

President's letter

A slightly brighter future is expected by the tantalum industry — this was the general feeling at our Twenty-eighth General Assembly in Brussels on October 20th 1987. Hopefully this improvement proves to be consistent and the T.I.C.'s services to the tantalum and the niobium community even more important.

A preliminary plan was given for a Symposium on the extraction, working and applications of tantalum and niobium, to be held in the fall of 1988.

The last major meetings on the two metals were held in 1978 in Rothenburg, Germany for tantalum, and in 1981 in San Francisco for niobium. In the intervening years there have been great changes in the technology and uses of the two elements, and we consider the time to be ripe for a new review. The T.I.C. will be organizing the Symposium, but we will be looking for sponsors from the industry to underwrite the exercise, which we can see as spreading over three days or so, and will be finally recorded in a formal volume of transactions.

I hope that everyone who reads this bulletin can persuade his company to help with sponsorship, so that the project can get off to a confident start. All we then need, is for all of you actually to attend the Symposium to ensure its professional (and financial) success.

On behalf of all of us, I express my thanks to Mr Theo De Cleyn and Mr Jean Levasseur for their contributions to this last meeting.

Finally, but most important, we all thank Mr R.J. Tolley very much for all the efforts and work during his year of office as President.

Yours sincerely,
H.J. Heinrich
President

Mr J.H. Langenberg

The T.I.C. was very sad to learn of the death on July 14th 1987 of Mr Jaap Langenberg, Managing Director of Thailand Smelting and Refining Co., Ltd., Mr Langenberg had been the delegate of Thaisarco to the T.I.C. since September 1985 and his contribution to the work of the association has been greatly appreciated.

Current trends in the tantalum market

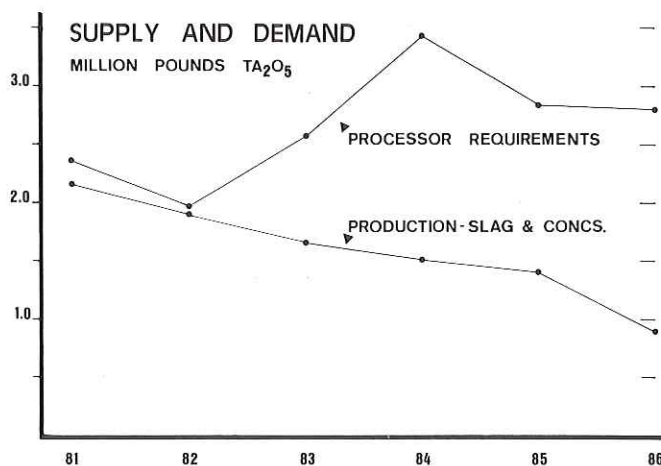
This is based on a presentation made at the T.I.C. meeting in Rio de Janeiro, June 2nd 1987, by Mr Andrew Jones, T.I.C. Technical Officer.

The purpose of this survey is to indicate some important trends in the tantalum market, especially the supply/demand balance and in the end-uses. T.I.C. data are used throughout except where stated to the contrary.

SUPPLY AND DEMAND

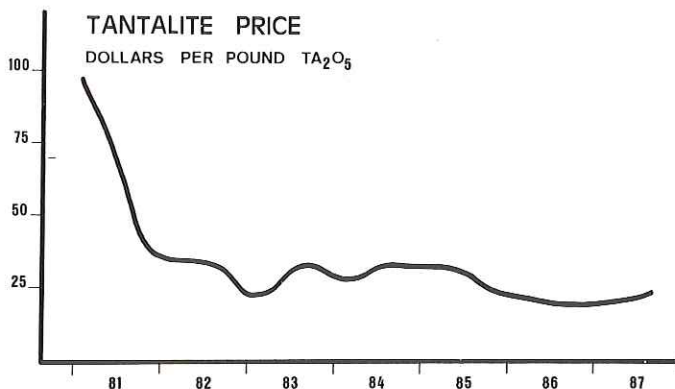
Supply and demand have been out of balance since 1982; this situation is likely to continue for the next two to three years. The shortfall between raw material production (in slag and concentrates) and processor shipments has been filled by inventories; these have now declined to such a level that the resumption soon of large-scale purchases of raw material would seem inevitable.

Processor shipments of metallic and compound products were curtailed by the worldwide recession of 1980-82, as well as by some substitution of tantalum caused by high prices for raw material. The generally favourable world economic conditions should benefit tantalum shipments this year for electronics and superalloys. The outlook for the individual end-uses will be explored later.



Production of concentrates and slag has declined every year since 1981, the onset of the "tin crisis" in 1985 steepening this decline last year. Prices for tin appear to have stabilised but are unlikely to recover to pre-1985 levels. Future tantalum supply will be more dependent on mined concentrates rather than by-product tantalum in tin slag.

The decline in tantalite concentrate prices (as quoted in "Metal Bulletin") reversed in June, and by September the quote was at \$ 20-24 / lb Ta₂O₅. But this price is still not sufficient to encourage large-scale operation by tantalite producers.



PRODUCTION

A comparison of production estimates of Ta₂O₅ in slag and concentrates for 1985 and 1986 shows a reduction of one-half million lb Ta₂O₅ due almost exclusively to the lower prices for tin. Tantalum production is often associated with either tin smelting (slag) or tin mining (concentrates).

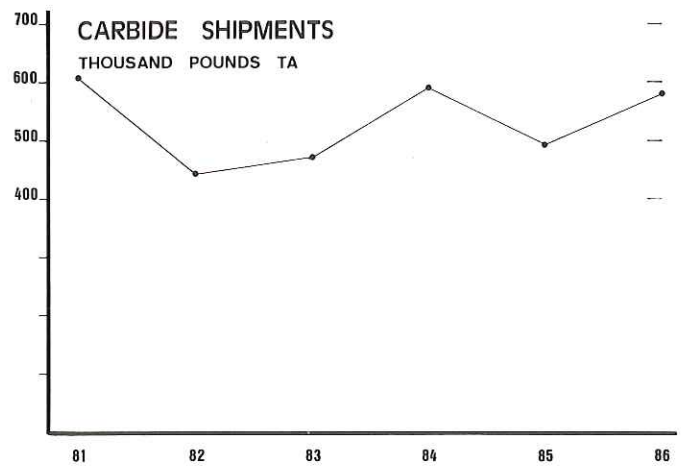
Production was worst affected in Malaysia, Nigeria, Thailand and Zaire, while the reductions in Australia and Brazil were more probably due to the poor state of the tantalite market. The sole Canadian mine, not a tin producer, is not producing tantalite for the same reason.

The year's production has so far remained similarly depressed. Around 200 000 lb Ta₂O₅ a year of current output is contained in low-grade slag, not an economic raw material at the current low prices for tantalite.

PRODUCTION ESTIMATES

THOUSAND POUNDS TA₂O₅; SLAG & CONCS.

