TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

BULLETIN Nº 48 OCTOBER 1986 FOURTH QUARTER

Twenty-sixth General Assembly and associated meeting

The meeting will be held on **Friday October 24th 1986** at the Ramada Hotel, Brussels, and will be preceded by a cocktail party on the evening of October 23rd, also at the Ramada Hotel.

PROGRAMME

9.30 a.m. Twenty-sixth General Assembly of the T.I.C., in the Bruxelles/St. Gilles room, for delegates of member companies.

10.30 a.m. Coffee break. Delegates of non-member companies join the meeting.

11 a.m. **Technical presentations**
Prof Dr Hugo M. Ortner, Metallwerk Plansee : "Ultrapure Refractory Metals — Facts and Fiction".
Dr K. Schulze, Max-Planck-Institut für Metallforschung : "Production of pure niobium and its possible applications".

12.30 p.m. Lunch.

2 p.m. **Panel discussion** on the topic :
"What influence do recent developments in tin have on the present and future tantalum supply".
Delegates who have agreed to join the panel are : Mr Rod Tolley (Datuk Keramat Smelting), Mr John Linden (Greenbushes), Mr Egberto Silva filho (Mamoré Mineração e Metalurgia), Mr Michael Herzfeld (Sominki), Mr Jaap Langenberg (Thailand Smelting and Refining) and Mr Noel Cook (Willan-Wogen Alloys).
Everyone present will have the opportunity to contribute to this exchange of views.
The meeting will end at about 4 or 4.30 p.m.

TWENTY-SIXTH GENERAL ASSEMBLY TO BE HELD AT 9.30 A.M. ON FRIDAY OCTOBER 24TH 1986 AT THE RAMADA HOTEL, BRUSSELS

AGENDA

1. **Voting proxies.**
2. **Address by the President of the T.I.C., Dr C. Hayashi, Vacuum Metallurgical Co.**
3. **Minutes of the Twenty-fifth General Assembly (held in Kobe, Japan, on May 20th 1986).**
4. **Membership : applications, resignations.**
5. **Financial matters : approval of audited accounts for the year ending June 30th 1986.**
6. **Report of Executive Committee.**
7. **Report of Technical Officer.**
8. **Statistics.**
9. **Statutory elections.**
10. **Forthcoming General Assemblies.**
11. **Other matters.**

President's letter

There are only a few months left in this year. The Twenty-fifth General Assembly has closed and the Twenty-sixth is just around the corner.

Recently, there has been no good news about the tantalum business in Japan. As you know, the economic situation in Japan is hardly fluctuating due to the Japanese yen strength in foreign exchange. Without exception, tantalum usage is influenced, and the demand from capacitors will change in 1987.

One of the biggest usages for tantalum in Japan is still for capacitors. For your information, let me show you the data from which you can compare production output for the period from January to May 1986 with that of January to May 1985. You cannot see any big change; however, a slight decline can be seen. Therefore, our supply of tantalum powder and wire is slightly decreasing.

Capacitor output

	A : 1986 (Jan.-May)	B : 1985 (Jan.-May)	A/B
Quantity (thousand pieces)	884 187	937 645	94.3 %
Value (million yen)	18 272	21 981	83.1 %

We are especially anxious about the trend in 1987 of the market and price for tantalum. It would be significant if we could discuss the forecast of tantalum demand for 1987 at the coming meeting.

Detailed information has been sent to members from the T.I.C. office in Brussels.

I am looking forward to seeing each of you soon.

Sincerely yours,
C. Hayashi
President

The Niobec mine

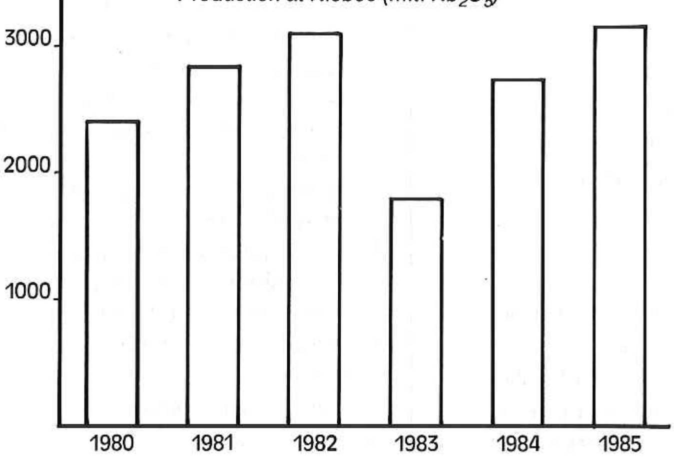
Niobec Inc., the world's second-largest primary producer of niobium, exploit a carbonatite deposit 525km north of Montreal, Quebec. Construction of the underground mine began in 1974 and was completed two years later. The initial production capacity of 5.5m lb Nb_2O_5 per year was expanded to 7.0m lb in 1981. This article is based on information gained from a visit to the mine-site by the T.I.C. Technical Officer earlier this year.

The underground operations consist of a three-compartment shaft, 1200 feet deep. Current production is from working levels at 300, 450 and 600 feet with levels under development at 700, 850 and 1000 feet. The established ore reserves of about 11m tonnes are equivalent to 14 years of current production, but ultimate reserves could be sufficient for the mine to operate well into the next century. Ore grades range from 0.6 to 0.7% Nb_2O_5 with an average grade of 0.63% Nb_2O_5. Most of the niobium is contained in pyrochlore minerals although a proportion is in columbite. The concentration of the ore is performed by a multi-step flotation process, thought to be the most sophisticated single-product flotation circuit in operation. The final concentrate contains about 60% N_2O_5 with a recovery of about 65%. Through innovation, improvement and expansion, costs have been kept under close control with the result that the Niobec mine is an exceptionally efficient operation. Employment at the mine is about 175 people, approximately one-third each in mining, milling and maintenance-administration.

The mine was established as a 50/50 joint venture between the Teck Corporation, a diversified mining group with holdings in metals and energy resources, and Soquem, a Quebec Crown Corporation. Recently, the Quebec government has announced plans to privatise all the mining assets of Soquem, including their 50% ownership of Niobec Inc. Management of Niobec Inc. is performed by a nine-member committee.

