_5 annually, so slag is an important raw material for tantalum processors. Most Ta_2O_5-containing slag is produced by smelters in Malaysia and Thailand, and tin mining in these countries has been among the worst affected anywhere.

Estimates of tantalum production (all forms : slag and concentrates) by region, thousand lb Ta_2O_5

	1985	*1986*
Africa	200	100
Australia	200	150
Brazil	350	300
Canada	nil	nil
South-east Asia	800	500
Total	1550	1050

Total production from slag and concentrates was down in 1986 from all sources, mostly due to the dramatic downturn in the tin market, but the tantalum market also worsened. Last year, the total quantity produced was comparable to that in 1986 : increased tantalite output was offset by a further fall in slag.



Tantalum grades in tin slag vary depending on the source and determine whether or not the slag is economic to process. Material over about 10 % Ta_2O_5 can be used as a direct feed for acid digestion, whereas slag less than 10 % Ta_2O_5 must first be upgraded into so-called "synthetic concentrates". This type of processing is only economic when the tantalite price exceeds the combined cost of the slag and of the upgrading process. The upgrading cost tends to increase with lower grades of slag.

Ten smelters have significant grades of tantalum in their slag : Datuk Keramat Smelting and Malaysia Smelting (Malaysia), Mamore (Brazil), Thaisarco (Thailand), Iscor (South Africa), Kamativi (Zimbabwe), Makeri Smelting (Nigeria), Greenbushes (Australia), and Mibra and Fluminense (Brazil), both owned by Cia. de Estanho Minas Brasil.

Most of the slag from the first three smelters is under 3 % Ta_2O_5 and so requires high tantalite prices to make upgrading into synthetic concentrates economic. At the low throughput of tin concentrates which the two Malaysian smelters are experiencing, it is not convenient to smelt several batches together, which are high in tantalum, to produce a higher grade of slag. At the end of 1986, Malaysian slag production was running at just over 100 000 lb Ta_2O_5 a year, almost half of the previous quantity.

The Thaisarco smelter has historically been the major source of high-grade slag, i.e. over 10 % : production peaked during 1979-80 at about 850 000 lb Ta_2O_5 a year, but has been declining more or less continuously ever since. In 1981 and 1982, about 750 000 lb and 650 000 lb Ta_2O_5 were produced, respectively. By 1987, Thai tin concentrate output had almost halved compared to 1982. Recently, the slag grade has been increased to 17 % Ta_2O_5.

Slag from the three African smelters is generally higher grade than the Malaysian material. Iscor produces 50-55 000 lb Ta_2O_5 a year in slag with an average grade of 6 % Ta_2O_5. Kamativi produced about 80 000 lb Ta_2O_5 last year in slag with an average grade of 9 % Ta_2O_5. Makeri's output has been very low over the past few years, because Nigerian tin concentrate production has been devastated by the lower prices. The average grade of Makeri's slag was 4 % Ta_2O_5. These slags still have to be upgraded before chemical processing, but are economic to use at a lower tantalite price than the Malaysian slags.

The major activity of Greenbushes and Cia. de Estanho Minas Brasil is mining tin-tantalum ores rather than tin smelting. In world terms, their plants are small-scale and primarily smelt the companies' own tin concentrates. By taking special measures, the slag from these smelters is upgraded to over 25 % Ta_2O_5. The quantity of concentrates smelted at Greenbushes has declined since 1985, and slag output is currently about 50 000 lb Ta_2O_5 a year, a reduction of 25 % from two years ago.

Tin consumption is currently estimated at just over 150 000 tonnes a year, so supply and demand were close to being in balance in 1985. According to one estimate, stocks have been run down from over 100 000 tonnes at the end of 1985 to around 40 000 tonnes currently. Tin mining in Malaysia and Thailand does not seem likely to gain much from any future upturn in the market due to its high-cost nature; sources elsewhere will probably benefit instead. Tantalum production in tin slag, therefore, is unlikely to exceed one million lb Ta_2O_5 a year again for some years to come.

TANTALITE CONCENTRATE PRODUCTION

The price increases for tantalite will stimulate extra production in 1988. There will be a delay, however, before the tantalite producers can utilise fully their available capacities, and tantalum has a long "supply line" compared to other metals due to the dispersed and small-scale nature of many sources.

No accurate data on processor inventories exist, but these are thought to consist largely of low-grade slag. As discussed previously, this material will only be economic to use when tantalite prices reach a certain level, depending on the grade of the slag. Material under 2 % Ta_2O_5 is discounted from T.I.C. production statistics as it is very unlikely to be economic to use in the future.