	1985	1986
AFRICA	200	100
AUSTRALIA	200	150
BRAZIL	350	300
CANADA	NIL	NIL
SE. ASIA	<u>800</u>	<u>500</u>
TOTAL	1550	1050

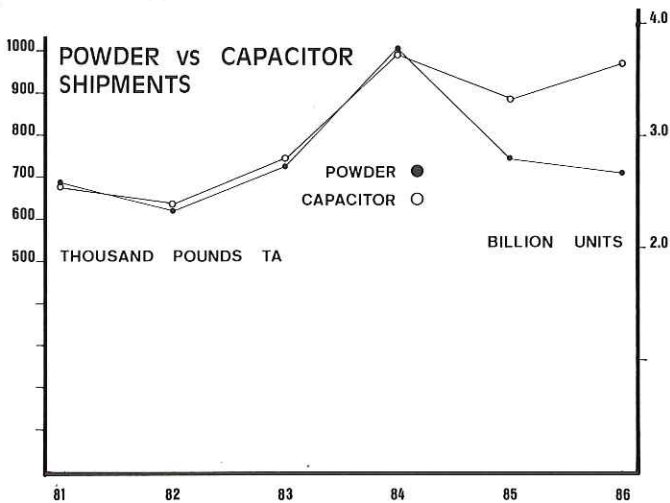


trend. Improved design is leading to longer tool life; there is a trend toward down-sizing machined components and producing these components at near net shape.

ELECTRONICS

Electronic capacitor manufacture currently consumes around 50 % of tantalum shipped, most usually in the form of powder for the production of sintered capacitor anodes.

World powder and capacitor shipment data exhibit a remarkably similar trend until 1984; thereafter, powder shipments decline relative to capacitor shipments. Whereas during 1984 electronic equipment manufacturers increased component stocks — including tantalum capacitors — and component manufacturers increased stocks of tantalum powder, 1985 saw de-stocking throughout the industry as optimism in the electronics business evaporated. The prevailing policy seems to be to keep stocks of electronic components to a minimum — the "JIT" (Just-In-Time) concept. However, capacitor shipments resumed an upward trend last year, and powder shipments should follow by the end of 1987.



Tantalum capacitor shipments should increase by 5-10 % a year over the next five years. But since the use of high-charge powders will reduce the average anode size by around 30 % over the same period, powder shipments will not increase proportionally.

CEMENTED CARBIDES

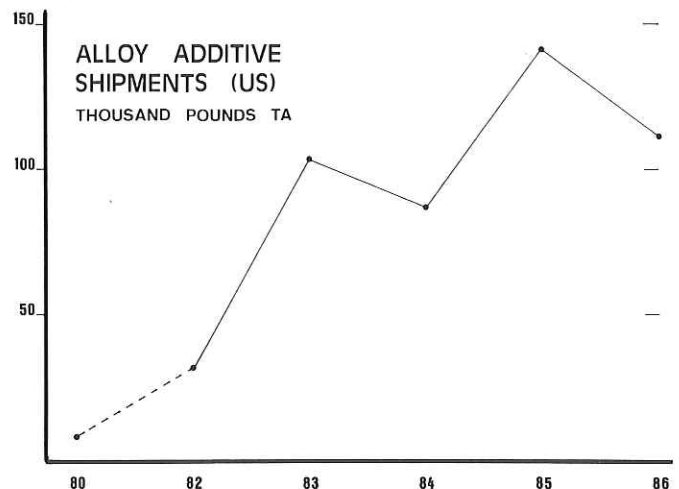
Carbide tools for metal cutting currently take 30 % of tantalum shipments. The chart shows the substitution for tantalum carbide after 1981 due to high prices at the time. These substitutions have now halted, and the data for recent years show some measure of stability. However, factors other than straightforward substitution will influence future tantalum carbide consumption.

- Firstly, recycling of used tools reduces virgin tantalum carbide requirements by 30 %. This figure could well increase in the future; there is no reason why it should decrease.
- Secondly, coated tools are gaining rapidly; this tool design needs less tantalum in the substrate material.
- Mixed carbides of tantalum and niobium, in the ratio of 90/10 and 80/20, are also gaining; these carbides displace pure tantalum carbide in the substrate.
- Finally, the overall market for cemented-carbide tools seems to be in decline — at a slow rate but this will be a long-term

SUPERALLOYS

The smallest market for tantalum but the fastest-growing in recent years is superalloy additive. Ten percent of tantalum is used for this purpose. Superalloys are used for heat-resistant parts in turbines, principally jet engines.

The rapid expansion in tantalum usage for superalloys since 1982 is demonstrated with TPA data showing US consumption. The equivalent T.I.C. statistic for 1986 was close to 200 000 lb. This rapid growth in demand is due to the introduction of single-crystal turbine components. The outstanding example, of course, is the 1480 alloy introduced by Pratt & Whitney into their jet engines, containing 12 % tantalum.



EQUIPMENT FABRICATION

Ten percent of tantalum is used for equipment fabrication, mainly for the manufacture of corrosive chemicals. About one-half of the tantalum used for this purpose goes into sulphuric acid equipment; the remainder goes into equipment for chemicals such as nitric acid and chlorine derivatives. Tantalum is also used for electronic and nuclear equipment.

In recent years, there has been a trend towards using tantalum in the form of a 2½ % tungsten alloy, although this cannot be seen as a major factor in influencing consumption, the general state of the chemicals industry playing the major role. The advance of materials technology in developing cheaper alternatives to tantalum threatens future consumption; this threat may be reduced by the use of tantalum-base alloys with high contents of other refractory metals, such as niobium, though there is no evidence yet of such a trend.

SUMMARY

The market for tantalum raw materials, tantalite and slag, should improve this year as processor inventories decline to more usual levels. By-product tantalum has been curtailed due to the collapse in the tin market: as a result, future tantalum supply will have to be met increasingly by tantalite concentrates.

On the demand side, 1987 holds better prospects from electronics and superalloys.

Working with tantalum and columbium

The conclusion of an article from Bulletin No 51 by Mr Sherwood Goldstein and Mr Louis E. Huber, both of Cabot Corporation.

RESISTANCE-WELDED CLADDING

Tantalum- and columbium-clad base metals can also be produced by the "Resista-Clad" process, developed by Showa Entetsu in Japan. The Pfaudler Co., Rochester, NY, is the prime US licensee; sub-licenses are also available.

Unlike explosive bonding, the Resista-Clad process does not produce a full-width bond between the cladding and the base metal; the cladding is resistance seam welded to the underlying metal at intervals determined by the intended usage. This is enough to eliminate the problems, such as fatigue and abrasive wear resulting from differential thermal expansion, that typically occur when a loose lining of a refractory metal is used inside a steel pressure vessel.