Unlike tantalum, niobium is not a traded commodity, but sold through organised selling channels under long-term contract. Niobec has exclusive agreements with Continental Alloys (Luxembourg), Mitsui Mining & Smelting (Japan) and Shieldalloy (USA). The total world demand for niobium was 20 250 tonnes Nb_2O_5 (44.7m lb) in 1985, broken down into 7980 tonnes in Europe, 3680 tonnes in Japan, 5670 tonnes in North America and 2920 tonnes elsewhere.

Production at Niobec (m.t. Nb_2O_5)



Andrew Jones
Technical Officer

Perspectives on the development of the tantalum industry

This paper was presented by Mr Larry O'Rourke, Vice President of the Cabot Corporation, at the Kobe T.I.C. meeting on May 20th 1986.

A tabulation of presentations made to past T.I.C. General Assemblies reveals that these papers have covered the full range of members' interests. Some conclusions may be drawn about specific interests from the topics covered.

Prior to the 1978 Tantalum Symposium, the papers presented at meetings were quite broad, only generally informing about the specifics of the business. But once the communication block was broken at the Symposium, members have shared their knowledge generously. It appears, when looking at the presentations specific to tantalum, that concerns have involved two principal topics : "How to use tantalum" and "Where to get it from". There have been only three presentations on the processing of raw material to tantalum products. This lack of emphasis on processing, however, does not result from the reticence of processors as a study of the individual speakers reveals that 20 out of the 70 presentations have been made by representatives of processor companies.

To determine what the major influences have been on the industry, an inquiry was performed into the background of how the industry collectively views itself, specifically :

— What the most important events have been during the last twenty years to affect the business;

— Why, in terms of these specific events, the industry is where it is today;

— How these events will shape the future of the business.

PRESENTATIONS

MADE TO THE T.I.C.

1975 - 1986

SUBJECT	NO. OF PAPERS
T.I.C. STUDIES & STATISTICS	9
GENERAL ECONOMICS	6
TANTALUM - GENERAL	10
- SOURCE MATERIALS	16
- PROCESSING	3
- PRODUCTS	20
NIOBIUM	3
COMPANY SPECIFIC	3
	70

To accomplish these objectives, a number of knowledgeable persons and long-time associates in the business, who as a group represent a true cross-section of the industry from miner to fabricator, were asked to provide their perceptions as to what forces and events have had the greatest influence in changing the structure of the business over the past 20 years.

First, however, a background of the tantalum business for the last 20 years is useful. In the late 1960's the major applications of tantalum were well-defined; tantalum was being used in cutting tools, capacitors, chemical equipment and as an alloy additive. The revolutionary developments of the 1950's, sodium reduction and electron-beam melting, were being widely used. The tin-related sources of raw material in South America, Europe, Africa, South-East Asia and Western Australia were yielding by-product tantalite and slag. The process for upgrading low-grade slag was being used to produce significant quantities of source material.

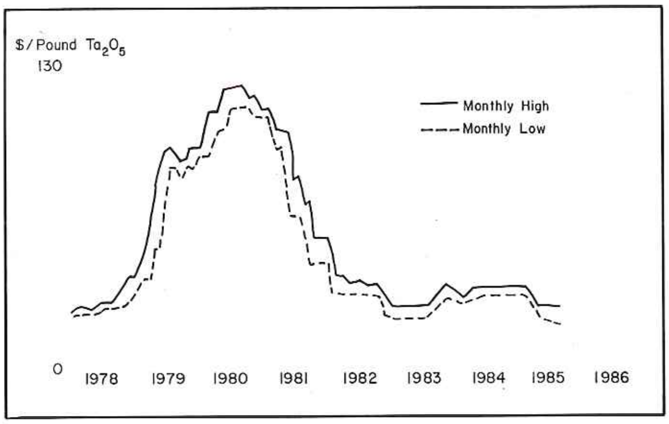
So the tantalum industry today is not much different in its markets, material sources or processing procedures from 20 years ago. The framework of change has been the increase in the size of the business, both in the volume of product and the number of active participants. Thus, an observer might say that the past 20 years have seen few dramatic excursions. Members of the tantalum industry know better.

Worldwide tantalum demand and supply 1970-78 (000's lb Ta_2O_5)

	1970	1971	1972	1973	1974	1975	1976	1977	1978
Free World Demand	1960	1890	2220	2575	2910	1670	2600	2760	2900
Supply									
Production	2000	2140	2090	1725	1910	1865	2230	2440	2535
GSA Sales	160	10	110	325	1080	165	0	0	0
Total	2160	2150	2200	2050	2990	1970	2240	2440	2535
To Russia, Per Year	120	120	120	120	120	120	120	120	120
Net Supply	2040	2030	2080	1930	2870	1850	2120	2320	2415
Surplus (Shortfall)	80	140	(40)	(645)	(40)	180	(480)	(440)	(485)

Significant changes to the supply situation took place during the 1970's. Current production never quite matched requirements. Part of the shortfall was filled by sales of ore from the GSA Stockpile from 1973 through 1975. While these sales had the effect of helping to prevent price increases in 1974, the resulting low prices deterred exploration. Some processors foresaw the coming production shortfall and began to stockpile inventories, particularly slags from South-East Asia. The process to pyrometallurgically upgrade slags into "synthetic concentrates", containing 20-25% Ta_2O_5 suitable for direct chemical processing, has had an enduring influence on industry economics. Processor inventories, plus material already accumulated in tin slag piles and trader inventories, supplied the balance of demand and, given these ongoing stocks, the situation did not appear to be commercially dangerous in 1970. Yet it proved to be dangerous indeed.

LMB Quotation - 30% tantalite



From the second half of 1978, raw material prices, as reflected in Metal Bulletin tantalite quotations, exploded, reaching a peak in 1980 of approximately $150 per lb Ta_2O_5. It has been argued that there was not an actual shortage of tantalum to cause this price explosion, but at that time there were three very real factors which drove the price escalation.