The two largest tantalite miners in terms of capacity are Greenbushes (Australia) and Tanco (Canada) : both have indicated that they will produce significant quantities of material over the next few years. Other sources for tantalite exist in Brazil, China, several African countries and Thailand. Potential sources will need a period of stable prices to be developed.

Greenbushes Ltd., the tantalite miner in Western Australia, produced 204 000 lb Ta_2O_5 from alluvials in the year to June 1988. The company intends to shift production emphasis from soft-rock to hard-rock, open-cut mining in the future.

Greenbushes' proposed production schedule (thousand lb Ta_2O_5)

	Year ending June			
	1989	*1990*	*1991*	*1992*
Soft rock	250	250	250	250
Tailings	50	100	140	140
Hard rock	—	90	250	250
Total	300	440	640	640

Tantalum Mining Corporation of Canada (Tanco) began producing tantalite again this year after a six-year suspension (see article in this issue of the "Bulletin"). The mine can produce 240 000 lb Ta_2O_5 a year, a lower capacity than before 1982.

Thailand is a significant source of tantalite, coming as a tin-mining co-product, and of struverite, another tantalum raw material produced by the further treatment of tin-mining waste (amang). Government statistics showed a marked increase in production of both these minerals last year : the bulk quantity of tantalite-columbite was 183 tonnes, compared to 121 tonnes in 1986 and 432 tonnes in 1985; struverite production was 423 tonnes in 1987, compared to 241 tonnes in 1986. Tantalite concentrates normally assay over 25 % Ta_2O_5, struverite concentrates at about 10-15 % Ta_2O_5. Tantalite output in 1986 was less than one-third of the 1985 level, according to these data : therefore it is apparent that Thailand has lost much of its previous importance as a tantalite producer, despite the increase noted last year. Amang is also processed in Malaysia to produce struverite, but there is no tantalite output from Malaysian tin mines due to the lower ore grades of tantalum.

African sources for tantalum-containing concentrates have included : Mozambique, Namibia/S.W. Africa, Nigeria, Zaire and Zimbabwe.

Minas Gerais de Mozambique produces microlite, a tantalum ore concentrate with no tin association. Little is known about its production, but most is believed to be shipped to Eastern Bloc countries.

Production in Namibia is centred at a region known as Tantalite Valley. In recent years, there has been only one producer, a small tin mine with an output of a few thousand lb Ta_2O_5 a year. There is interest in starting up other tantalite productions again, but these are likely to be on a small scale.

Columbite is produced in Nigeria as a tin-mining by-product and contains over 60 % Nb_2O_5 and only 6-7 % Ta_2O_5 : current output is very much lower than previously due to the fall in tin prices after 1985. In any case, columbite is not so attractive to process due to the lower prices for refined niobium oxide since 1981.

Tin-tantalum mining in Zaire is of a small-scale, high-cost nature and hence was badly affected after 1985. Tantalite output fell to about 30 000 lb Ta_2O_5 in 1986, one-third of the previous level. Production has been declining ever since due largely to internal rather than market factors. The improvement in the tantalite market is unlikely to reverse this trend.

Kamativi Tin Mines Ltd., by far the major producer in Zimbabwe, has a small tantalite concentrate output which uses a stockpiled residue as its source. By 1989, however, Kamativi intends to be producing about 60 000 lb Ta_2O_5 a year in concentrates. Currently, most of Kamativi's tantalum output is contained in tin slag.