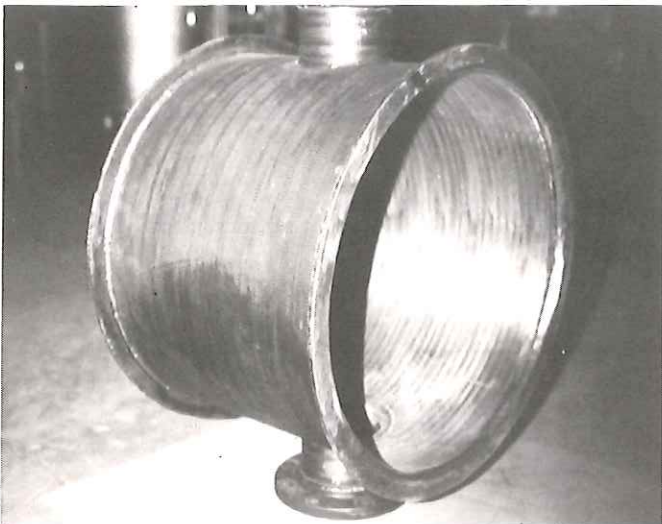
An additional advantage, according to Pfaudler, is that the Resista-Clad process can clad semi-finished pieces. For example, a pressure vessel would be fabricated by first making the shell and domed head out of carbon steel, then applying the tantalum or columbium cladding to these pieces. Nozzles and other internals are also clad this way. Whether clad or not, their attachment imposes little or no stress on the liner.

Since they are working with semi-finished pieces in any case, Pfaudler and their sub-licensees normally complete the fabrication. Final fabrication can be done elsewhere when desired.

Pfaudler believe that the techniques involved with Resista-Clad material are sometimes easier than those for explosively-bonded pieces: for example, since the cladding is not bonded to edges of the underlying metal, it is simple to peel it back and prepare a weld joint. In other words, the weld is built into the fabrication process.

Pfaudler maintain the design and preparation techniques for further fabrication of Resista-Clad material as proprietary: this is largely to avoid the problems that might occur if unqualified individuals were to attempt to work with the unfamiliar material. When a contract calls for final fabrication to code specifications, it is relatively easy for Pfaudler to work with a code steel fabricator and build to ASME Code Section VIII.

The Resista-Clad process was used to line the inside of this 30 inch by 24 inch spool piece with tantalum.



TTIC to rebuild tantalum processing plant

The Thailand Tantalum Industry Corporation (TTIC) are to start the reconstruction of their tantalum processing plant in December 1987; commercial operation is scheduled for the second quarter of 1990.

The first plant, located on Phuket Island, was destroyed by a fire in June 1986. The finance for the new plant has been provided by the Thai government which has taken a 20% interest in TTIC, as well as supplying soft loans and an eight-year tax exemption. The new site will be the Mab Ta Phud Industrial Estate in the south-eastern

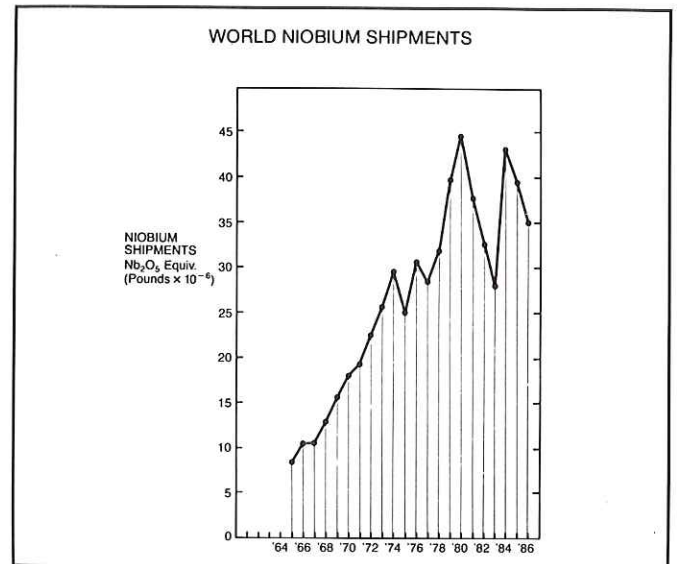
province of Rayong. Plant capacity will be unchanged at 660 000 lb Ta₂O₅ a year, and the products will be potassium fluotantalate and tantalum and niobium oxides using hydrofluoric acid digestion and MIBK solvent extraction. A facility to pyrometallurgically upgrade Ta₂O₅-containing tin slags into 'synthetic' concentrates is scheduled to be operating in 1994.

The principal material feed for the plant will be the Ta₂O₅-containing slag from the Thaisarco tin smelter at Phuket. This slag contains over 10% Ta₂O₅ and so can be used as direct feed. However, tin production at Thaisarco has declined in recent years, so that the output of tantalum in slag is less than half of that being produced during 1979-80 when production was around 850 000 lb a year. In Thailand, tantalite is produced by some tin mines as a by-product, and processors of tin-mining waste ('amang') produce struverite, a tantalum-containing mineral. But current output from these sources is very low due to the depressed prices for both tin and tantalum, so TTIC intend to import suitable raw material to complete requirements.

Niobium in perspective

This paper was presented by Dr Harry Stuart, Niobium Products Co., at the T.I.C. meeting in Rio de Janeiro, June 2nd 1987.

The nature of the niobium market has changed quite dramatically since 1980. There was the euphoria of the 1970's which might have gone on for ever, but unfortunately it did not. For three successive years after 1980, shipments declined. Since then, the market has recovered but has now essentially matured.

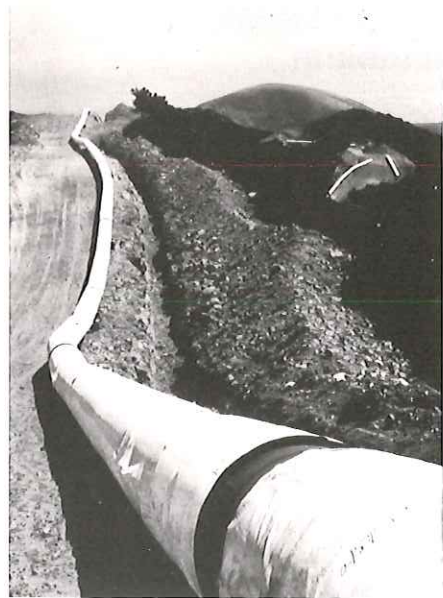
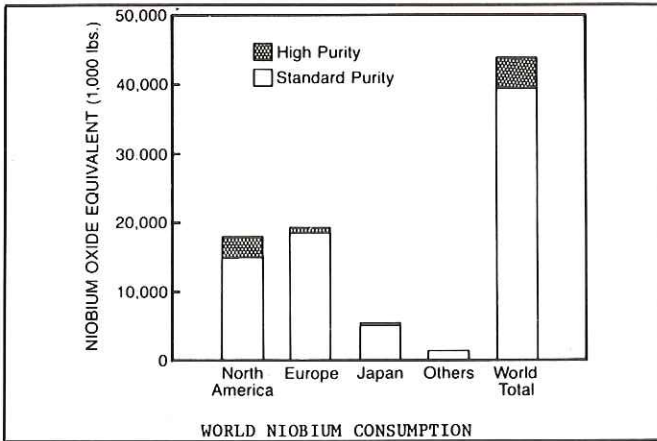


Where does niobium come from? These are the producers round the world: CBMM, Niobec in Canada, Catalao, some in Nigeria and Thailand, and now there is a newcomer in Zaire which is producing some material, not very much, but it can be expected to be a force in the future. There are many potential niobium sources, which is not always realised. Potential resources exist in Canada, Africa, Brazil, China and the Soviet Union, and even the U.S. has niobium deposits, not particularly exploitable, but they do exist. Canada has at least three deposits that could be exploited, and there is one not listed here which is in Greenland.