First, there was the continuing failure of current production of both ore concentrates and useable slags to meet demand, resulting in continued inventory reduction. With the optimistic forecasts of market growth, even the low-grade slag accumulations in South-East Asia were recognized as a finite resource. It became evident that the reserves identified in Zaire, Canada and Egypt would require many years and high prices to develop and so processors found themselves in a bidding contest for material to protect their individual companies and customers.

The second important factor was a structural capacity situation within the processing industry. To achieve the higher throughputs demanded by the market with no time to increase capacity, the processors were forced to use scarcer materials with high Ta_2O_5 contents. The higher assay ore became a prized commodity with a limited supply.

A third factor was the linking of the pricing basis for slags to the Metal Bulletin tantalite price quotations which caused a powerful upward influence on all feedstocks.

Other factors contributed to the market condition. The slag upgrading facilities in West Germany reached capacity limits and the inherent lead times prevented their expansion. Then there was an unfounded concern over the future structure of Thailand's production, an increase in U.S. niobium requirements for aerospace applications, and the inevitable entry of traders to arbitrage the situation.

All of these threatening supply conditions inevitably led to reactions on the market side. Because of escalating prices, consumers began to substitute other materials, modify products, decrease tantalum content and recycle scrap. As a defensive measure to maintain a competitive position, processors greatly improved the quality of their products, particularly of capacitor powder. The net effect of all of these efforts has been about a one-third reduction in the demand for tantalum from the peak of 1979 to a reasonably stable level during the 1983-1985 period.

Worldwide tantalum demand and supply 1979-85 (000's lb Ta_2O_5)

	1979	1980	1981	1982	1983	1984	1985
Capacitors	1,977	1,767				1,340	978
Cemented Carbides	950	942				768	647
Mill Products	386	3,265	2,282	1,902	2,480	476	382
Alloy Additives	180	170				133	215
Other	-	-				594	523
Russia	120	120	120	120	120	120	120
Total Demand	3,595	3,325	2,400	2,020	2,600	3,430	2,865
Supply	2,840	2,820	2,250	1,930	1,650	1,500	1,400
Industry Stocks				11,000	10,050	8,120	6,655
Potential Supply		2,900	2,900	3,000	3,200	3,200	3,200
% Utilized		100	78	64	52	47	44

The downturn from 1979 was painful. Large inventories purchased at high prices burdened processors and traders with record interest rates compounding the effect. The mining sector of the industry now bears the burden of that over-supply scenario : the drop from 100% utilization of their materials in 1980 to under 50% in recent years was traumatic for the entire industry.

Tin slag inexorably produced as a low-cost by-product of tin production currently remains available, although it is being used at a reduced rate. Therefore, the ore concentrate producers with a far higher cost structure than the tin slag producers (tin smelters) will not have a viable market until stocks are further in balance. Both Tanco and Greenbushes have curtailed underground development until a more favorable climate emerges.

Yet events other than the price excursion have affected our industry and certainly some have had more impact than others. So what does the T.I.C. membership perceive these to be ?

The overall results of the survey show that the forces that have shaped the business are seen to be numerous, with a 55% vote of the respondents being the best any one item could muster. The responses most frequently presented are discussed below.

THE T.I.C.

This carries the highest proportion of responses – 55%. Prior to 1974, there was little communication among the segments of our business, but when Tanco and Thaisarco began to sell directly to processors, other producers recognized the benefits of direct communication. From this, the concept of the T.I.C. was born. Official statistics were unavailable or unreliable. The U.S. Bureau of Mines officially reported the main reserve to be in unstable Zaire. At that time, it occurred to Mr Herman Becker-Fluegel, involved with Tanco, that a worldwide forum was needed to provide a base of fundamental information. He investigated the special laws of Belgium permitting the incorporation of a study group and, with the co-operation of others, especially Mr Cor Herkstroeter of Billiton and Mr Louis Landa and Mr Paul Leynen of Geomines, formed the T.I.C., this group creating the bonding activities which assured active member participation and statistical reporting, also the quarterly Bulletins and General Assemblies.

Twenty years ago, very few, if any, persons had a good knowledge of the total business. No one could make a worthwhile forecast of the market, determine the adequacy of supply or even make knowledgeable statements about facets of the business outside their own particular interests. But we have now left behind our provincial attitudes and become truly cosmopolitan : the T.I.C. by providing the channels of communication has accomplished this.

EVENTS RELATED TO SOLID CAPACITORS

PRE-1965

* APPLICATION OF E.B. FURNACES
* APPLICATION OF SODIUM REDUCTION

1966

* ADVENT OF RESIN-DIPPED CAPACITORS

1970-72

* INTRODUCTION OF CAPACITANCE-RELATED PRICES FOR CAPACITOR POWDER
* BEGINNING OF WIDE-SCALE USE BEYOND MILITARY AND AEROSPACE

1980

* INTRODUCTION OF HIGH CV POWDERS

1985

* RAPID BUILD-UP OF DEMAND FOR CHIP CAPACITORS

SOLID CAPACITORS AND HIGH-CV POWDERS

These two factors are closely linked as the high-CV powders are the logical result of the demand of an expanding solid capacitor market. Although the solid capacitor was developed prior to the beginning of this twenty-year study period, only in the last fifteen years has the volume market been developed. The solid capacitor is widely recognized as the foundation of the tantalum business.

PRICE ESCALATION AND CONSERVATION

Once again, these two survey factors are discussed together as conservation was certainly a result of the price increase. The substitution by ceramic and aluminum capacitors in consumer electronic devices, the commercialization of coated carbide tools, the improvement of material utilization by fabricators and a number of other factors all made permanent changes in this consumption pattern. Even though the period of price escalation has ended, hopefully for all time, its effects remain.

USE OF UPGRADED TIN SLAGS

On more than one occasion the seemingly unlimited piles of low-grade slags have rescued the business from even worse supply crunches than have occurred. But the slags alone would have been useless without the persistence of the companies which developed the upgrading process needed to convert these slags into useable material.