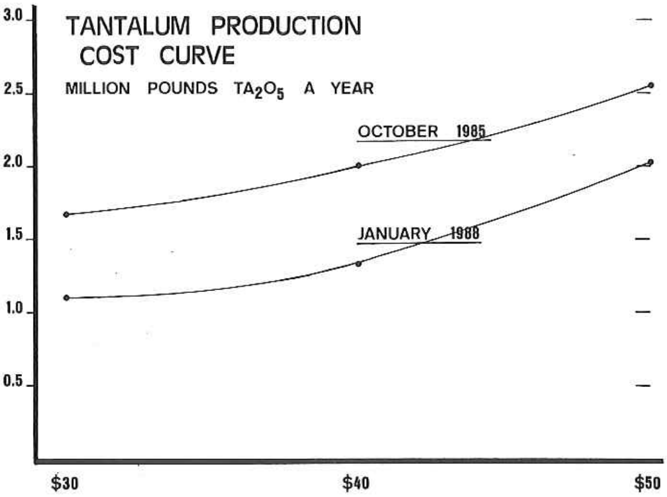
Tantalite production in Brazil is centred in several specific regions and has been at a low level over the past few years. Cia. de Estanho Minas Brasil has historically been the major producer, but its output is primarily shipped to other Metallurg companies for conversion into refined products. This year, Paranapanema began to produce niobium and tantalum oxides as a tin by-product : its plant's annual capacity is two million lb of oxides, according to the company, of which less than 200 000 lb is tantalum oxide. Elsewhere, tantalite is produced by small groups of prospectors using comparatively basic mining techniques. In 1987, total Brazilian tantalite exports were about 40 000 lb Ta_2O_5, less than half of the previous year's quantity. However, it has been reported that there is increased activity this year due to the higher prices.

China has a potential production base of several hundred thousand lb Ta_2O_5 a year, but most tantalite produced is shipped to domestic processors rather than abroad. At least two tantalite mines are known to exist in China — Limu and Yichun — but there are thought to be others. However, the quantities currently being exported are low : it seems that the Chinese are having difficulty in increasing tantalite production or even maintaining it at previous levels.

Another effect of the higher tantalite prices, besides increasing production from existing sources, will hopefully be to encourage source development. For example, there is reported interest in exploiting tin-tantalum ores in south-west Venezuela. Apart from the Greenbushes mine, a number of potential producers exists in Australia : Goldrim Mining began production in 1988, and next year it may be joined by Pilgan Mining and the Bayer-Greenbushes Bynoe joint venture. The combined output of these new operations could exceed 100 000 lb Ta_2O_5. Pancontinental Mining may also start tantalite production next year : the intended output is 150 000 lb Ta_2O_5 annually.

COST OF PRODUCTION

The T.I.C. has been publishing estimates of future tantalum production from all known sources — tin slag, concentrates etc. — for one year ahead at price scenarios of $ 30, $ 40 and $ 50 per lb Ta_2O_5. The estimates are obtained from individuals knowledgeable about tantalum production in each significant region of the world. Two sets of data are contrasted : those made in October 1985 — immediately before the "tin crisis" — and those made in January 1988 — just over two years later. Obviously, at higher tantalite prices, production increases because more sources become economic.



This chart shows that 0.6 million lb Ta_2O_5 of potential output has been lost from two years ago. As this does not appear to be price-related as it occurred at all price levels, most was probably in by-product tin slag.

SUMMARY

Less tin-associated production of tantalum after 1985 : the effect on tantalite prices during the two years after was negligible, because demand for tantalum raw materials was low.

More tantalite output both in 1988 and 1989 : increases are likely to occur in Australia, Brazil and Canada rather than in African and S.E. Asian countries.

LITERATURE

"Production of tantalum-containing slags at Thaisarco", J.R. Lay, T.I.C. Bulletin No. 35 (September 1983).

"The influence of recent developments in tin on present and future tantalum supply", A. Jones, T.I.C. Bulletin No. 49 (January 1987).

Greenbushes Ltd. Annual Report 1988.

Andrew Jones
Technical Officer

Ceramic capacitors containing niobium and tantalum oxides

A relatively new type of ceramic dielectric for electronic capacitors being developed and marketed worldwide contains niobium oxide : the widespread adoption of this dielectric, which is based on lead oxide, could increase demand for extra-purity (99.9 %) niobium oxide significantly within the next two to three years.

Ceramic-grade niobium and tantalum oxides are used to a limited extent in conventional dielectrics, principally barium titanate-based compositions, to control grain growth and modify electrical characteristics. Contents vary from one to five per cent. Total usage of barium titanate is probably declining due to improvements in material utilisation, analogous to the trend towards smaller-sized tantalum capacitor anodes because of the introduction of high-charge powders. So although the market for multi-layer ceramic capacitors (MLC's) is increasing by 25-30 % a year, the market for niobium/tantalum oxides in conventional dielectrics could be said to have matured. In any case, tantalum oxide is not generally favoured because of its high cost compared to alternatives, notably niobium oxide; its use is essentially confined to high firing temperature compositions. Niobium oxide has also been added to dielectrics based on strontium titanate since the late 1970's, primarily by a Japanese manufacturer, Taiyo Yuden. Worldwide current usage of ceramic-grade niobium oxide probably does not exceed 70 tonnes Nb_2O_5, around half of which is consumed in Japan. The market for ceramic-grade tantalum oxide is at least an order of magnitude less.

