TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

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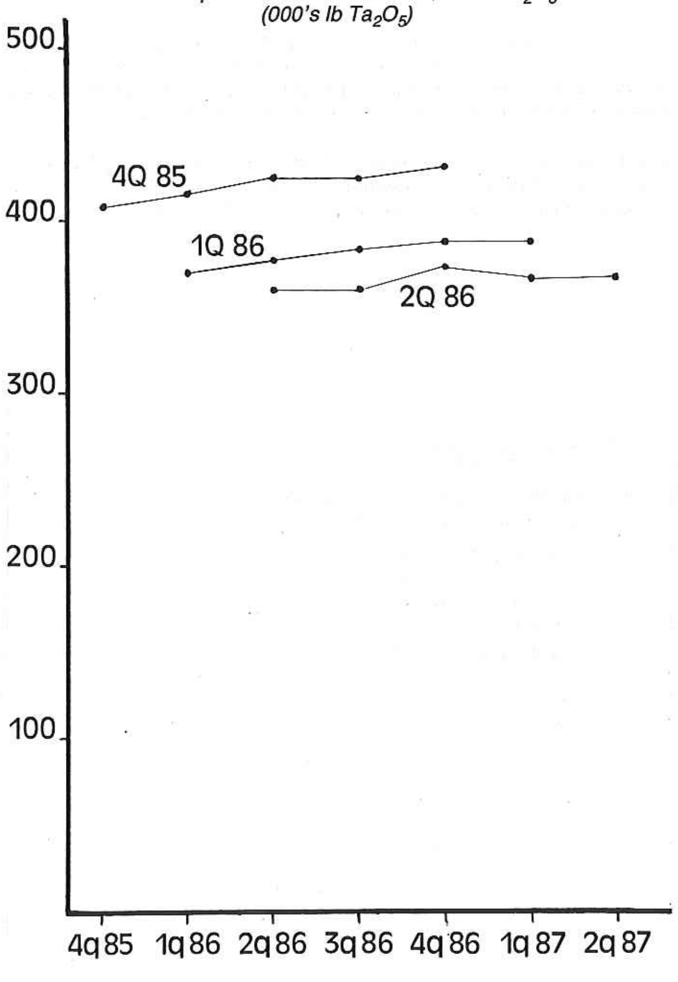
The tin crisis

Tantalum raw materials — ore concentrates and tin slags — come extensively as a co- or by-product with tin, and so the current crisis in tin will obviously be influencing tantalum production : this article seeks to examine this effect in the major producing regions of the world.

The recent problems in the tin market began last October when the International Tin Council (ITC) ran out of money to support the existing price level on the London Metal Exchange (LME). A key factor in the rundown of ITC funds was the massive increase in supply from non-ITC countries, most notably from Brazil, whose exports were not subject to ITC controls. Tin prices have fallen since that time from over £ 8000 per tonne to around £ 3500 per tonne in June. The main reason for this is not over-supply but the dumping on to the market of tin inventories held by banks as collateral for loans made to the ITC. These stocks are estimated at around 130 000 tonnes, equivalent to nine months' demand. At current prices, a large proportion of the world's tin mines are uneconomic to operate, and so closures are taking place. To what extent these closures are going to be temporary, awaiting an upturn in prices, or permanent cannot be determined yet. What is certain is that tin prices will never again be sustained at artificially high levels by ITC purchasing on the LME as it has been indicated that the ITC will not exist in its present form after June 1987. Tin producers in the future will have to compete in a free market.

The effect of all this on tantalum production in the short term can be seen from the progressive decline in T.I.C. production estimates since the last quarter of 1985, when the crisis was still in its infancy, to the most recent forecasts made during the second quarter of 1986. This downward trend is illustrated below at the $ 30 per lb Ta_2O_5 price scenario, but decreases also occurred at $ 40 and $ 50 prices.

Forward production estimates at $ 30/lb Ta_2O_5
(000's lb Ta_2O_5)



The three largest tin smelters, in terms of capacity, in the world are Thaisarco in Phuket (Thailand) and the two Penang smelters, Datuk Keramat and Malaysia Smelting, between them accounting for 35% of world tin output in 1985. They produce an even larger proportion of the Ta_2O_5 in slags – 70 % or more. In recent years, they have been toll-smelting for miners, but many of these mines have now closed down as they cannot cover their costs at current prices.

In Thailand, 221 out of 587 mines have closed since January, with 164 operating at reduced output. As a result, tin production at Thaisarco, although at a high level so far this year, is set to fall by 30 % in 1986 over the previous year, this situation continuing into 1987. Thaisarco is the major producer of high-grade slags (i.e. over 10 % Ta_2O_5) in the world.

In Malaysia, miners have been experiencing cash flow problems due to the Penang smelters ceasing to make advance payments on ore received. Penang slags, for the most part, are of a very low grade, less than 3 % Ta_2O_5 against a current marketable grade of 2.5 %. During the past few years of low throughput, it has been difficult for the smelters to produce slags greater than 1.5 % to 2 % Ta_2O_5. To obtain a saleable slag, they have to smelt several high Ta-content ore batches together, and this is not practicable at the present low level of operation, a situation which shows no sign of changing within the foreseeable future. Material which is less than 1.5 % Ta_2O_5 is normally dumped and so permanently lost to the market.

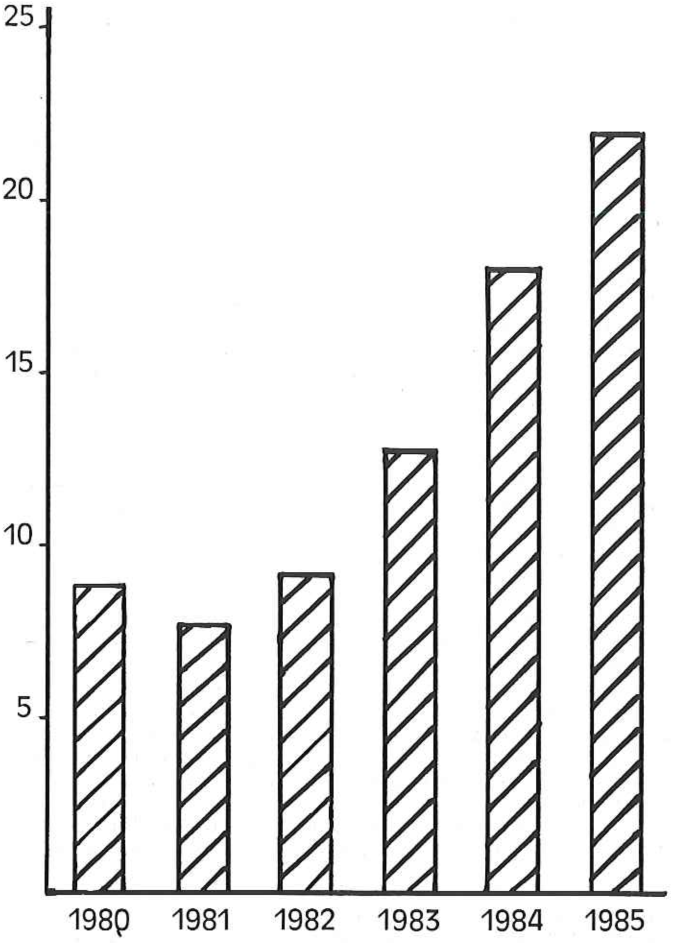
The only other smelter in S.E. Asia which has produced slags with a significant Ta_2O_5-content, Kimetal in Singapore dealing largely in illegally-smuggled concentrates, is thought to be facing imminent closure.