NIOBIUM SOURCES - 1987				
LOCATION	CAPACITY (Lbs. Nb ₂ O ₅ x 10 ⁶)	ORE GRADE	RESERVES (tonnes Nb ₂ O ₅ x 10 ⁶)	PRODUCTION (Lbs. Nb ₂ O ₅ x 10 ⁶)
Araçá, Brasil	55	3.0	500+	21
St. Honore, Quebec	7	0.7	11	7
Catalão, Brasil	5.5	1.5	50	5.5
Nigeria	2	-	-	-
Thailand	1-2	-	-	-
Zaire	Pilot Scale	2-3	Extensive	0.5

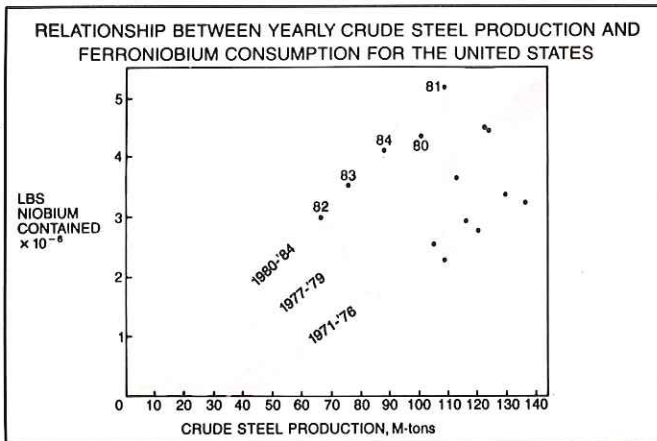
POTENTIAL NIOBIUM SOURCES	
CANADA	- At least three commercial deposits
AFRICA	- Many deposits
BRAZIL	- Three very large deposits
CHINA	- Extensive deposits
USSR	- Significant deposits
USA	- Several small deposits

Where does niobium go geographically? It goes to Europe, North America and also to Japan. North America uses much more high-purity niobium than anywhere else; Europe uses much more steel-making, HSLA-grade niobium.

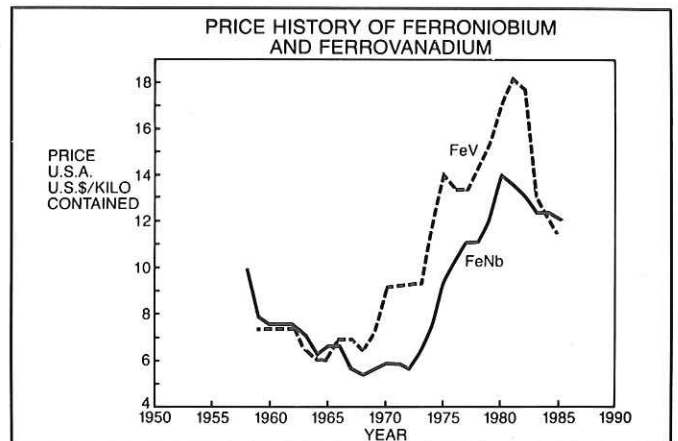


Where does it go by industry? It goes into the metallurgical industry. Niobium is essentially a steel-making metal, but if you include superalloys it is a metallurgical element, nothing more than that.

This is the annual crude steel production in the U.S. against the annual niobium consumption: as you can see, where steel goes, niobium goes, a very close correlation. So when steel is up, niobium is up, and vice versa. Niobium is a steel-making metal.



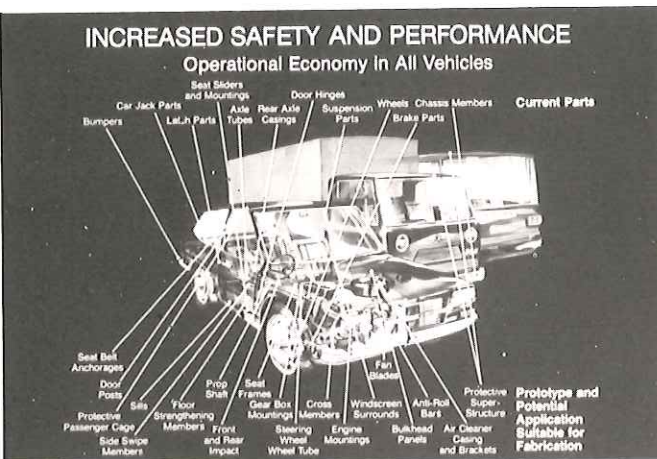
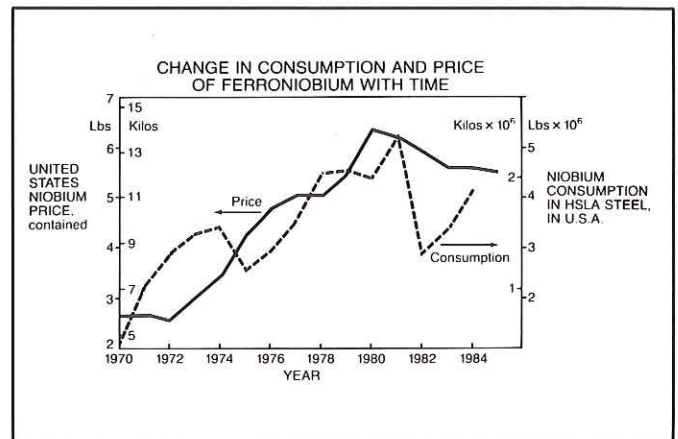
This is the price of niobium compared to vanadium, another steel-making metal; there is a very similar relationship between the two as they are both tied to the same industry.



Then if you look at the consumption of niobium and compare it to its price, naturally there is a relationship: if consumption goes up, the price goes up, and vice versa.