MLC's are essentially composed of very thin (20-25 μm) ceramic layers interleaved with precious metal electrode layers. This formulation is pressed and sintered to produce a compact and volumetrically efficient capacitor dielectric, which the forms the basis of the MLC device. Around 30 % of the total capacitor market is held by MLC's, and their growth rate (25-30 % a year) is much higher than that of the total capacitor market. Their volumetric efficiency is suited to surface mounting, a rapidly evolving assembly technique. Also, MLC's are capturing markets previously held by ceramic disc capacitors.

Dielectrics based on lead oxide, containing between 5 and 25 % Nb_2O_5 as well as other additives, are apparently capable of taking at least 20-25 % of the total MLC market. Their major advantage is their volumetric efficiency due to the high niobate dielectric constant. Already at least three manufacturers, Kemet Electronics, NEC and Toshiba/Marcon, have niobate MLC's on the market, and Tam Ceramics offers niobate dielectric powders. The effect on consumption of ceramic-grade niobium oxide is very difficult to determine with estimates varying considerably, but it seems that the current demand level of under 70 tonnes Nb_2O_5 a year could increase several times over within the next three to five years.

Within the overall MLC growth rate of 25-30 % a year, there are several internal trends. First, niobate MLC's primarily cover "Z5U-type" characteristics, one of the three basic capacitor types : the proportion of the MLC market accounted for by Z5U-type devices will probably decline from 45 % today to around 30 % in 1992, which is a negative trend for niobate MLC's. Second, the cost competitiveness of niobates is achieved mainly in large-sized MLC's over 1 μF : requirements for these components may grow at a faster rate than the overall MLC market as they take over applications from other capacitor types, which is a positive trend for niobate MLC's. The use of lead oxide in these dielectrics may impose worker/environmental safety considerations on manufacturers, but it is too early to say whether this will prove a significant impediment to the development of this market.

Niobium and tantalum oxides used for ceramic capacitor applications have extra-purity requirements, nominally 99.9 %. The actual specification depends on the formulation in which the oxide is used, but impurities not compatible with existing phases in the dielectric composition should not usually exceed 500 ppm (0.05 %). The dielectric powder for pressing and sintering is prepared by calcining. A recently developed niobate powder is prepared in three stages : calcining magnesium oxide and niobium oxide at 1050 °C; mixing the crushed MgO/Nb_2O_5 with lead oxide, then calcining at 700 °C; finally, mixing this composition with other additives and calcining at 700 °C.

LITERATURE

1. J.H. Alexander, D.A. Jackson, E.L. Bush; "The preparation and properties of relaxor multi-layer capacitors"; IEEE Transactions, Vol. 9, No. 4 (Dec. 1986).
2. M. Baker; "Capacitor technologies compared"; "Electronics and wireless world" (July 1987).

Andrew Jones
Technical Officer

Niobic acid as an unusual acidic solid material

This is a report of January 1987 by Professor Kozo Tanabe, Hokkaido University (Japan), to Cia. Brasileira de Metalurgia e Mineração (CBMM).

Hydrated niobium pentoxide, usually called niobic acid, was found to exhibit a high acid strength corresponding to 70 % H_2SO_4 when calcined at relatively low temperatures (100-300 °C), though the surface of niobic acid calcined at 500 °C was almost neutral. Since any acidic metal oxide shows acidity on calcination at about 500 °C and the acidity is lost or decreased by absorbing water, niobic acid which shows high acid strength on the surface, despite containing water, is an unusual solid acid. The unusual solid acid is expected to show a stable catalytic activity for acid-catalyzed reactions in which water molecules participate or are liberated. In fact, it showed an excellent stability as a catalyst for esterification, hydrolysis and hydration reactions.

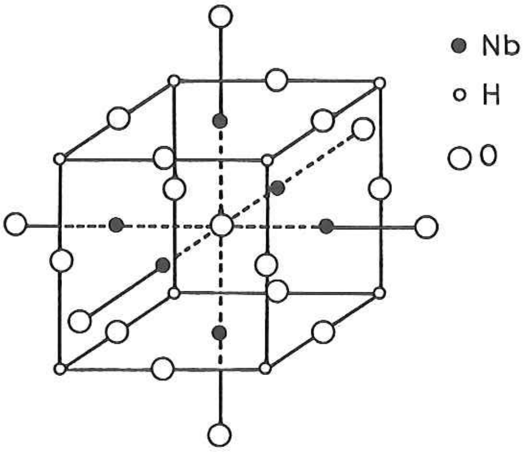
In this article, the structure, surface property and catalytic behaviour of niobic acid are demonstrated and the characteristics of the unusual solid acid material are emphasized.