In S.E. Asia, tantalum-containing raw materials have also been extracted from tin mining waste in treatment plants. There is no immediate threat to the supply of this mining waste ("amang") since adequate sources exist. But there is little production of tantalite and struverite taking place at present because of the low demand, the plants concentrating on more saleable minerals.

African tantalum production is likely to fall by around 75 % from 330 000 lb Ta_2O_5 (slags and concentrates) in 1985 to 80-100 000 lb during 1986, this being mainly attributable to the tin crisis. Cutbacks are likely in production of slags in Nigeria, Zimbabwe and Zaire. Zimbabwe's main tin-tantalum producer, Kamativi Tin Mines, was forced to close down one of their two mines earlier this year, apparently on a permanent basis, and have their other hard rock mine on care and maintenance with only mining of alluvials continuing. At Kamativi, cassiterite is smelted to produce tin and slag assaying around 9 % Ta_2O_5. The Zairetain smelter in Manono (Zaire) has been operating at a very low level since Geomines, the owners of the smelter, were declared bankrupt last year. Hence production of tantalum in slags is likely to be significantly less in 1986 than 1985 (30-50 tonnes at 10-12 % Ta_2O_5, from "Tantalite production in Zaire and Rwanda", T.I.C. Bulletin No. 45). Production of tantalite concentrates in Zaire, Rwanda and South Africa is likely to decline because they are associated with cassiterite production. However, the microlite deposit of Minas Gerais de Mozambique has no tin content and so tantalite production there will not be affected by the crisis.

The major tantalite miner in Brazil, Cia. de Estanho Minas Brasil, also produce tin but not at a level to rate as a significant producer. Once the ore has been mined, tantalite and cassiterite concentrates are separated out, the cassiterite then being smelted to produce tin and a high-grade tantalum-containing slag. The tin is sold predominantly into the domestic market where current prices are more favourable than international ones. Brazil, as mentioned previously, contributed to the demise of the ITC price support mechanism through its increases in production in recent years. One company in particular, the Paranapanema Group, had been producing increasingly larger quantities of concentrates from an extremely rich ore deposit at Pitinga in the Amazon. But, although reports indicate large quantities of Ta_2O_5, no tantalite production has commenced as yet. The collapse of tin prices has recently forced Paranapanema, Brazil's largest producer, to concentrate on increasing efficiency rather than output.

Growth in Brazilian tin production
(in 000's tonnes) 1980-1985



Tin metal sales by Greenbushes (Australia) are actually likely to increase because of the closure of the 7400 tpy ATS smelter at Sydney, which has opened up the domestic Australian market. The Greenbushes smelter is used to recover tantalum from cassiterite, the slag obtained having a 25-30 % Ta_2O_5 content. So although mining operations remain at a low level awaiting the recovery in the tantalite market, emphasis has been diverted to high-grade tin-bearing alluvials. During the 16 weeks to April 5th this year, the company produced 124.4 t of tin and 23 470 lb Ta_2O_5, as opposed to 104.0 t of tin and 56 650 lb Ta_2O_5 during the 12 weeks to December 14th 1985.

The long-term structure and size of the tin industry cannot be fully determined until the outstanding inventories have been exhausted which could take two to three years. In 1985, it was estimated that supply was exceeding demand by around 15 %, but lower prices could stimulate greater tin demand in the next few years.

Tin production by country in 1985
(000's tonnes)

Australia	9
Bolivia	19
Brazil	22
Indonesia	23
Malaysia	38
Thailand	20
Others	34
	165

(excluding Eastern Bloc)

Which countries emerge as the major tin suppliers will not depend solely on economics, Brazil being the most efficient producer and Bolivia the least efficient, but also on government policies. The Bolivian state-owned industry will continue to operate as long as it can in order to bring foreign currency into the country, the only limiting factor being the shortage of spare machinery parts. The Indonesian government also continues to operate its tin industry at close to 1985 levels in defiance of economic logic.

Tin prices have fallen far below the levels of £ 5000-6000 per tonne anticipated at the outset of the crisis. In the period of the next two to three years, this will lead to a change in emphasis for tantalum production away from Africa and S.E. Asia towards Australia and Brazil.

Andrew Jones
Technical Officer

TWENTY-FIFTH GENERAL ASSEMBLY

The Assembly was held at the Kobe International Convention Center, Japan, on May 20th 1986.

The delegates voted to accept a new charter for the T.I.C. which extends the same membership rights to niobium producers, processors and consumers as companies involved in tantalum-related activities enjoy. The name of the association was changed accordingly to the "Tantalum-Niobium International Study Center", the abbreviation — T.I.C. — being retained. It was also envisaged that collection of statistics on niobium would be under way by the end of the year at the latest as tantalum and niobium became "equal partners" in the association.

Three companies were admitted to T.I.C. membership :

- Corning/Components, Inc., a manufacturer of tantalum capacitors in Maine, USA.
- Intelligent Controls, Inc., a manufacturer of equipment for the automatic monitoring of the anodization of tantalum powder for the capacitor industry, located in Maine, USA.
- V-Tech Corporation, a company established in June 1984 to market tantalum products in the Far East. Recently V-Tech entered into an agreement with Fansteel, Inc. to market niobium and tantalum products in Japan and the Far East, and also to construct a manufacturing facility in Japan for tantalum capacitor powder and wire.

With one company resigning from the T.I.C., total membership now stands at seventy-four.

It was announced that Mr Bob Franklin, STC, had resigned from the Executive Committee.

It was decided that all future T.I.C. meetings should be financially self-supporting, and so the General Assembly agreed that the fee for all participants, including voting delegates, should be set at such a level that the total cost of the meeting would be covered.

The Twenty-sixth General Assembly will be held on October 24th 1986 in Brussels. The Twenty-seventh General Assembly will be in Brazil, probably in Rio de Janeiro, during the first half of 1987.

Membership

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

Corning/Components, Inc.,
One Components Drive,
Airport Industrial Park,
Biddeford, Maine 04005, U.S.A.

Intelligent Controls, Inc.,
297 North Street,
P.O. Box 638,
Saco, Maine 04072, U.S.A.

V-Tech Corporation,
2F Mita Maruhachi Bldg.,
1-10, 3-Chome, Mita,
Minato-Ku,
Tokyo 108, Japan.

The resignation of **Brandeis Intsel Ltd.** was accepted by the same Assembly.

President's letter

I am pleased to announce that the Twenty-fifth General Assembly (May 19th-21st 1986 held in Kobe, Japan) has closed with great success. I would like to express my warmest thanks for all of your kind co-operation during this assembly.

The Japanese host companies, Vacuum Metallurgical Co., Showa Cabot Supermetals KK and Mitsui Mining & Smelting Co., have been happy to do their best in holding this assembly in Japan. We believe that the plant tours must have been useful and valuable, being welcomed with kindness by Sumitomo Electric Industries and NEC Kansai, Ltd. The tour for ladies also must have been enjoyable.