LOW-GRADE TIN SLAGS

1950's: U.S. NATIONAL STOCKPILE ACQUISITIONS

- * CHEMICAL UP-GRADING IN U.S.
  - SINGAPORE SLAGS
  - NIGERIAN SLAGS & LOW TA COLUMBITES

1960's: PROCESSOR INVENTORY BUILD-UP

- * PYROMETALLURGICAL UP-GRADING IN EUROPE
  - PENANG SLAGS

LATE 1970's: TIGHT SUPPLY CONDITION WITH HIGH PRICE

- * INCREASED UP-GRADE CAPACITY IN EUROPE
  - PENANG SLAGS
  - THAI SLAG DUMPS
  - SINGAPORE DUMP
- * RECOVERY OF STRUVERITE FROM TIN DUMPS
  - MALAYSIA AND THAILAND

NEW SOURCES OF SUPPLY

The development of Canadian and Thai sources (Tanco and Thaisarco) in the late 1960's was essential to the rapid expansion of the solid capacitor market from 1970 to 1974. Without sufficient supply to support the demand, this growth would have probably not occurred. The Greenbushes development in the early 1980's played exactly the same role in the overall tantalum business as Tanco in 1969-1970. Potential supply sources exist from mineral deposits in Brazil, Greenland, Egypt and Canada.

ADDITIONAL EVENTS OF IMPORTANCE

The survey respondents offered numerous individual events that seemed most important to them. These included : GSA buying and selling activities; the use of capacitors in computers; the effect of ITC export controls; the internationalization of the industry; Thai processing development (TTIC); the lack of volume-related new applications over the period; availability of niobium oxide from pyrochlore; acquisition of U.S. processors by larger companies; and the growth of markets for metal products and alloy additive. Although each of these events has had an effect on the business in some way, they clearly were not universally perceived to be dominating influences.

SURVEY CATEGORIES

To discover the percentage of respondents who emphasized various factors, the replies have been categorized into five fundamental areas : general, market, processing, supply and future. Looking through these factors for percentage of replies, emphasis on the factors previously detailed can be deduced.

GENERAL FACTORS	% REPLIES
* T.I.C.	55%
* TPA	10%
* GOVERNMENT INVOLVEMENT	15%

MARKET FACTORS	% REPLIES
* SOLID CAPACITORS	50%
* PRICE ESCALATION	45%
* CONSERVATION	35%
* NIOBIUM USEAGE	10%

PROCESSING FACTORS	% REPLIES
* HI CV POWDERS	50%
* SLAG UP-GRADING	45%
* NA-REDUCTION & EB MELTING	20%

SUPPLY FACTORS	% REPLIES
* LOW GRADE SLAG	45%
* GREENBUSHES	40%
* LMB QUOTATION USE	25%
* THAI SOURCE DEVELOPMENT	25%
* TANCO DEVELOPMENT	20%

FUTURE FACTORS	% REPLIES
* TIN MARKET STABILITY	25%
* NEW RESOURCES	45%
* FORWARD INTEGRATION	15%

Finally, one other matter may be of interest. The respondents can be put into four groups :

- Producers (miners and tin smelters);
- Merchants or traders;
- Processors (convertors of concentrates and slags into useful products);
- Consumers (the manufacturers of capacitors, cutting tools, alloys and chemical equipment).

	Producers	Merchants	Processors	Consumers
Market Factors				
Solid Caps	50%	0%	70%	70%
Price Escalation	60%	30%	70%	0%
Conservation	25%	0%	60%	35%
Niobium Use	0%	0%	30%	0%
Processing Factors				
HI CV Powder	40%	35%	70%	70%
Slag Upgrading	50%	30%	90%	30%
Na - Red & EB Melt	25%	0%	30%	0%
Supply Factors				
Low Grade Slag	50%	30%	75%	30%
Greenbushes	60%	0%	40%	0%
LMB Quotation Use	50%	0%	30%	0%
Thai Sources Devel.	40%	0%	30%	0%
Tanco Development	40%	0%	30%	0%
Future Factors				
Tin Market	25%	100%	0%	0%
New Resources	75%	35%	70%	0%
Forward Integr.	25%	30%	0%	0%

SURVEY RESULTS
MAJOR FORCES AND EVENTS
IN THE TANTALUM BUSINESS
1966 - 1986

	REPLIES FROM			
GENERAL FACTORS	PRODUCERS	MERCHANTS	PROCESSORS	CONSUMERS
* T.I.C.	75%	0%	70%	30%
* TPA	0%	0%	30%	0%
* GOV'T INVOLV.	25%	0%	0%	0%

These show the proportion of each group which enumerated the principal events. Each respondent could be quite parochial, although a significant commonality of feeling between the producers and processors seems to exist, both feeling they have benefited most from the T.I.C. Only the processors recognize the influence of the TPA, undoubtedly due to the fact that the TPA is an association of U.S. processors only.

CONCLUSION

It is hoped that this survey exercise has provided an internal perspective of the T.I.C. membership helpful to all in managing the events of the future so that the tantalum business will remain stable and progressively improve.

Behavior of oxygen in tantalum

(Continued from Bulletin N° 47)

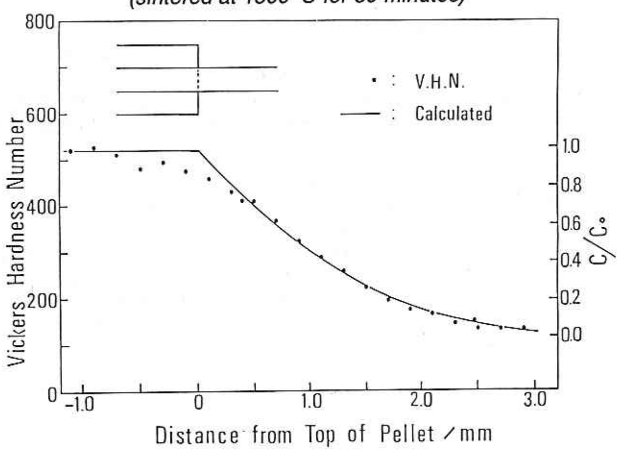
DIFFUSION OF OXYGEN

When tantalum wire is embedded in the powder pellet for a capacitor, it is often proposed that the oxygen in tantalum is responsible for cracking of the wire sintered at temperatures higher than 1400°C. The oxygen content of the wire is usually about several tens ppm and about 40 000 ppm in the tantalum powder, so that the oxygen in tantalum diffuses from powder to wire during the sintering. For a cylinder, e.g. wire, the diffusion process is complete when $Dt/L^2 = 1$, where L is the cylinder radius. This is very convenient for a rapid estimate as to whether a diffusion process occurs slightly or significantly or goes to thermal equilibrium.