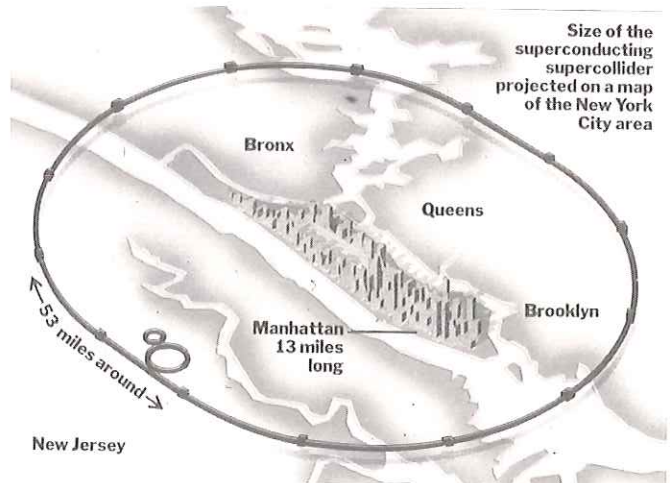
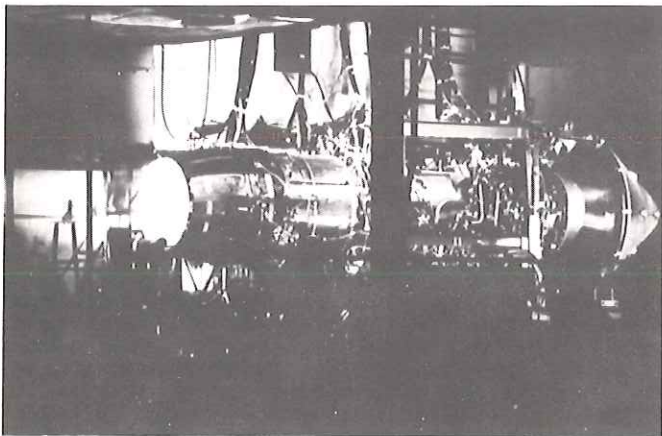
Steel goes into cars, particularly in the U.S.: to make cars lighter, you use stronger steel and you use niobium to do this. It goes into pipelines. These are the two biggest consuming areas for niobium. It goes into ships, bridges and offshore construction ... it goes into steel.

HSLA steel in cars and pipelines



There are other uses for niobium; it is not just for steels. It goes into superalloys for aircraft engines, and it goes into other parts of aerospace paraphernalia. It goes into lithium niobate for electronic devices. It goes into chemical alloys for corrosion resistance. And it goes into superconductors.

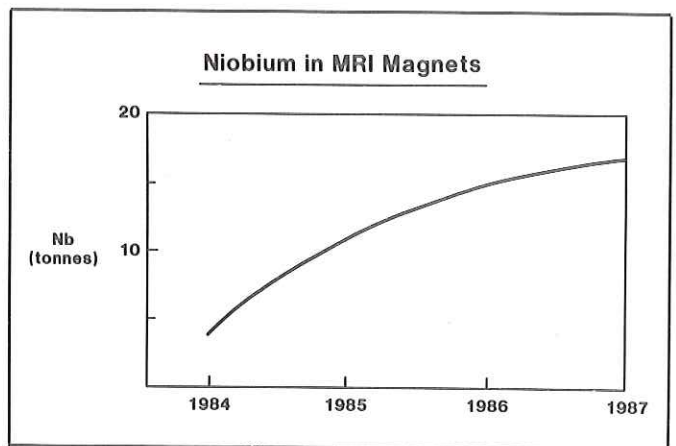
Some other applications for niobium : superalloys;



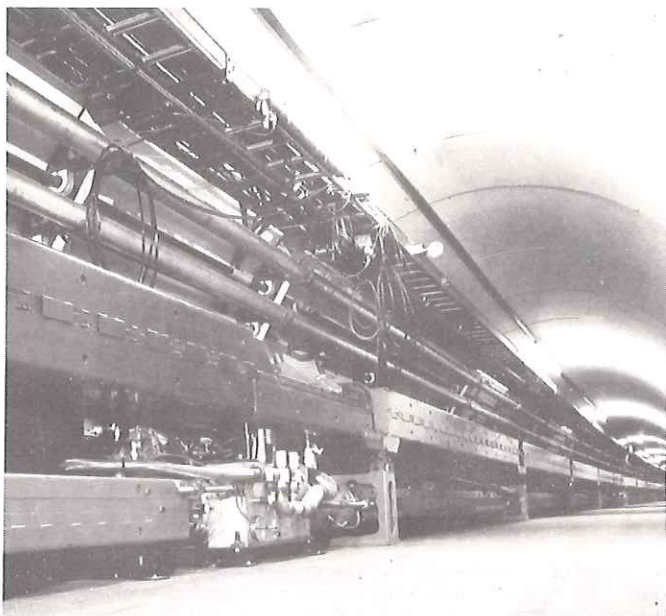
lithium niobate;



There are body scanners, the only commercial application for superconductivity. They cost about three million dollars each; it is not easy for a hospital to acquire these devices. And as a consequence you can see that the consumption of niobium in body scanners in 1987 was only 17 tonnes.



and superconductors.



Ceramic superconductors (high T_c superconductors) even made the front page of 'Business Week' and 'Time' magazines. There is a tremendous amount of money being spent on these new superconductors that can operate at liquid nitrogen temperatures. These materials are here, and they will get better. They will take over the applications for superconductivity from niobium. IBM recently said that they had developed a superconductor that could carry much larger amounts of electric current, removing a big obstacle to commercial use.

So where does it leave niobium? It leaves niobium in steel; it leaves niobium in the metallurgical industry. So what of the 'strategic importance' of niobium? There are references to niobium being a 'strategic material' or a 'critical metal'. Here is a series of tables which look at the various niobium products, their consumption and estimated future growth, their areas of application, and the many possible replacements for niobium in each application. Niobium is not of strategic importance to the world or to Brazil.

PRODUCT	MARKET GROWTH**			APPLICATIONS	REPLACEMENTS	STRATEGIC IMPORTANCE		
	WORLD MARKET*	1970 to 1980	1980 to Future			FOR THE WORLD	FOR BRAZIL	
PERKONIOBIUM STANDARD GRADE (made from pyrochlorite concentrate)	10,500	9	0-2	0-3	STRUCTURAL STEEL FOR: Automobiles Pipelines Construction Appliances etc.	TITANIUM VANADIUM MOLYBDENUM BORON COPPER NICKEL CHROMIUM	NOT STRATEGICALLY IMPORTANT 1) There are very many substitutes for niobium in these applications 2) HSLA steels are not essential materials 3) There are other sources of niobium in the world	NOT STRATEGICALLY IMPORTANT 1) There are very many substitutes for niobium in these applications 2) HSLA steels are not essential materials
	1,000	0-2	5	5	STAINLESS STEEL FOR: Automobiles Appliances Chemical Plant	TITANIUM MOLYBDENUM COPPER OTHER STAINLESS STEELS	NOT STRATEGICALLY IMPORTANT 1) There are very many substitutes for niobium in these applications 2) There are other adequate sources of niobium in the world 3) There are many alternative stainless steels which do not contain niobium	NOT STRATEGICALLY IMPORTANT 1) There are very many substitutes for niobium in stainless steels 2) There are many alternative stainless steels which do not contain niobium

* Tonnes of contained niobium per year
** Percent change per year

What is the future going to have in store for niobium? Steel will grow, modestly. There may be some new applications for niobium in things like ceramics, catalysis and paint pigments.

But what of superconductivity? This is the proposed Superconducting Super Collider, fifty miles in circumference, compared to Manhattan Island. This will consume 400 or more tonnes of niobium, almost 1000 tonnes of niobium-titanium alloy. But already it is doubtful if this device will ever be built.