Meanwhile, the General Assemblies have progressed to the Twenty-fifth and have contributed to the improvement of communications within the tantalum and niobium industries. We can now get a better focus on what to do for the future of tantalum. However, there are still difficult problems with regard to tantalum business in general so that we cannot be optimistic for its future.

We should continue making efforts to exchange opinions among members through this organization so that we may get a better future for our business. The T.I.C. formally added to its activities the subject of niobium, and it is hoped that this action will increase the value of the T.I.C. Let us make efforts to establish professional activities in the T.I.C. to serve the niobium world. It is hoped to hold the Twenty-seventh General Assembly in Brazil, the niobium country. We are going to have the Twenty-sixth General Assembly in Brussels on October 24th, where we will hopefully discuss more on niobium.

Again, I wish to express thanks to all participants and speakers for their kind co-operation throughout the Twenty-fifth meeting.

Sincerely yours,
Chikara Hayashi
President

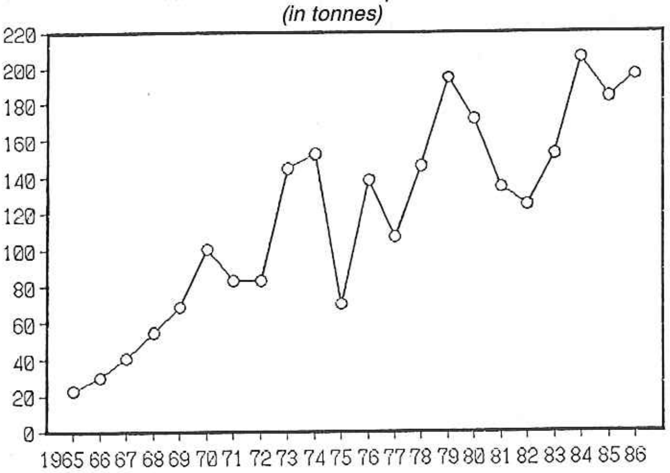
History of the tantalum industry in Japan and its problems

This paper was presented at the T.I.C. meeting in Kobe on May 20th 1986 by Mr Yoichiro Takekuro, President of the Japan Society of Newer Metals Tantalum Committee.

Japanese interest in tantalum dates from 1935 when the Toshiba Corporation and others tried to produce tantalum plates for nozzles used in artificial silk manufacture. In Germany, the production of tantalum metal started in 1902, 33 years earlier than the initiation of Japanese research, and in the US, tantalum rods were being manufactured as of 1929. In 1940, Fansteel Inc. commenced production of tantalum capacitors. It was during the 1950's that the Japanese also began to manufacture these capacitors for communications equipment, the raw material, tantalum powder, being imported from the US. In 1957, these imports of tantalum products were about 200 kg of wire and foil and about 100 kg of powder. Powder consumption in Japan has now grown to approximately 120 tonnes during 1985.

The history of the tantalum industry in Japan can be divided into three periods, the first being from 1950 through 1965, an inauguration era when many companies started tantalum production anticipating a prosperous future for the new metal. During the second period, which was the following ten years, one company after another, from amongst more than a dozen which were involved with tantalum at that time, withdrew from the business. The third period is the ten years from 1976 to date : an era of oligopoly by those who survived.

Tantalum demand in Japan 1965-86
(in tonnes)



There are different backgrounds to each of these three periods. However, factors that are common to each era are the movement and behavior of the European and US producers, as well as the natural resources preservation issue which played an important role in the development of the industry in Japan.

INITIAL DEVELOPMENTS

The period from 1950 through 1959 was centered on research and development. In 1960, tantalum powder was produced by Showa Denko, Shinetsu Chemical Co., Komatsu and Nihon Soda. The year after, Tokyo Denkai Co. began fabricating tantalum items and Mitsui Mining & Smelting Co. started to produce tantalum compounds. ULVAC Corporation advanced into processing of tantalum by electron-beam melting, Kobe Steel also entering this field. The present Vacuum Metallurgical Co. was founded in 1966 when a new organization was created from the Tantalum and Titanium Division of ULVAC Corporation.

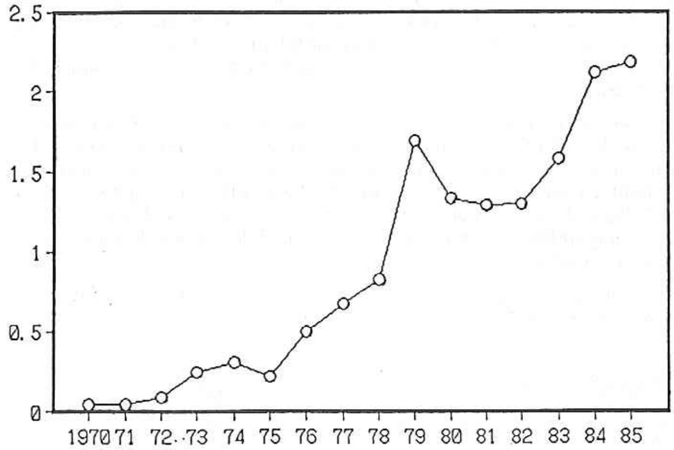
Later on, several companies, including Tohoku Metal Industries, commenced tantalum processing. Although chemical products such as carbide for cemented carbide tools and oxide for optical glass were accepted by users comparatively easily, Japanese tantalum powder and wire manufacturers were experiencing a very hard fight in the capacitor market. In 1962, MITI (Ministry of International Trade and Industry) made the unusual proposal to the domestic capacitor industry that they should use more tantalum products manufactured in Japan and went so far as to resort to protectionism resulting in wire imports being restricted. But this failed to have any noticeable effect, and the industry's situation did not improve. Amidst such circumstances, price competition from the US manufacturers of tantalum powder became harder, and concurrently the price of ore soared which dealt another blow to the industry. Also, sales by overseas manufacturers of potassium tantalum fluoride, which is an intermediate material for powder, became so brisk that the Japanese tantalum producers had to decide whether they should purchase this material from abroad, process ore themselves or leave the tantalum business completely.

On that occasion also, MITI gave advice to the domestic producers in an effort to help them survive, by, for instance, implementing a reorganization of the industry. But they failed to succeed in this goal.

PERIOD OF RECESSION

Finally, the Japanese tantalum industry suspended production of powder in 1965. The tantalum market in Japan was not depressed at that time nor during the period that followed. The production of tantalum capacitors, which was 600 000 pieces in 1960, reached 2200 million pieces in 1985.

Tantalum capacitor production 1970-85
(in billion pieces)



But, at a time when US demand for tantalum reportedly exceeded 500 tonnes a year, the Japanese domestic demand was only 50 tonnes, and half of this quantity was imported. Indeed, the production scale of tantalum producers in Japan was less than one-twentieth of that of their US equivalents and so it was not surprising that no competitive power arose from such a base. Every year, one domestic producer disappeared. The year 1976 saw the end of this period of hardship with the withdrawal of Shinetsu Chemical Co. from the industry. In 1971, the only powder manufacturer left in Japan was Showa KBI, a joint venture between Showa Denko and KBI, who continue to lead the industry in high CV powders. (Now renamed Showa Cabot Supermetals.)