NATURE AND STRUCTURE OF NIOBIC ACID

Niobic acid is polymerized $Nb_2O_5.nH_2O$ with an uncertain composition as the water content is not constant. The gradual formation of the species is represented by the following scheme :

$$H_8Nb_6O_{19}.18H_2O \to H_8Nb_6O_{19}.12H_2O \to H_8Nb_6O_{19}.6H_2O \to H_8Nb_6O_{19}.3H_2O \to H_8Nb_6O_{19} \to [H_2Nb_6O_{16}]_n \to [Nb_6O_{15}]_n \to [NbO_{2.5-2.33}]_n$$

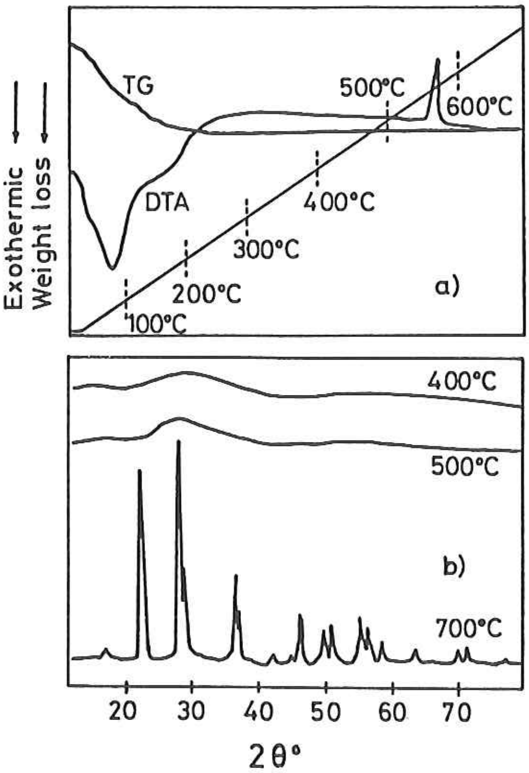
Model structure of niobic acid



The structure of hydrated niobium oxide is an isopolyacid of composition $H_8Nb_6O_{19}$. The structure of the free acid, $H_8Nb_6O_{19}$, can be depicted by the presence of eight protons above eight triangular faces of the octahedron formed by six niobium atoms. Thus, each hydrogen is embedded in the electron cloud produced by three bridging oxygens, three terminal oxygens and the central oxygen. The protons in niobic acid are not present in the form of water molecules but in the form of hydroxyl groups attached to the niobium atoms.

The results of differential thermal analysis (DTA) and thermogravimetry (TG) of niobic acid are shown. At around 90 and 180 °C, two endothermic peaks with the decrease of gravity were observed which could be ascribed to the dehydration process of niobic acid. The dehydration was completed by heating up to 300 °C; gravity change of the sample was not observed between 300 and 700 °C. The exothermic peak at 550-570 °C with no gravity change could have been due to a phase transformation. According to X-ray diffraction patterns, a good crystallinity was observed by heating at 700 °C, and the diffraction pattern corresponded well to the T.T.-phase Nb_2O_5. The crystallization begins on calcination at 400 °C.

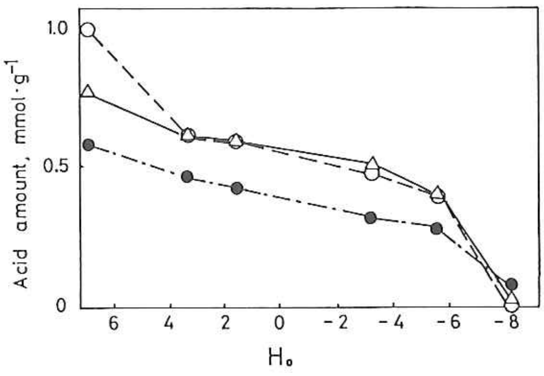
Thermogravity and differential thermal analysis of niobic acid (a) and X-ray diffraction patterns of niobic acid heat-treated at various temperatures (b)



SURFACE AND ACIDIC PROPERTIES

The surface areas of niobic acid were 164, 126 and 42 m^2/g after evacuation at 100, 300 and 500 °C, respectively. The ion-exchange experiment showed that only 1.2 % of the protons of $H_8Nb_6O_{19}$ could be exchanged with sodium ions. The exchange process of protons was very slow.