A tantalum wire of 0.15 mm radius, embedded in a pellet, was sintered at 1500°C in vacuum. Taking the diffusivity (D) of oxygen in Ta as 5.9×10^{-6} cm² /s, the time (t) required to thermal equilibrium can be estimated as 38 seconds. The pellet size is large compared to the wire so the average oxygen concentration may be almost constant even if oxygen diffuses from the Ta pellet to the wire.

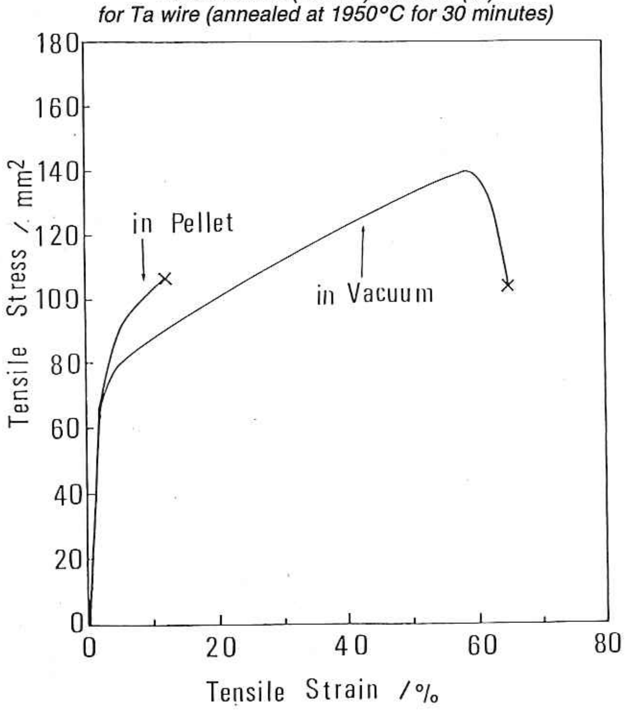
The hardness of the wire in the pellet sintered at 1500°C for 30 minutes was measured : the results are demonstrated graphically below. It was found that the distribution of hardness along the wire axis agrees very well with that of oxygen concentration calculated by the laws of diffusion. Therefore, the hardness of the wire is proportional to the oxygen concentration.

Hardness profile of Ta wire in pellet (sintered at 1500°C for 30 minutes)



The stress-strain curves of tantalum wire at room temperature which has been annealed at 1950°C for 30 minutes are shown below. The specimen annealed in vacuum could be deformed more than 55 % in tensile strain and exhibited a very ductile fracture. The specimen annealed in the pellet, however, showed brittle fracture with only 10 % in tensile strain. The ductile fracture was intergranular and the brittle fracture intercrystalline.

Tensile stress (N/mm²) vs strain (%) for Ta wire (annealed at 1950°C for 30 minutes)



As shown previously, the hardness of the wire in the pellet sintered at 1500°C for 30 minutes is proportional to the oxygen content. The excess oxygen above the solubility limit precipitates as tantalum oxide during furnace cooling. The plastic deformation in the wire is induced by dislocation motion, the following mechanisms being considered for the resistance against the dislocation motion : Cottrell locking, precipitation hardening and solid solution hardening. Among these mechanisms, the contribution to hardening from solid solution oxygen is very small because of the very low solubility at room temperature. Cottrell locking makes a very strong contribution to the hardening. Precipitation hardening is important because of the large amount of oxide. Therefore, the hardening proportionality to the oxygen concentration can be explained by the Cottrell locking and precipitation hardening mechanisms.

When impurity atoms segregate along crystal grain boundaries, the grain boundary strength can either be increased or decreased. Oxygen atoms in tantalum segregating along the grain boundaries decrease the grain boundary strength, the following mechanisms being proposed to explain the phenomena :

- The cohesive strength between oxygen atoms is smaller than that between tantalum atoms. So when the oxygen atoms segregate along the tantalum grain boundaries, the cohesive strength of the grain boundaries decreases and intercrystalline cracking is induced.
- The oxygen atoms segregated at grain boundaries are supposed to form a layer of covalent bond character with tantalum atoms. Then the tantalum atomic bonding in the neighbouring metal layers is weakened as a result.
- The distortion of the crystal lattice along grain boundaries increases with increasing misfit angle up to 45°. Probability of fracture at grain boundaries is very high at the large-angle boundaries compared with small-angle boundaries. The mechanical strength of the oxide of tantalum is weak, so if the thin films of oxide are formed along grain boundaries, then intercrystalline cracking may be induced.

To suppress intercrystalline cracking in tantalum wire the segregation of oxygen must be suppressed during sintering. One way is to introduce elements which have a higher affinity with oxygen than tantalum does, so using the internal oxidation or scavenging effect. Oxide formed by internal oxidation is normally so stable, even at high temperatures, that it may suppress crystal grain growth during heat treatment. The mechanical strength of polycrystalline materials increases with decreasing crystal grain size.

DEOXIDATION

Suitable deoxidation agents for tantalum are Al, Ca, Mg, Th, Ti, Si and Zr. One disadvantage with these deoxidants, however, is that the oxide remains on the tantalum crystal surface and must be removed by acid leaching before the material can be used. Gases of H_2 and Na are sometimes used as the deoxidizing agents : H_2O and Na_2O can be removed from the outside of the furnace during the deoxidation treatment.