The general business mind in Japan postulates that any concern once started should be sustained without being easily abandoned. And so it is quite unusual that so many Japanese companies suspended production of such a prospective commodity as tantalum.

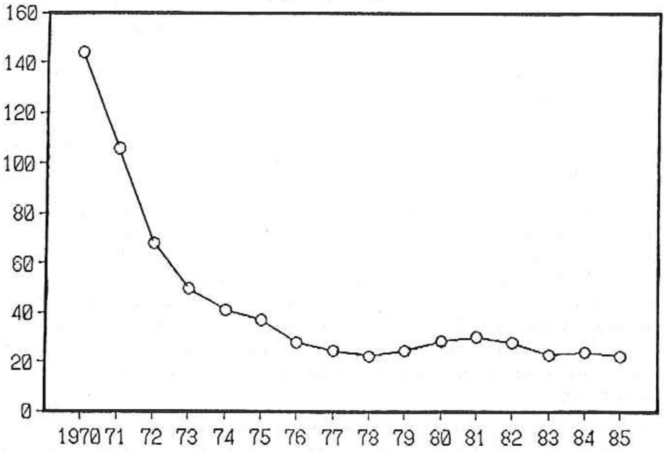
PERIOD OF OLIGOPOLY

After some difficult times, there are now four members of the Japan Society of Newer Metals Tantalum Committee : Showa Cabot Supermetals specialising in powder, Mitsui Mining & Smelting Co. for compounds, Tokyo Denkai Co. as a processor and Vacuum Metallurgical Co. engaged in the processing of mill products and as NRC's sales agent in Japan. Unlike other realms of Japanese industry where there is a strong tendency for a number of manufacturers to coexist, the tantalum industry, in which oligopoly persists, is a rare exception.

FUTURE PROBLEMS...

If the price of tantalum had not soared in the latter half of 1979, a market of a greater scale could have been secured. This historical fact is a good precept whereby such events should not recur, this being possible to achieve through the efforts of those involved.

Tantalum capacitor average unit price 1970-85
(yen/piece)



In 1981, at the T.I.C. meeting held at Goslar in West Germany Mr Hidehiro Okuda (NEC) emphasized the possibility of strong demand for compact tantalum capacitors and forecasted that the CV value of powder would reach 30 000 CV/g in four to five years hence. Five years have passed, but this level has not yet been achieved for practical use. However, powder of 20 000 CV/g is now being produced and accomplishment of 30 000 CV/g, once regarded as impossible, may soon be realized. In this respect, it can be said that the tantalum industry in Japan has gone beyond the technically-lagging stage.

The domestic tantalum industry, when viewed as a whole, is still in a developing phase. Japan is being criticized for its great trade surplus : as far as tantalum is concerned, there is an overwhelming deficit. The significance of this problem is that the industry's activities are limited to a domestic market without any significant exports.

First of all, Japan has no capacity to influence international prices : this inclination is strengthened further due to the appreciation of the Japanese yen. Also, the establishing of a reasonable price level for tantalum powder produced domestically is difficult despite the fact that Japan leads the field in high CV powder. This can be considered as being indirectly attributable to our inability to control the international quotation.

At the same time, further efforts must be made in the area of material development.

Present tantalum and niobium operations of Mitsui Mining & Smelting Co.

This paper was presented by Mr Takao Mori of Mitsui Mining & Smelting Co. at the T.I.C. meeting held in Kobe on May 20th 1986.

In recent years, tantalum and niobium, because of their special physical, chemical and electrical properties, have become widely-used in "leading-edge" industries. Niobium, for example, has become prominent as a superconductor material. Oxides of Ta and Nb are in demand as materials for lenses in high-quality cameras that demand high refraction and low dispersion. And high-purity Ta_2O_5 and Nb_2O_5 are gaining attention as materials for lithium tantalate and niobate single crystals. The demand in these applications is growing rapidly.

But at the same time, Ta_2O_5 for use in optical products is relatively expensive, so other oxides, such as Nb_2O_5 and Y_2O_3, are being substituted for it : this is producing a structural change in the demand trend for this product in Japan.

HISTORICAL DEVELOPMENT

Tantalum and niobium operations at Mitsui Mining & Smelting started in 1958 with the manufacture and testing of oxides at the Kamioka zinc and lead mine in Gifu Prefecture. It was here, in 1960, that a pilot plant was built with a 30 kg per month capacity. Five years later, oxide production commenced at a 1.2 t per month capacity plant which was located at the Central Research Laboratory in Mitaka, a suburb of Tokyo. This plant's capacity was increased to 3 t per month in 1969.

Carbide production started in 1967 at the rate of 0.2 t per month, increasing steadily to a capacity of 3.2 t per month in 1970.

In 1975, oxide production was moved to Omuta in Fukuoka Prefecture, to what is now the Miike Rare Metal Plant. Production rose in line with demand, until the present capacity of 14 t per month was achieved. Then, in 1980, the company also moved their carbide production to Miike and increased output to the present 5.5 t per month capacity. In 1981, the company started manufacturing high-purity Ta_2O_5 and, in 1985, high-purity Nb_2O_5.

PROCESSES AND PRODUCTS

The process used at Mitsui Mining & Smelting is an extremely common one : tantalite, columbite and other ores are dissolved in hydrofluoric acid and the solution is then conditioned with sulfuric acid. After that, the solvent extraction process using MIBK separates Ta and Nb from the solution and eliminates impurities. Ammonia solution is then added to neutralize and precipitate the Ta and Nb and, finally, the precipitates go through the drying and calcination processes with hydroxides to obtain Ta_2O_5 and Nb_2O_5. A special feature of the process at MM&S is that the solvent extraction does not use the Mixer-Settler method but the Column method. Both have advantages and disadvantages, but with the Column method the damage to the solvent is less, nothing has to be moved and relatively little floor space is needed. Also the manufacturing conditions can be easily changed to allow production of oxides for ceramic use to any individual customer's specifications.

Specification for Ta_2O_5

Element	High-purity grade	Optical grade	Ceramic grade
Ta2O5 (%)	> 99.99	> 99.8	> 99.8
Nb2O5 (ppm)	< 5	< 50	< 50
Fe2O3 (ppm)	< 5	< 20	< 20
SiO2 (ppm)	< 10	< 200	< 200
Al2O3 (ppm)	< 5	< 15	< 20
TiO2 (ppm)	< 5	< 10	< 10
NiO (ppm)	< 5	< 10	< 10
SnO2 (ppm)	< 5	< 10	< 10
Cr2O3 (ppm)	< 5	< 10	< 10
MnO (ppm)	< 5	< 10	< 10
L. O. I. (%)	< 0.1	< 0.1	< 0.2
Average particle diameter (μm)	—	—	0.6 ~ 1.0

Specification for Nb_2O_5

Element	High-purity grade	Optical grade	Ceramic grade
Nb2O5 (%)	> 99.99	> 99.8	> 99.8
Ta2O5 (ppm)	< 20	< 1,000	< 1,000
Fe2O3 (ppm)	< 5	< 20	< 20
SiO2 (ppm)	< 10	< 200	< 200
Al2O3 (ppm)	< 5	< 15	< 20
TiO2 (ppm)	< 5	< 10	< 10
NiO (ppm)	< 5	< 10	< 10
SnO2 (ppm)	< 5	< 10	< 10
Cr2O3 (ppm)	< 5	< 10	< 10
MnO (ppm)	< 5	< 10	< 10
L. O. I. (%)	< 0.1	< 0.2	< 0.3
Average particle diameter (μm)	—	—	0.7 ~ 1.5

The process for high-purity Ta_2O_5 is the following : tantalum hydroxide goes through an oxidation process. The same MIBK method is used to separate and refine the solution to obtain oxide of a very high purity. According to the distribution coefficients of each of the components present, it should be easy to obtain both high-purity Ta_2O_5 and Nb_2O_5 using this basic method. But on an industrial scale obtaining high-purity products with this method is very difficult, even when the extraction process is repeated many times. So careful attention is paid to the working environment, and to the quality of the industrial water and chemicals used.