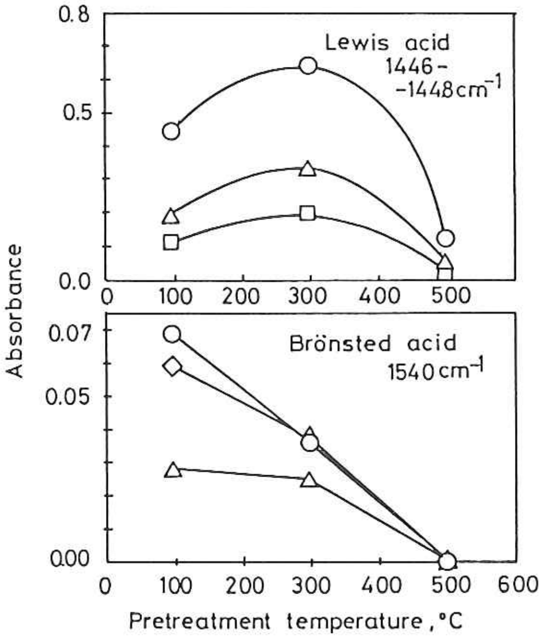
Acid amount vs acid strength of niobic acid (calcined at 120, 200 and 300 °C, from top to bottom, respectively)



The acidic property of niobic acid was measured by n-butylamine titration using Hammett indicators. Considerable acid amounts at H_0 of −5.6 were observed for niobic acids pre-treated at 120-300 °C, although a niobic acid calcined at 500-600 °C did not show any acidic property.

According to infrared spectra of pyridine adsorbed on niobic acid, the Brönsted acid band intensity was strongest on the sample evacuated at 100 °C and decreased with increasing evacuation temperature. However, Lewis acid band intensity showed a maximum on the niobic acid which had been evacuated at 300 °C.

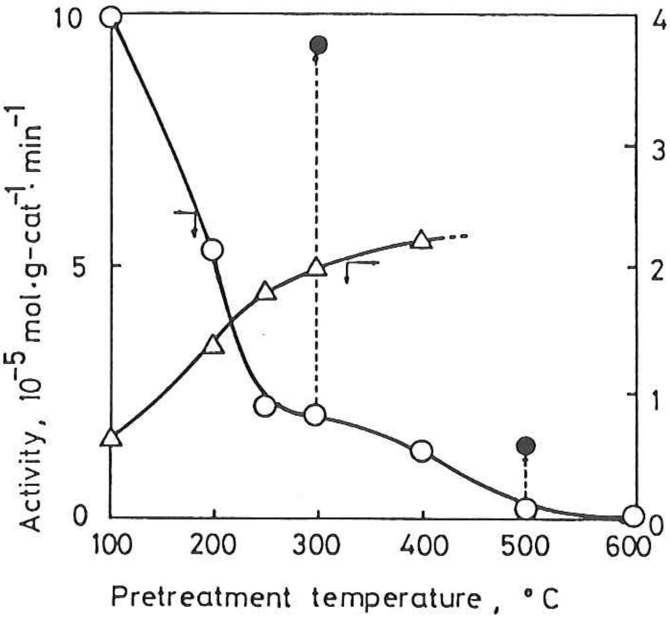
Acidity change of niobic acid with pre-treatment temperature. Lewis acid : evacuated at 100, 200 and 300 °C, from top to bottom, respectively. Brönsted acid : evacuated at 100 °C, room temperature and 200 °C, from top to bottom, respectively.



CATALYTIC BEHAVIOUR

The isomerization of 1-butene, the dehydration of 2-butanol, and the polymerization of propylene are reactions known to be catalyzed by acids and so were studied over niobic acid to characterize the acidic nature of niobic acid. The catalytic activity and selectivity of niobic acid evacuated at various temperatures for isomerization of 1-butene are shown. The niobic acid evacuated at 100 °C for two hours exhibited the highest activity. The selectivity indicates that Brönsted acid is behaving as active sites. The activity decreases with increasing evacuation temperature and the selectivity becomes almost equal to two, suggesting that Lewis acid is also behaving as active sites. On evacuation at 500-600 °C, the activity almost disappeared. It was interesting to notice that the activity of niobic acid evacuated at 300 °C, followed by exposure to water vapour and evacuation at 100 °C, became almost the same as that evacuated at 100 °C; whereas the niobic acid once evacuated at 500 °C did not increase the activity even if exposed to water vapour. This indicates that the transformation of amorphous to T.T. phase interferes with the regeneration of Brönsted acid by water addition.