When the deoxidation treatment is conducted for tantalum powder, the following processes are considered as the rate-controlling steps :

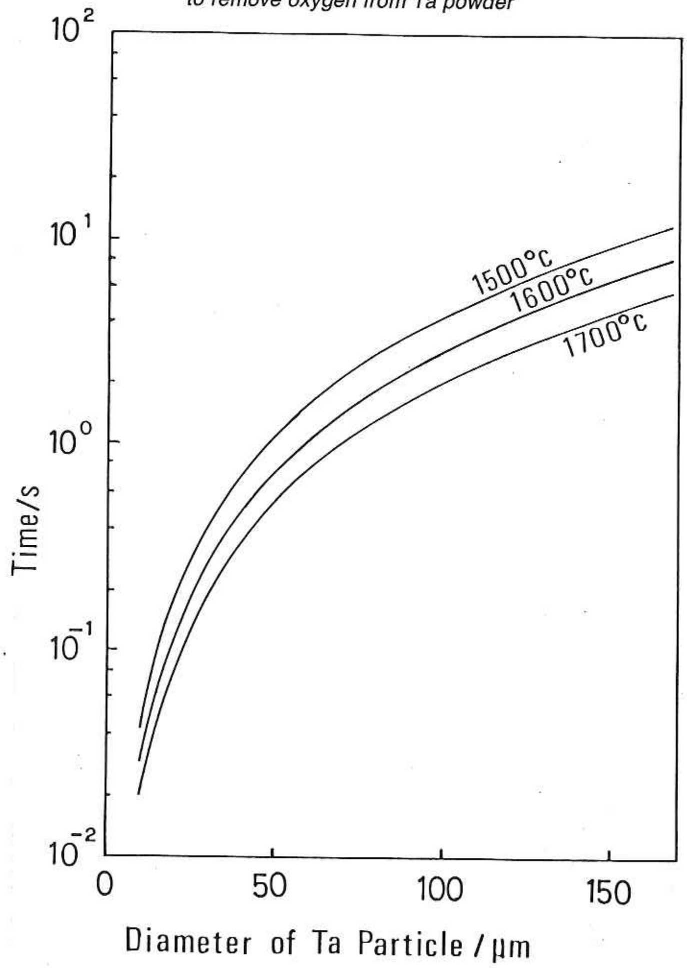
- diffusion rate of solute oxygen;
- resolution rate of oxide;
- deoxidation reaction at the particle surface;
- efficiency of exchange between reductive gas and oxidation product.

The rate of deoxidation is so fast at high temperatures that the surface reaction is not the rate-controlling step. As the mean free path and mean velocity of H_2 and H_2O or Na and Na_20 gases at high temperatures are large, the exchange between these gases in the powder is probably very effective. Therefore, the first two mechanisms are the most likely main rate-controlling steps.

When the oxygen content is less than the solubility limit, the rate-controlling mechanism is the diffusion rate of solute oxygen. It can be demonstrated that the time required for complete deoxidation is a function of powder particle size.

When the oxygen content is higher than the solubility limit, the purification rate is determined by the processes of diffusion of solute oxygen and of resolution of tantalum oxide. The oxygen content is less than the solubility limit towards the outside of a powder particle and higher towards the center. The interface between these two regions moves to the center of the particle in the progress of deoxidation, and so as the loss of oxygen toward the outside of the particle by diffusion is supplied equally from the oxide, the change in oxygen content in the outside region is very slow. Consequently, it can be assumed that the region is in a quasi-stationary state.

Particle size dependence of time necessary to remove oxygen from Ta powder



TTIC plant fire

The damage caused by fire to the newly constructed plant of the Thailand Tantalum Industry Corporation (TTIC) in June will mean that the start-up planned for October this year will not now take place. Although press reports have stated that there would be no reconstruction at the old site on Phuket Island, it would seem unlikely that any definite decisions on the future of the project will be taken until negotiations have been completed between all the interested parties : International Finance Corporation, Hermann C. Starck, the Thai government and the TTIC themselves. Also, there is the question of insurance claims to be dealt with.

Construction commenced in 1984 and was nearing completion before a fire destroyed a large part of the processing facility but left the civil structure largely intact. Built with $25m of IFC money, the plant was to process Thaisarco tin slag into intermediate products : tantalum and niobium oxides and potassium fluotantalate, at a capacity of 660 000 lb Ta_2O_5 per year. Hermann C. Starck, supplying technology, were to take 50% of the production with Mitsubishi Corporation also reportedly interested in a quantity of potassium fluotantalate. The processes to be used were the same as are employed throughout the tantalum industry : hydrofluoric acid digestion followed by liquid-liquid extraction with MIBK. Construction of the smelter for converting low-grade tin slag into so-called "synthetic concentrates" (as reported in "Current status of the Thailand Tantalum Industry Corporation", Bulletin N° 35) had not been started.

Recent progress in high-field superconductor research in Japan

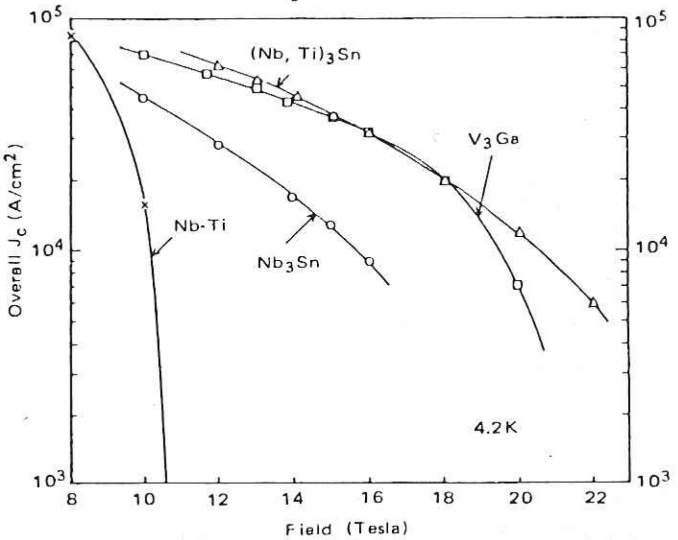
This paper was presented at the Kobe T.I.C. meeting by Dr Kyoji Tachikawa of Tsukuba Laboratories, National Research Institute for Metals (NRIM).

Recently, multifilamentary Nb_3Sn, $(Nb,Ti)_3Sn$ and V_3Ga have achieved commercial status, and 15T-class magnets have been successfully constructed using these superconductors. Now, superconducting materials with different crystal structures having superior performance to Nb_3Sn and V_3Ga are being developed as the next generation superconductors. However, these advanced superconductors can not be synthesized by the bronze process which has been applied to Nb_3Sn and V_3Ga. Thus, the development of new fabrication processes is proceeding. In this article some of the recent researches in Japan on the development of practical and emerging high-field superconducting materials are reviewed.