To produce carbide at the Miike Plant, Ta_2O_5 (Nb_2O_5) and carbon black are first mixed. This is followed by carbonization : either a hydrogen atmosphere or vacuum heating furnace is used to keep the carbonization temperature between 1500 and 2000 °C. The product is then pulverized to produce TaC (NbC).

RAW MATERIAL SUPPLY

Tantalum and niobium processors are trying to take some measures to deal with problems related to raw material supply.

To ensure a steady supply they are trying, to some extent, to negotiate long-term ore buying contracts. They are also evaluating the political and economic stability of the individual raw material producing countries and trying as much as possible to diversify their supply sources.

Also, they are considering scrap circulation as one of the most important sources of raw material and looking to establish the technologies for recovering many different types of scrap as efficiently as possible. It is especially urgent to establish the technology for recovering niobium scrap at low cost.

TECHNOLOGY-RELATED PROBLEMS

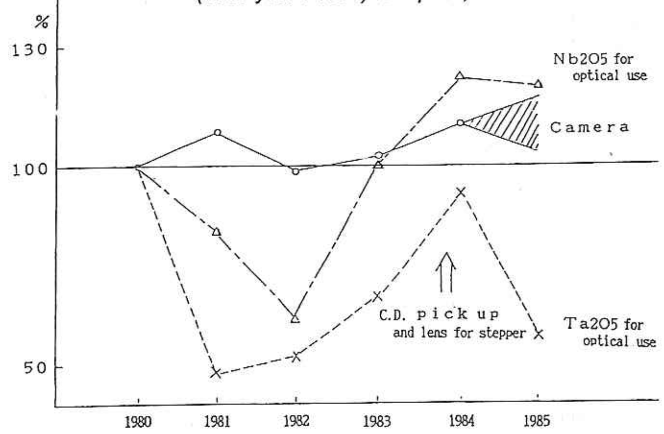
The cost of raw materials accounts for a large percentage of the total cost of producing and refining Ta and Nb products. So, naturally, the technology must be developed which can maximize the extraction yield of Ta and Nb from raw material, and every company in the industry is expending a lot of energy in this. Also, the technology for treating low-grade ores and a wide range of scrap at minimum cost must be perfected, and so lower the percentage that the cost of raw material takes up of the total cost. The present refining and manufacturing technology (as described previously) has not basically changed in the last 20 years. But recently processors have been taking a second look at the method. For example, they have been trying to clarify the dissolution mechanism that occurs when hydrofluoric acid is used to dissolve the raw material; they have been studying how to shorten the dissolution time; and they have been researching how to make use of the ammonium fluoride, which is generated as a by-product of the present process, as a substitute for hydrofluoric acid.

A number of different research projects are underway to develop new organic solvents for use in the separating and refining processes, such as Tributyl Phosphate (Japan), Dialkyl Acetamide (China) and Quaternary Amine (MM&S, Japan). Likewise, as the demand for extremely high-purity Ta_2O_5 and Nb_2O_5 increases, further research must be done on new extraction processes, such as the Chelate and ion-exchange methods which can replace organic solvent methods. In Japan, the Government Industrial Institute at Tohoku has been performing the main research in this area.

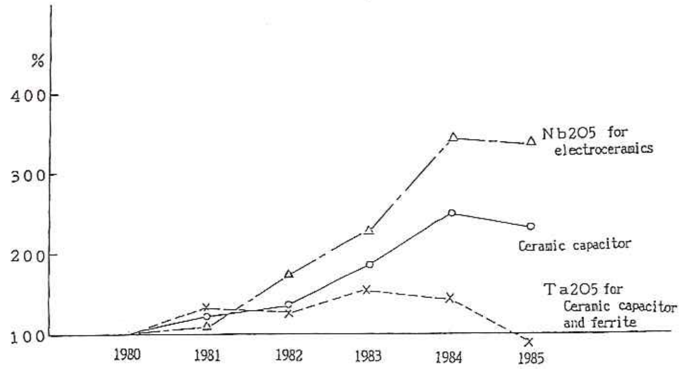
MARKET TRENDS

The tantalum and niobium markets have been changing tremendously in the last few years : consumption in existing markets is levelling off or decreasing due to replacement by new products. For example, although the production of cameras continues to rise, usage of Ta_2O_5 in optics is decreasing, Nb_2O_5 and Y_2O_3 being substituted instead. As the electronic components industry becomes more competitive, Nb_2O_5 is being used instead of Ta_2O_5 as the material for ceramic capacitors. And, while the production of facsimile devices is increasing, the consumption of Ta_2O_5 as an anti-abrasive material in sputtering targets for thermal head printers is levelling off, Si_3N_4 being used as a substitute.

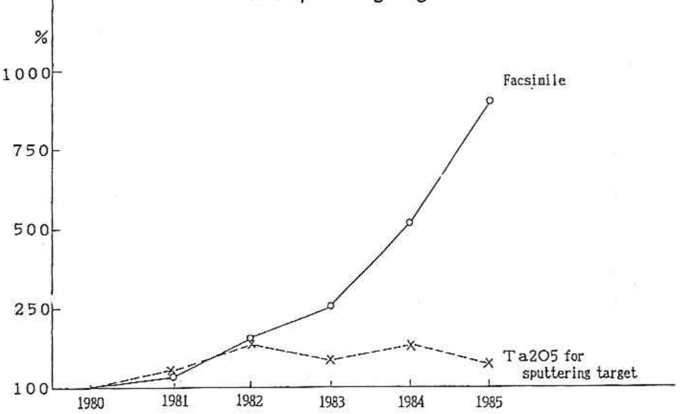
Consumption trends of Ta_2O_5 and Nb_2O_5 (base year : 1980) for optics;



— ceramic capacitors;