Activity and selectivity of 1-butene isomerization (H_2O added after pre-treatment and evacuated at 100 °C)



In the case of dehydration of 2-butanol, the activity of niobic acid was high and competed with that of SiO_2-Al_2O_3 when evacuated at 150 °C, but markedly decreased when evacuated at 300 °C. Thus, the active sites are considered to be Brönsted acid from the comparison with the previous data. For polymerization of propylene, niobic acid showed a high activity on evacuation at 100 °C; the activity decreased on evacuation at 150-200 °C, increased on evacuation at 250-300 °C, and finally disappeared on evacuation at 500 °C. This activity change can be interpreted by taking into account that the main active sites are Brönsted acid in the case of low-temperature evacuation, but Lewis acid in the case of high-temperature evacuation.

For hydration of ethylene, the activity of niobic acid was very low in the early stage of the reaction, but increased gradually as the reaction proceeded and reached a steady state in six hours. The de-activation of the catalyst was not observed when the run was repeated. The steady-state activity of niobic acid calcined at 300 °C was higher than that of solid phosphoric acid which is widely used in industry. When niobic acid was calcined at a high temperature of 500 °C, the activity was low and did not increase even in the later stage of the reaction. It is interesting and important that the niobic acid, calcined at relatively low temperatures, showed a high activity and a long life. The selectivity for the formation of ethyl alcohol at 220 °C over the niobic acid catalyst was more than 97 %, a small amount of the other product being acetaldehyde.

Activities and selectivities of niobic acid and other solid acids for esterification of ethyl alcohol with acetic acid (catalyst weight : 1 g; volume ratio of acetic acid to ethyl alcohol : 1; reaction time : 1 hour)

Catalyst	Reaction temp. °C	C_2H_5OH basis		By-products
		Conversion, %	Ester selectivity, %	
$Nb_2O_5 \cdot nH_2O$[a)]	120	72	100	
	140	86	100	
resin[b)]	120	38	< 99	
	140	50	< 98	
ZrO_2-SO_4^{2-} [c)]	140	56	90	$(C_2H_5)_2O$
Fe_2O_3-SO_4^{2-} [c)]	140	13	93	$(C_2H_5)_2O$
TiO_2-SO_4^{2-} [c)]	120	95(54)[d)]	99(98)[d)]	
	140	100	95	C_2H_4
SiO_2-Al_2O_3[c)]	120	4	99	$(C_2H_5)_2O$ $+C_2H_4$
	140	14	98	
HZSM-5[c)]	120	82	92	$(C_2H_5)_2O$ $+C_2H_4$
	140	99	72	

a) Calcined at 200 °C, b) Calcined at 120 °C, c) Calcined at 500 °C, d) After 2 h's reaction time.

For esterification of ethyl alcohol with acetic acid, the catalytic activities and selectivities of niobic acid and the other solid acids are shown. The niobic acid showed higher activity than resin, ZrO_2-SO_4^{2-}, Fe_2O_3-SO_4^{2-} and SiO_2-Al_2O_3. The selectivity for the formation of ethyl acetate was 100 %. In the case of resin, the selectivity was high, but the resin became black after one hour's reaction so that repeated use was impossible under the reaction conditions. In comparison, the activity of niobic acid did not change even after use for 60 hours. The TiO_2-SO_4^{2-}, a solid super acid, showed a high activity, but the activity rapidly decreased and became much lower than the activity of niobic acid after two hours' reaction. The HZSM-5 catalyst also exhibited a high activity, but formed considerable amounts of diethyl ether and ethylene as by-products, the selectivity being less than 92 %. It is concluded that niobic acid pre-treated at relatively low temperatures is highly active for the esterification with 100 % selectivity and that the catalyst life is long enough.

Niobic acid pre-treated at 200-400 °C showed a high activity and selectivity (100 %) and a remarkably good stability also for the hydrolysis of acrylic ester in which a large amount of water exists in the reaction system.