PRODUCT	MARKET GROWTH**			APPLICATIONS	REPLACEMENTS	STRATEGIC IMPORTANCE		
	WORLD MARKET*	1970 to 1980	1980 to Future			FOR THE WORLD	FOR BRAZIL	
NICKEL GRADE NIOBIUM MASTER ALLOYS (Fe-Nb, Ni-Nb) (made from high purity niobium pentoxide)	950	5	5-10	5-10	SUPERALLOYS MANUFACTURE FOR Aircraft engines Oil wells	TANTALUM TITANIUM MOLYBDENUM ALUMINUM OTHER SUPERALLOYS	NOT STRATEGICALLY IMPORTANT 1) There are a number of other superalloys available which do not contain niobium 2) Superalloys research continues to develop non-niobium containing superalloys 3) There are other sources of high purity niobium in the world	NOT STRATEGICALLY IMPORTANT 1) There are a number of other superalloys available which do not contain niobium 2) Superalloys research continues to develop non-niobium containing superalloys

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PRODUCT	MARKET GROWTH**			APPLICATIONS	REPLACEMENTS	STRATEGIC IMPORTANCE		
	WORLD MARKET*	1970 to 1980	1980 to Future			FOR THE WORLD	FOR BRAZIL	
NIOBIUM METAL (made from high purity niobium pentoxide)	50	0	0-5	0-5	NIOBIUM BASED ALLOYS FOR SUPERCONDUCTORS	Ceramics Pd Ba CuO Sr Ba CuO Eu Ba CuO Gd Ba CuO Yb Ba CuO Dy Ba CuO Ho Ba CuO Tm Ba CuO Y Ba CuO La Ba CuO	NOT STRATEGICALLY IMPORTANT 1) Within five years the world's superconductors will be manufactured from the newly discovered ceramic materials which are cheaper and better than niobium.	NOT STRATEGICALLY IMPORTANT 1) Brazil's needs for superconductors will be satisfied by the new ceramic materials. The materials for these new superconductors exist in abundance in Brazil.
NIOBIUM METAL	120	0	0-5	0-5	NIOBIUM BASED ALLOYS FOR CHEMICAL AND NUCLEAR ENGINEERING	Titanium Tantalum Molybdenum	NOT STRATEGICALLY IMPORTANT 1) Small market 2) Small growth 3) Many replacements 4) Sufficient niobium outside Brazil.	NOT STRATEGICALLY IMPORTANT 1) Small market 2) Small growth 3) Many replacements.
SPECIAL NIOBIUM OXIDES (made from high purity niobium pentoxide)	30	0	5	10	MISCELLANEOUS NIOBIUM CONTAINING COMPOUNDS AND ALLOYS	Titanium Tantalum Molybdenum	NOT STRATEGICALLY IMPORTANT 1) Very small market 2) Many replacements.	NOT STRATEGICALLY IMPORTANT 1) Very small market 2) Many replacements.

* Tonnes of contained niobium per year
** Percent of change per year

granites. The age of this basement fluctuates between 1950 m and 2600 m years. The young, non-tectonized granitic province of Parguaza in the mineralized area comprises: rapakivi granites, orbicular granites, leucogranites, syenites, pegmatites, late basaltic dykes and thick veins of hyaline quartz. The rapakivi granite is the most abundant with a typical pink colour, coarse-grained, non-tectonized and unweathered; the rock consists essentially of potassic feldspar in ovoidal crystals or alternating rings, subhedral quartz crystals, well-developed biotite, hornblende, epidote and metallic minerals, but no Nb, Ta or Sn minerals. The orbicular granite is a massive rock which is dense, biotite, coarse-grained and mineralogically rich in pink potassic feldspar, quartz and biotite. The leucogranite is a minor part of the granitic bodies and characterized by a fine grain and white feldspar. The pegmatites are located within the granitic zone in the form of large bodies with sharp contacts, highly weathered and rich in large orthosa, biotite and quartz crystals. The thick quartz veins, normally showing rutile needles, are located in the lower zones of the hills. The largest crystals of columbite-tantalite have been found associated with these pegmatitic and quartz zones. The syenites are rocks characterized by a typical grey colour and medium grain and consist almost entirely of a perititic microcline without visible orientation, a few plagioclase and some metallic minerals, such as hematite, titanite and probably some grains of tantalite.

ORE MINERALS

The Nb-Ta-Sn mineralization detected in the granitic units is associated almost exclusively with the pegmatitic and quartz veins. The minerals exist in masses or disseminations of crystals varying from less than 1 mm up to 200 mm. Tropical weathering has caused the formation of extensive economic alluvial/eluvial sediments showing rich levels of cassiterite, tantalite-columbite and rutile. No hydrothermal alteration, greisenization, tungsten or sulphide minerals have been detected with the primary mineralization zones. According to detailed investigations, all the main metallic phases contain high proportions of at least one of the following oxides: FeO, MnO, Nb₂O₅, Ta₂O₅, SnO₂ and TiO₂. Except for some inclusions, no other elements have been detected. The main ore minerals detected were: cassiterite, rutile, tantaliferous-columbiferous rutile, tantalite-columbite and stanniferous tantalite.

The one area where niobium could have had strategic significance — superconductivity — has disappeared with the new high T_c superconductors. Niobium is a metallurgical metal and not of strategic importance to anybody.

Secondary deposits of tantalum and niobium ores in south-west Venezuela

This paper was presented by Dr Simon E. Rodriguez, Geological Survey of Venezuela, at the T.I.C. meeting in Rio de Janeiro on June 2nd 1987.

Exploration work by the Mineral Resources Branch of the Ministry of Energy and Mines over an extensive area of the Amazonas federal territory and western Bolivar state, southern Venezuela, revealed niobium, tantalum, tin and titanium mineralizations associated with granitic rocks, specifically the Parguaza group. This unit of acid rocks is responsible for the formation of large bauxite deposits, but never before had metallic minerals been located in association with these units.

The mineralization zone is located in hilly country with large alluvial and eluvial valleys rich in hyaline quartz boulders. Located about 45 km from Puerto Ayacucho, the capital city of the Amazonas territory, the area is crossed by good roads and has air links with other Venezuelan cities.

The Parguaza group covers large areas of western Bolivar state and northern Amazonas territory and is one of the most important granitic units of the Precambrian Guyana Shield. Several important ore deposits have been located and outlined: Nb-Ta-Sn pegmatites; granitic rocks showing Mo mineralization; large carbonatite complexes; and possible kimberlite dykes. Between 1975 and 1986, several of these zones were studied in detail, and a large reserve of Fe, Pb, Nb, P, Th and Zn ore associated with carbonatites was outlined, as were important alluvial zones showing economic levels of Nb, Ta, Sn and Ti minerals.