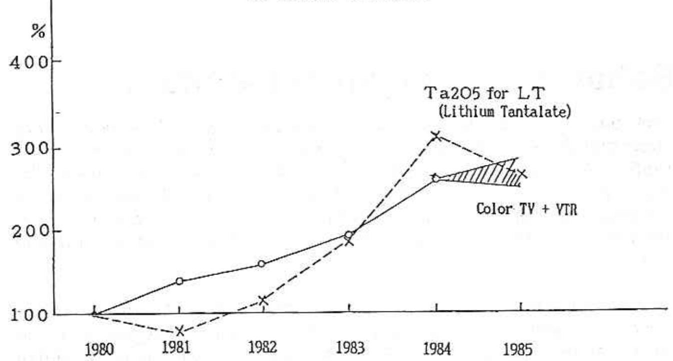


— and sputtering targets



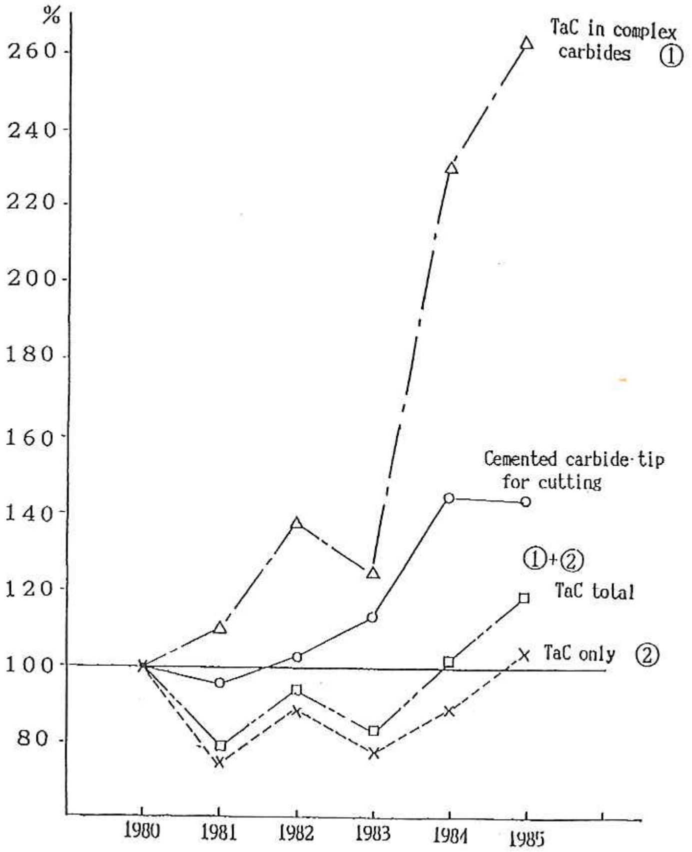
However, consumption of lithium tantalate and niobate (from high-purity Ta_2O_5 and Nb_2O_5) as single crystals for surface acoustic wave filters continues to rise.

Consumption trend of Ta_2O_5 for lithium tantalate

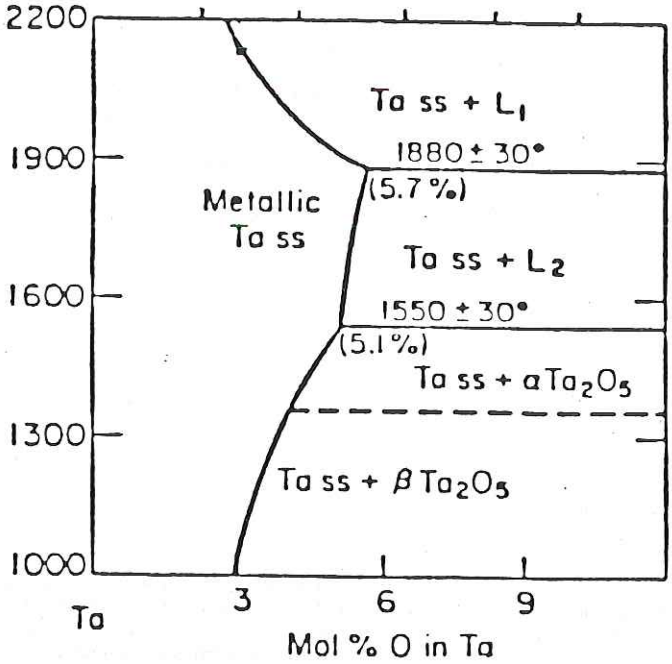


As an example of a demand arising for existing products in new markets, high-purity Ta_2O_5 and Nb_2O_5 are in demand for optical modulators. And in existing markets, existing products are in demand in new ways and new products are in demand as substitutes for existing products. Some examples : high-purity Ta_2O_5 and Nb_2O_5 are being used in optical lenses; and co-precipitated materials such as BZNT and PZNT, which contain Ta and Nb, are being used as ceramic raw materials in microwave dielectrics. (BZNT is an oxide of the four elements, barium, zinc, niobium and tantalum; PZNT is an oxide of lead, zinc, niobium and tantalum). New applications for tantalum and niobium are being developed : some examples are NbTi for superconductors; Nb, NbN and Nb_3Ge for Josephson devices; and high-purity Ta and TaSi as LSI-gate electrode materials. Similar good prospects are in store for carbides as the demand for cemented carbide cutting tips is rising. The consumption of pure TaC for cutting tips is falling, whereas the demand for TaC in complex carbides (WC-TiC-TaC) or for cermets is rising.

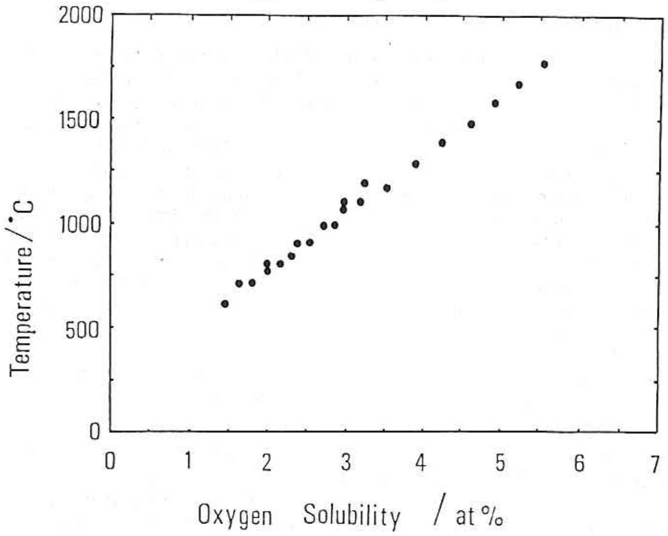
Consumption trend for TaC



Ta-O phase diagram



Oxygen solubility in Ta



CONCLUSIONS

The tantalum and niobium industries have to deal with raw material, technology and marketing problems. But both metals have excellent properties that no other material can replace and so processors must continue in every way possible to provide customers with a steady supply of tantalum and niobium products at competitive prices. Maximum effort must be expended to perfect ultra-high purification and ultra-fine pulverization technologies so that the need for high-quality products can be satisfied. Finally, new demands for such products should be investigated.

Behavior of oxygen in tantalum

This paper was presented by Dr Hiroaki Wada of Showa Cabot Supermetals at the T.I.C. meeting held in Kobe on May 20th 1986. Considerable editing has been necessary to meet the requirements of the Bulletin and in particular all discussion of scientific formulae has been omitted. Any reader with an interest in this field can obtain an unedited copy of Dr Wada's paper from the T.I.C.