PRACTICAL SUPERCONDUCTORS WITH IMPROVED HIGH-FIELD PERFORMANCES

Studies on Ti additions to the CuSn matrix and Nb core in bronze-processed Nb_3Sn conductors were performed at NRIM. This method is the most effective and economical way of improving B_{c2} and J_c at high fields. The optimum Ti concentration to be added to the bronze or Nb core is 0.4-0.5 at% or 2-3 at%, respectively.

Overall J_c versus B curves for multifilamentary NbTi, Nb_3Sn, $(Nb,Ti)_3Sn$ and V_3Ga conductors



Multifilamentary Nb_3Sn conductors with Ti added to the matrix have already been used for the construction of several high field superconducting magnets in Japan. An example is a 180mm-bore, high-stability Nb_3Sn/NbTi magnet which has been excited up to a central magnetic field of 14.2 T with a current of 1180 A. The specification of the $(Nb,Ti)_3Sn$ conductor used for this magnet is as follows : width 9.5mm, thickness 1.8mm, number of Nb filaments 125 987, filament diameter 5μm, Ic (at 16T) 1700A.

Internal diffusion processed Nb_3Sn conductors with Ti additions to the Sn core and Nb filaments are being developed at NRIM in collaboration with Mitsubishi Electric Co. The composite wire is easily drawn down to the final size without intermediate annealings. The wire, with Sn-4.8 at% Ti core and 5.6μm diameter Nb filaments, shows overall J_c of 3×10^4 A/cm^2 at 16T after reaction at 675°C for 168 hours.

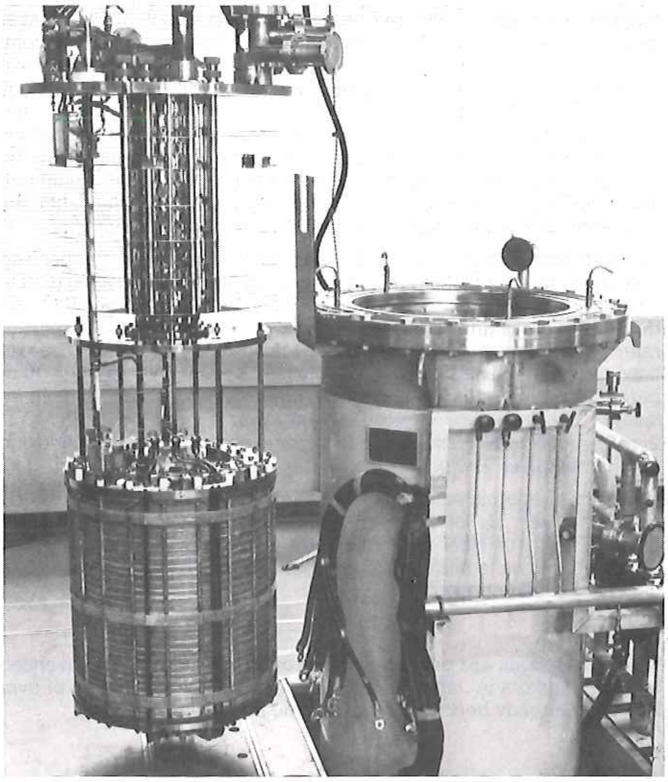
The Nb tube method has a few advantages compared to the conventional bronze method, such as no intermediate annealings, high tin concentration and no diffusion barrier. The wire, fabricated at Toshiba and Showa Electric Wire & Cable Co., using Nb-1.9 at% Ti tube shows an overall J_c (without Cu) of 7.4×10^4 A/cm^2 at 15T after the heat treatment at 725°C for 240 hours. This extremely high overall J_c is mainly due to the small areal fraction of the bronze.

The infiltration process using SnTi alloy cores has also been studied. The sintered Nb was infiltrated with Sn-9.0 at% Ti alloy at 700°C and fabricated into a tape. The tape, after being heat treated at 950°C for 15 minutes, showed an overall J_c of 3.2×10^4 A/cm^2 in a parallel field of 16T.

V_3Ga tape produced by the surface diffusion process shows the largest overall J_c in the field range of 15-18T among practical superconductors and has been used for winding the insert pancake magnet of a 180mm-bore 14.2T $(Nb,Ti)_3Sn$/NbTi magnet. The insert magnet has generated an incremental 3.9T with an excitation current of 130A. The magnet was wound by Hitachi Ltd. and installed at NRIM.

The in-situ process is a much simpler one because most of the intermediate annealing in the conventional bronze process is eliminated. Also, the in-situ processed conductors show superior mechanical properties to the bronze processed ones. In Japan, studies have been made on in-situ processed V_3Ga and Nb_3Sn. With this process, a homogeneous and fine distribution of V or Nb fibers in the Cu alloy matrix is essential. To achieve this, a special consumable electrode for arc melting is prepared to make CuV and CuNb ingots. These ingots were cold-worked to thin tapes followed by coating of Ga and Sn and subsequently heat treated to form V_3Ga and Nb_3Sn fibers in the matrices. Typical overall J_c's for the in-situ V_3Ga tape is 5×10^4 A/cm^2 at 16T and 4.2K. The in-situ processed V_3Ga tape has been used in the outer section of the insert of the 18.1T magnet.