GENERAL GEOLOGY

The rocks showing Nb-Ta-Sn-Ti mineralization intrude a basement consisting of: tonalitic gneisses, highly metamorphosed; mafic rocks of the gabbro series; pyroclastic volcanic rocks; and alaskitic

Chemical analyses of primary ore (percentages)

Cassiterite			
	Sample ATF-1	Sample ATF-2	Sample ATF-3
TiO ₂	0.07	0.15	0.11
MnO	0.00	0.02	0.12
FeO	0.12	0.75	1.01
Nb ₂ O ₅	0.08	1.33	2.22
SnO ₂	99.10	96.00	94.60
Ta ₂ O ₅	0.68	2.70	3.92

Rutile-Tantaliferous/Columbiferous Rutile			
	Sample ATF-10	Sample ATF-15	Sample ATF-17
TiO ₂	94.70	43.90	56.20
MnO	0.01	0.50	0.32
FeO	1.39	9.35	6.73
Nb ₂ O ₅	1.66	6.85	5.38
SnO ₂	1.12	4.10	3.05
Ta ₂ O ₅	0.66	37.40	28.50

Tantalite-Columbite				
	Sample ATF-9	Sample ATF-11	Sample ATF-2	Sample ATF-20
TiO ₂	1.07	2.70	2.98	3.42
MnO	14.10	9.91	5.66	1.69
FeO	2.53	6.11	10.70	12.50
Nb ₂ O ₅	38.40	38.60	42.60	40.70
SnO ₂	0.23	0.73	0.69	0.13
Ta ₂ O ₅	43.30	42.40	35.30	36.10

In several of the sediments, the cassiterite content is up to 73 % of the ore. The light-coloured variety contains almost 100 % of SnO₂ while the dark ones contain high amounts of Fe, Nb and Ta with only traces of Mn and Ti. Samples of rutile and tantaliferous-columbiferous rutile were detected in several pegmatites and secondary alluvial zones. They are steel-grey in colour and can comprise up to 10 % of the heavy fraction in the sedimentary alluvial zones.

The tantalite-columbite is easily recognized because of its brilliant black colour and can be in large crystals associated with the pegmatitic and quartz veins. In the alluvial zones, they constitute up to 10 % by volume of the ore zone. Usually they show few inclusions in polished sections, and the chemical analyses show high amounts of FeO and MnO.

Generally this type of deposit does not contain large ore zones, but in tropical countries, like Venezuela or Brazil, the mineralized rock is easily decomposed and washed away, forming extensive alluvial or eluvial young deposits. This is the case with the ore deposit in western Bolivar and northern Amazonas territory. Drilling was carried out by the Mineral Resources Branch on several zones of the sedimentary valley near the granitic rocks and showed economic values of Nb, Ta and Sn. The whole area will probably be evaluated in the near future.

ORIGIN

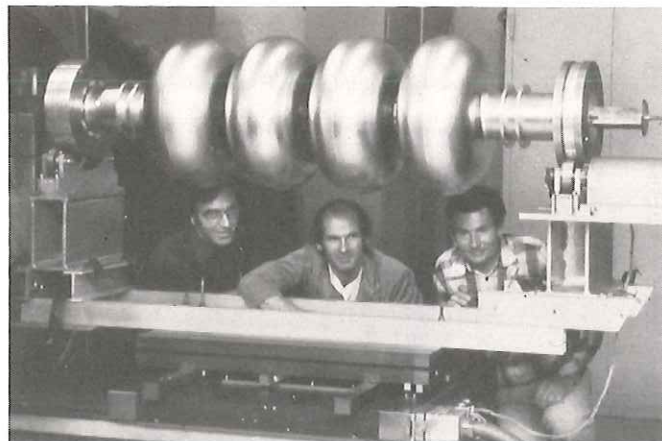
The Venezuelan deposits represent classic rare-metal tin pegmatite and quartz veins associated with granitic intrusions generated in late- and post-tectonic precambrian terrains. Only cassiterite, columbite and tantalite have been detected as the main ore minerals in the pegmatitic zone. No evidence of the typical high-temperature tin deposits, such as intensive greisenization, albitization, sulphides, tungsten minerals or tourmalinization have been detected. These complex pegmatites are located near large faults with a general north-south trend, and several carbonatite complexes have been outlined in association with these structures. These faults represent an important reactivation of the old Precambrian Guyana Shield and continue to Brazil where important ore zones have been outlined. These primary Nb-Ta-Sn pegmatitic deposits can be the source of large secondary alluvial and eluvial ore zones, especially in tropical areas. In the Venezuelan case, very important Nb-Ta-Sn secondary deposits have been formed quite near to the granitic zone and, according to preliminary drilling, they are in different levels associated with sand and clay which is very rich in lateritic material.

Chemical analyses of secondary ore

Drill site	Sn %	Nb %	Ta %
1 E00	0.02	0.04	0.01
1 E02	0.77	0.17	0.01
2 E02	0.43	0.16	0.02
04	0.19	0.12	0.01
05	0.12	0.20	0.01

Not least of the problems is that no suitable industrial equipment exists in which the required qualities can be produced economically on a tonnage scale. The aim was therefore to find a production route based on economic process steps available on an industrial scale, such as aluminothermic reduction, electron-beam melting, forging and rolling and vacuum heat treatment.

Four-cell cavity structure at CERN



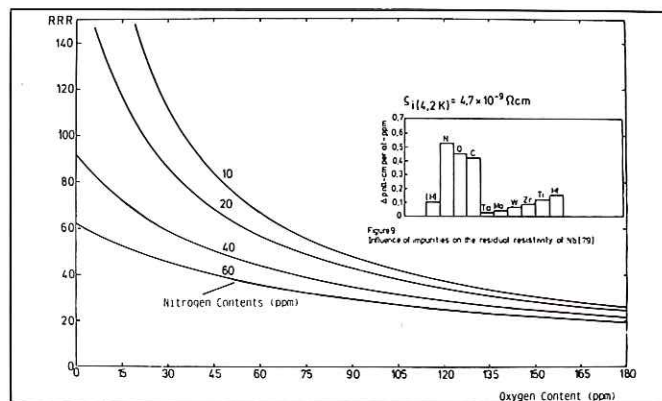
FUNDAMENTAL CONSIDERATIONS AND METROLOGICAL REQUIREMENTS

Niobium ingots are obtained by electron-beam melting of ATR-Nb bars, i.e. aluminothermally-reduced Nb₂O₅. Due to the high melting point of Nb (2415 °C), evaporation of impurities by EB melting in a vacuum is very effective, achieving better than 3 × 10⁻⁴ mbar after the first melt. A minimum of four melts is normally necessary to produce commercial-grade Nb.

To check the interstitial contents after various process steps, the determination of the residual resistivity ratio by gas analysis is particularly advantageous. The substitutional impurity atoms such as Ta and Zr contribute much less to the electrical resistance than the interstitials O, N and C.

Because of the marked oxygen affinity of niobium in gas-metal reactions, the dependence of RRR on the oxygen concentration was first calculated using residual resistance coefficients.

Simulated RRR vs oxygen concentration



Production of high-thermal conducting niobium on a technical scale for high-frequency superconductivity

This paper was presented by Dr Michael Hörmann, W.C. Heraeus, at the T.I.C. meeting in Rio de Janeiro, June 2nd 1987.

In the early 1950's W.C. Heraeus (WCH) in Hanau, West Germany, were developing vacuum-melting techniques, i.e. vacuum arc and electron-beam melting for processing refractory metals and their alloys. In 1963 the activities were split between two companies: Leybold Heraeus were founded to produce vacuum fabrication facilities; while W.C. Heraeus concentrated on mill production of refractory and precious metals and are now the leading European producer of electron-beam-melted niobium and tantalum.