As the tantalum crystal has a strong affinity for oxygen, tantalum powders readily absorb a considerable amount of oxygen from the environment. The surface of tantalum is covered with an oxide film of about 40 atomic layers, and so the oxygen content of Ta powder increases with decreasing particle size. About 30 000 ppm oxygen is contained in the normal-grade powder whose size is several μm in diameter.

It has been reported that non-metallic atoms, such as boron, carbon, nitrogen, phosphorus or sulfur, and metallic atoms, such as vanadium or nickel, when added to tantalum, improve the electrical, thermal and mechanical properties of the capacitor, but oxygen atoms decrease these properties. Therefore, it is very important to understand the behavior of oxygen in tantalum when we use the powder as the starting material for capacitors.

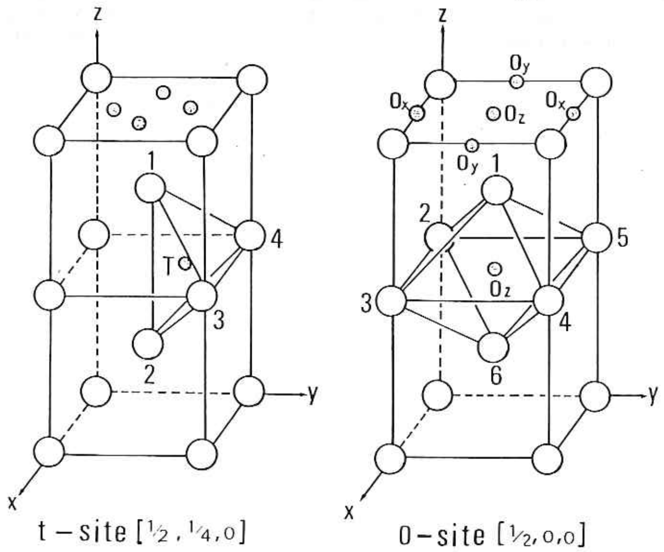
PHASE DIAGRAM OF OXYGEN-TANTALUM SYSTEM

The phase diagram of the oxygen-tantalum system has already been studied, but measurements of oxygen solubility have not been made in the low temperature region. Values of oxygen solubility at temperatures lower than 500°C must be obtained by extrapolation from high-temperature data.

MIGRATION OF OXYGEN IN SOLID SOLUTION

When non-metallic atoms with small radii, such as hydrogen, carbon and nitrogen, are dissolved in metals, they occupy interstitial lattice sites. In tantalum, whose structure is body-centered cubic, two different kinds of site can be distinguished : octahedral and tetrahedral interstices (o- and t- sites).

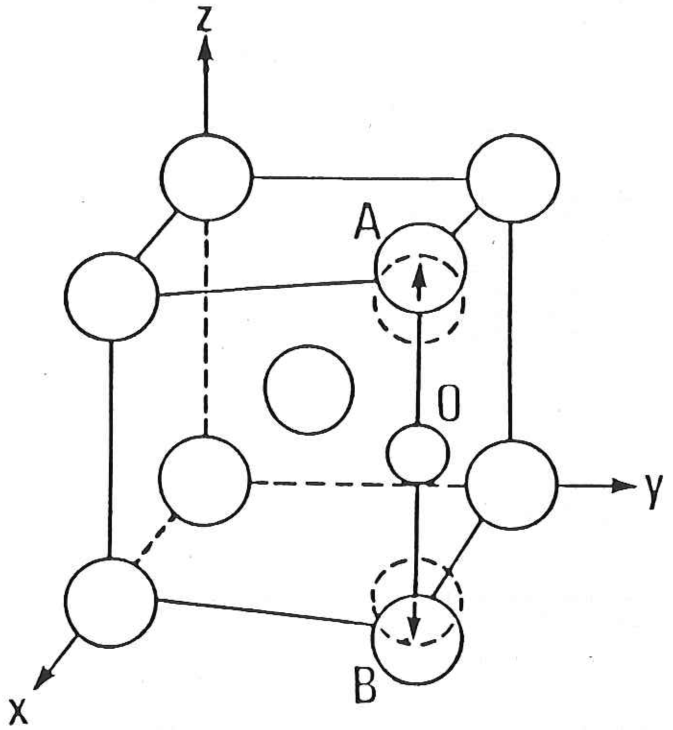
Ta crystal unit cell with sites of interstitial oxygen



It is often proposed that solute nitrogen and oxygen in the Ta crystal occupy o-sites of which there are three, x, y, z-sites, all equivalent in potential level under stress-free conditions.

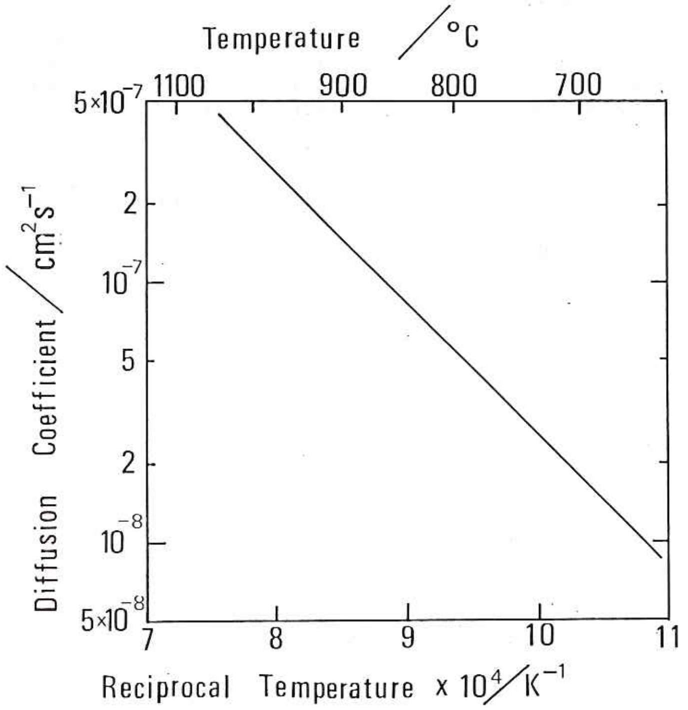
The lattice parameters of tantalum are markedly increased by the dissolution of nitrogen or oxygen. The local distortion created by interstitials can be discussed using the theory of elasticity. In BCC structures, interstitially-dissolved atoms create local distortions of the tetragonal symmetry and, with the aid of this concept, some phenomena observed in Ta which contains dissolved oxygen can be understood. For example, internal friction is caused by the relaxation of interstitial defect oxygen in a periodically changing stress field. The internal friction causes a damping of macroscopic vibrations : this damping is related to non-elastic behavior. This means that as a result of an external stress, in addition to the elastic strain, an inelastic strain occurs caused by lattice imperfections such as interstitially or substitutionally dissolved atoms, vacancies, dislocations and grain boundaries.