CHARACTERISTICS OF NIOBIC ACID

The most striking feature of niobic acid is that it possesses a high acid strength corresponding to that of 70 % H_2SO_4 despite containing a considerable amount of water. Such a hydrated metal oxide has never been reported before, since the acidity of metal oxides is lost or decreased by absorbing water. The generation of the strongly acidic sites on the surface of niobic acid cannot be explained by the structure mentioned above. The elucidation is an important future problem which would give information for developing new types of acidic solid materials.

Niobic acid, which contains water but has a high acidity, exhibited not only a high activity and selectivity, but also a high stability for hydration, hydrolysis and esterification in which water molecules participate or are liberated. The application of this unusual solid acid as catalyst to other reactions is also promising.

TANTALUM/NIOBIUM PRODUCTS SURVEY

T.I.C. member companies offer for sale the following products based on tantalum and niobium.

	Raw Materials						Compounds								Carbides				Alloy additives						Metallurgical-grade products										Capacitor-grade products					
	Tantalite	Columbite	Struverite	Tin slag	Pyrochlore	Synthetic concentrate	Tantalum oxide, standard-grade	Tantalum oxide, optical-grade	Tantalum oxide, ceramic-grade	Potassium fluotantalate	Niobium oxide, standard-grade	Niobium oxide, optical-grade	Niobium oxide, ceramic-grade	Potassium fluoniobate	Tantalum carbide	Niobium carbide	Binary carbides	Mixed carbides	Nickel-tantalum	Tantalum (unalloyed)	Nickel-niobium	Ferro-niobium (steel-grade)	Ferro-niobium	Niobium (unalloyed)	Tantalum melting stock	Tantalum ingot, unalloyed	Tantalum ingot, alloyed	Tantalum mill products, unalloyed	Tantalum mill products, alloyed	Niobium melting stock	Niobium ingot, unalloyed	Niobium ingot, alloyed	Niobium mill products, unalloyed	Niobium mill products, alloyed	Powder, sodium-reduced	Powder, EB-melted	Foil	Wire	Cases	Anodes
Cabot Corporation - Refractory Metals							●	●		●	●	●	●						●	●	●	●		●	●	●	●	●	●	●	●	●	●	●	●	●	●	●		
Cambior Inc.					●																																			
Datuk Keramat Smelting Sdn. Bhd.				●																																				
Derby & Co., Division of Philipp Brothers Ltd.	●	●	●	●	●	●																																		
Minera del Duero S.A.	●																																							
Cia. de Estanho Minas Brasil	●	●	●				●				●																													
Fansteel Inc.							●		●	●	●		●							●				●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Gesellschaft für Elektrometallurgie mbH	●	●			●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●			●	●	●			●	●				
Greenbushes Ltd.	●			●			●		●	●					●		●								●	●		●												
W.C. Heraeus GmbH																										●	●	●	●	●	●	●	●	●						
Intersteel Com. Ext. Ltda.	●	●								●	●																													
Kamativi Tin Mines (ZMDC)	●	●		●																																				
Liarte Metalquimica	●					●	●								●	●	●	●																						
Lien Metals, Inc.							●	●	●		●	●	●																											
Malaysia Smelting Corporation Bhd.				●																																				
Metallurg, Inc.	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●			●	●	●			●	●				
Metamin Sdn. Bhd.			●																																					
Mitsui Mining & Smelting Co. Ltd.							●	●	●		●	●	●		●	●	●	●																						
National Resources Trading Inc.	●																																							
Niobium Products Co. Inc.											●	●	●								●	●	●	●						●	●									
Norore Division of Sogem Corp.	●	●	●	●	●	●																																		
NRC Inc.							●		●	●	●		●							●				●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	
Sassoon Metals & Chemicals, Inc.	●	●	●	●		●	●			●										●			●		●	●														
Showa Cabot Supermetals K.K.																				●					●	●		●							●	●				
Hermann C. Starck Berlin	●	●	●			●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●		●	●	●	●			●	●				●	●	●	●		●
The Straits Trading Co. Ltd.				●																																				
Tantalum Mining Corporation of Canada Ltd.	●																																							
Teledyne Wah Chang Albany											●											●		●						●	●	●	●	●						
Thailand Smelting and Refining Co. Ltd.				●																																				
Treibacher Chemische Werke AG							●	●	●		●	●	●		●	●	●	●			●	●	●																	
Vacuum Metallurgical Co. Ltd.																								●	●	●	●	●	●	●	●	●						●		
V Tech Corporation																									●										●					●

PRINTED BY PUVREZ, avenue Fonsny 59, 1060 Brussels.