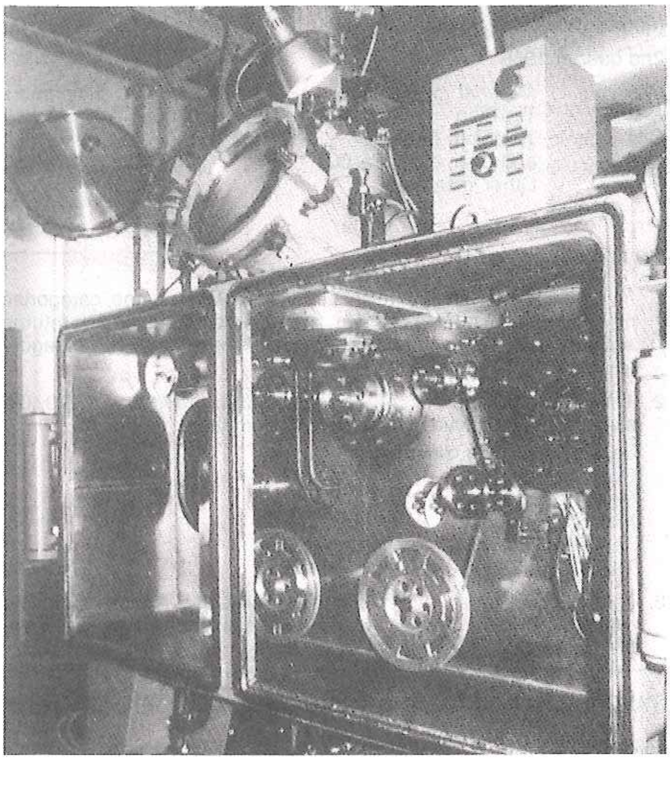
18.1T superconducting magnet at NRIM



EMERGING MATERIALS AND NEW FABRICATION PROCESSES

The rapid quenching technique from the liquid state is useful for the preparation of Nb_3Al, $Nb_3(Al,Si)$ and $Nb_3(Al,Ge)$. Liquid quenching on a hot Cu substrate improves wettability between the melt of high melting point materials and the substrate, resulting in a higher cooling rate than that by conventional quenching techniques. The $Nb_3(Al, X)$ supersaturated BCC solid solution phase produced in this way transforms to A15 phase after annealing above 800°C. This A15 phase has grain size of only a few hundred angstroms leading to a large J_c in high magnetic fields.

Continuous molten alloy quenching facility for producing composite tapes of high-performance superconducting materials and Cu



Continuous irradiation of high-energy beams, such as electron and laser, on to a moving tape enables successful high-temperature, short-time annealing. This is expected to result in rapid localized quenching leading to the retention of stoichiometric A15 phase, stable only at high temperatures. As starting materials, Nb_3Al and $Nb_3(Al,Ge)$ micro-composite tapes were prepared by powder metallurgical techniques. Electron beam irradiation at 300-500W or laser beam irradiation at 1-2kW have been performed on the micro-composite tape moving at a speed of 10-20cm/s. T_c's above 17.0K have been obtained after the irradiation and can be increased by 1-2K by annealing at 700-750°C. Maximum T_c's attained for Nb_3Al and $Nb_3(Al,Ge)$ tapes are 18.4K and 19.8K, respectively. These values are appreciably higher than those of the specimen prepared by the powder metallurgical process using conventional heat treatment. The overall J_c's for Nb_3Al and $Nb_3(Al,Ge)$ tapes annealed after the irradiation are nearly constant up to 23T, exceeding 10^4 A/cm^2.

The A15-phase Nb_3Ge compound with high T_c has been synthesized only by deposition techniques, i.e. chemical vapour deposition (CVD), vacuum evaporation and sputtering. The CVD process seems to be the most promising because it has the largest Nb_3Ge growth rate. There are, however, many deposition parameters, such as gas flow rate and mixing ratio, tape moving speed and reaction temperature, which must be precisely controlled to obtain a uniform layer. The synthesis of Nb_3Ge tape with T_c of 20K, and J_c of 2×10^4 A/cm^2 at 20T, has recently become reproducible by employing an improved gas flow pattern.

NbN films approximately 3000Å thick have been produced by sputtering with J_c of 1.5×10^5 A/cm^2 in a perpendicular field of 20 T. The J_c of NbN degrades rather rapidly with increasing film thickness but is sufficient to suggest the feasibility of NbN as a high-field superconductor.

SUMMARY

Many challenges are being overcome on the processing of advanced superconductors in Japan as mentioned briefly here. Fields of over 20T have already been obtained in some advanced materials.

T.I.C. Statistics

Price Waterhouse report the following collected statistics :

QUARTERLY PRODUCTION ESTIMATES

(quoted in lb Ta_2O_5 contained)

LMB quotation :	*$30*	*$40*	*$50*
3rd quarter 1986	265 850	330 600	435 350
4th quarter 1986	267 100	336 850	451 600
1st quarter 1987	275 850	350 600	465 350
2nd quarter 1987	275 850	360 600	465 350
3rd quarter 1987	275 850	360 600	495 350

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

PRODUCTION AND SHIPMENTS

(quoted in lb Ta_2O_5 contained)

2nd quarter 1986

Category	*Material grade*	*Production*	*Shipments*
A/B	Tin Slag	233 581	191 285
C/D	Tantalum under and over 25 % Ta_2O_5	33 760	78 860
F	Other materials	0	0
		267 341	270 145

Notes :

1. In accordance with the rules of confidentiality, some categories 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 17/19; 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 000 lb tantalum (after processing).

PROCESSORS' SHIPMENTS

(quoted in lb tantalum contained)

2nd quarter 1986

Product category	*Shipments*
Tantalum oxide/K_2TaF_7	32 227
Alloy additive	50 266
Carbide	148 225
Powder/anodes	170 671
Mill products	84 651
Scrap, ingot, unworked metal and other	23 479
Total	509 519

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 18/18; 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

EUROPEAN TANTALUM CAPACITOR SHIPMENTS

(thousands of units)

1st quarter 1986	132 369
2nd quarter 1986	139 376

(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*
2nd quarter 1986	552 661	136 623

(Data from JEIDA)

U.S. TANTALUM CAPACITOR SALES

(thousands of units)

Data shown in Bulletin No. 47 for 1st quarter 1986 were incorrect : the correct figures are given below.

1st quarter 1986

	U.S. sales	*Exports*	*Total*
Foil	297	24	321
Metal cased	36 219	10 266	46 485
Non-metal cased	125 145	28 100	153 245
Chips	13 540	2 697	16 237
Wet slug	2 611	303	2 914
Total	177 812	41 390	219 202

2nd quarter 1986

	U.S. sales	*Exports*	*Total*
Foil	322	10	332
Metal cased	33 127	10 978	44 105
Non-metal cased	133 681	30 661	164 342
Chips	17 299	1 816	19 115
Wet slug	2 214	244	2 458
Total	186 643	43 709	230 352

(Data from EIA)

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