Distortion due to solute oxygen

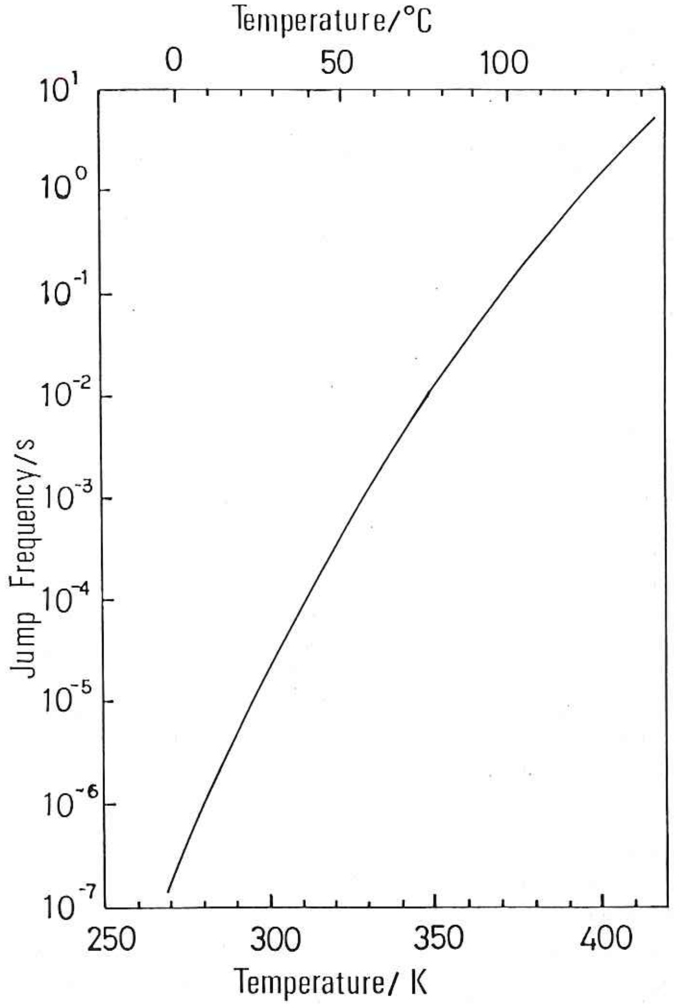


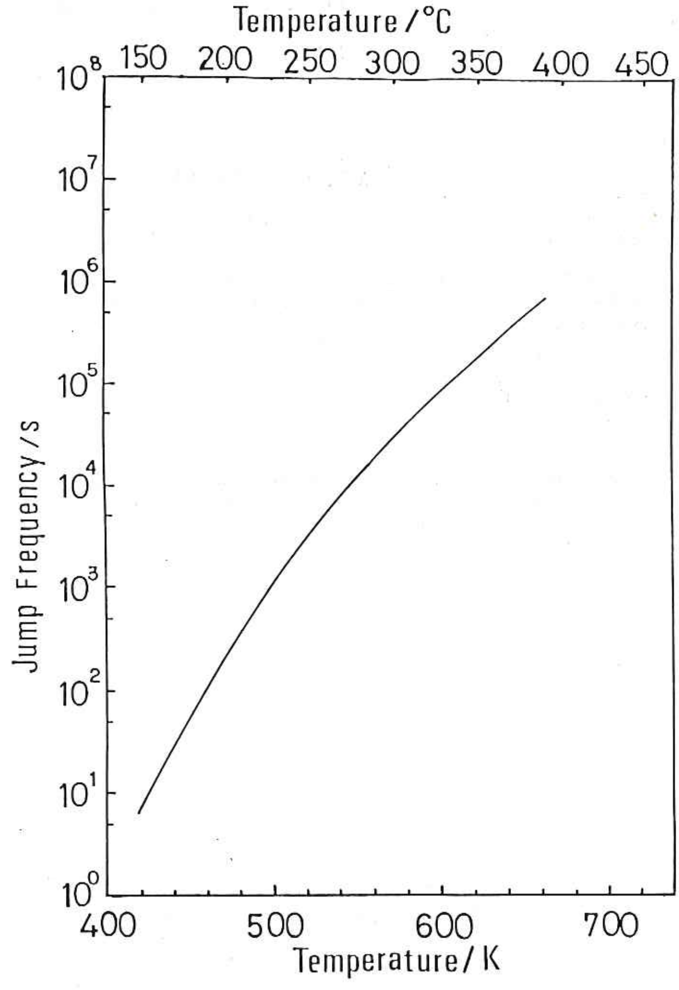
In the BCC lattice of Ta, oxygen atoms occupy octahedral sites and cause distortion of tetragonal symmetry. Three types of octahedral interstice exist as mentioned previously, so, if there are no external stresses, each of the three types of site is occupied by one-third of the interstitials.

Diffusion coefficient of oxygen in Ta



Temperature dependence of jump frequency of oxygen in Ta





However, if an uniaxial tensile stress is applied in the z-direction, for example, then the z-edge of the crystal is elongated, and the z-sites are favoured energetically. Therefore, the number of occupied z-sites rises while the number of occupied x- and y-sites decreases. This redistribution of interstitials results in an additional elongation in the z-direction occurring after instantaneous initial elastic elongation.

The diffusion coefficient of solute oxygen in Ta is shown below, together with the temperature dependence of the jump frequency of oxygen.

The jump frequency at 200°C is more than 10^7 times that at 27°C : this remarkable increase in jump frequency may be responsible for the degradation in life properties of the tantalum capacitor when used in the high-temperature range, 150°C to 250°C.

(to be continued in Bulletin no. 48)

T.I.C. Statistics

Price Waterhouse report the following collected data :

QUARTERLY PRODUCTION ESTIMATES

(in lb Ta_2O_5 contained)

LMB quotation :	*US $ 30*	*US $ 40*	*US $ 50*
2nd quarter 1986	357 965	424 915	548 015
3rd quarter 1986	357 965	439 915	563 015
4th quarter 1986	372 965	459 915	583 015
1st quarter 1987	367 965	454 915	588 015
2nd quarter 1987	367 965	464 915	628 015

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

PRODUCTION AND SHIPMENTS

(in lb Ta_2O_5 contained)

1st quarter 1986

Category	*Material grade*	*Production*	*Shipments*
A/B	Tin slag	236 367	98 866
C/D	Tantalite under 25 % & over 25 % Ta_2O_5	37 560	68 776
F	Other materials	0	0
		273 927	167 642

Notes :

1. In accordance with the rules of confidentiality, categories A and B, and C and D, 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 17/20; the statistics given above include reports from these producers :
   Datuk Keramat Smelting
   Greenbushes
   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 124 179 lb tantalum (after processing).

PROCESSORS' SHIPMENTS

(in lb tantalum contained)

1st quarter 1986

Products	*Shipments*
Ta_2O_5/K_2TaF_7	23 448
Alloy additive	29 044
Carbide	130 364
Powder/anodes	180 769
Mill products	69 742
Scrap, ingot, unworked metal and other	60 625
	493 992

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 16/18; 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

Capacitor Statistics

JAPANESE TANTALUM CAPACITOR PRODUCTION AND EXPORTS

(thousands of units)

	Production	*Of this, exports*
1st quarter 1986	526 587	107 301

(Data from JEIDA)

U.S. TANTALUM CAPACITOR SHIPMENTS

(thousands of units)

1st quarter 1986

	US Shipments	*Exports*	*Total*
Foil	130	3	133
Metal cased	12 683	3 811	16 824
Non-metal cased	50 421	10 852	61 273
Chips	6 146	522	6 668
Wet slug	802	113	915
Total	70 512	15 301	85 813

(Data from EIA)

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