In addition to the production of commercial- and reactor-grade niobium rod, tube and sheet (for application in Nb₃Sn superconductors, for example) WCH started producing high-grade niobium in 1983 — the defined 'Nb 100' quality, with a RRR value better than 100 (RRR - residual resistivity ratio). This material is used in the form of sheet for the construction of superconducting high-frequency cavities for accelerators in high-energy particle physics. Superconductors such as niobium used as the wall material for cavities lead to a ten-fold reduction in high-frequency losses.

Investigations of superconducting niobium show that thermal conductivity in the temperature range 2-10 K depends largely on interstitial impurities. By ultra-high vacuum techniques, such as high-temperature degassing, electron-beam zone melting and/or molten-salt electrolysis, it was possible to produce extremely pure niobium on a laboratory scale. These processes used in fundamental research cannot be applied simply to the production of large niobium sheets (1 to 2 m²) required for the construction of cavities.

To achieve high RRR values by decreasing oxygen concentration, low nitrogen and carbon contents become necessary. Examination of this idea by means of production samples shows that the influence of the structure and metallic impurities can be neglected. Thus a correlation between the analytically-determined oxygen, nitrogen and carbon contents and the RRR values could be established.

Calculated and measured RRR values of niobium

Sample	O (µg/g)	N (µg/g)	C (µg/g)	RRR (measured)	RRR (calculated from eq)
1 F/83	155	52	10	20	21
2 F/83	60	33	17	33	40
3 F/83	100	52	13	22	27*
4 F/83	85	66	2	33	31
5 F/83	22	16	16	70	79

* not recrystallised

The good correlation between RRR values and analytically-determined gas contents for pilot-scale samples provided the basis for the large-scale melting.

Gas contents ($\mu\text{g/g}$) calculated from P-T-C relationships

Nb-O ₂	Nb-H ₂ O	Nb-CO	Nb-N ₂	Nb-H ₂
C _O	C _O	C _O	C _N	C _H
1.2	4.5	1.3	8.7	0.006

INGOT PRODUCTION

The starting material for the electron-beam melting electrodes consisted of ATR-Nb slabs with defined interstitial and metallic impurity contents.

Impurity content of ATR niobium

Element	Wt %	Element	Wt ppm
Zr	<0.002	O ₂	6,800
Ta	0.031	N ₂	300
Fe	0.051	H ₂	< 10
Si	0.021		
W	<0.010	C	120
Ni	<0.002		
Mo	<0.002		
Hf	<0.003		
Ti	<0.002		
V	<0.002		
Al	5.500		

(Average values from top, middle and bottom)

The ingots were melted in an electron-beam furnace (type ESP 100/450 from Leybold-Heraeus). A final vacuum of about 10^{-6} mbar can be achieved in the cold furnace after cleaning. The effective melting rate is 450 kW; two electron guns can be used at up to 400 kW each with an accelerating voltage of 30 kV. The furnace has a magazine for the continuous charging of starting material in the form of slabs. Crucible dimensions can be between 150 mm and 300 mm diameter for final ingot lengths up to 2300 m.

In contrast to nitrogen, oxygen forms oxides of various compositions with the metal atoms of the melt surface during degassing at temperatures over 1600 °C. These oxides evaporate, condense on the cold walls of the vessel and are thus removed from the reaction system. The oxygen concentration decreases at first, then adjusts itself to the value given by the stationary state. Therefore, marked metal losses result from the evaporation of oxides with very long melting times. The oxygen content after the sixth melt approached the stationary state of approximately 6 $\mu\text{g/g}$; a significant reduction of the dissolved oxygen content is not to be expected until after six melting cycles at the given furnace pressures.

The nitrogen degassing of niobium also occurs via the recombination of nitrogen atoms to molecules at the surface of the melt. The degassing rate decreases strongly with decreasing concentration so the thermodynamic final content (8.7 $\mu\text{g/g}$) cannot be achieved with the finite melting times used. Furthermore, for a given partial pressure which is dependent on the equipment, the solubility of nitrogen in liquid is greater than that in solid.

Besides the gas contents, RRR and λ (4.2 K) measurements were carried out on selected samples from the final ingot. These measured values showed good agreement with those calculated previously.

SUPERCONDUCTING AND MECHANICAL PROPERTIES OF SEMI-FINISHED PRODUCTS

When sheets were produced from the EBM ingots, a comparison of the values showed that the gas contents achieved by melting could be sustained during the subsequent deformation and annealing processes.

Parameters for electron-beam melting

Starting material:	ATR-Nb slabs
Starting quantity:	ca. 800 kg
Melting cycles:	6
Melting temperature:	ca. 2400°C
Melting rate:	60 - 70 kg/h
Working pressure:	3×10^{-6} mbar
Ingot diameter:	225 mm
Yield:	81 %

Summary of properties of Nb ingots and sheets

Ingot Heat No.	Sheet		RRR	(4.2K) (W/mK)	
	COHN ($\mu\text{g/g}$)	RRR			
3042	140	38	150	33	8.5 ^{a)}
906	60	112	65	105	25.0
873/1	50	114	52	137	29.5
873/2	40	145	42	179	44.0
3074	20	350	25	300	70

a) Nb - commercial grade

Contents ($\mu\text{g/g}$) after each melting cycle

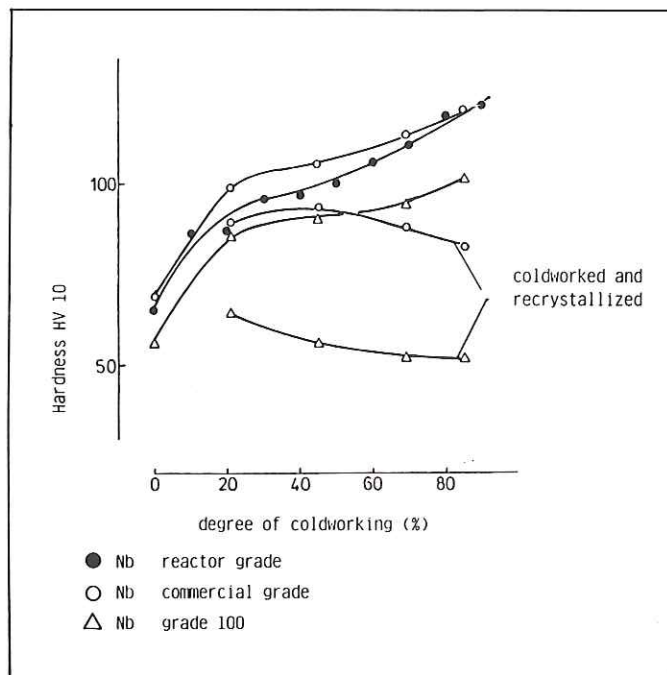
Melting Cycle	1	2	3	4	5	6
C	8	8	7	10	6	8
O	675	128	54	32	17	10
H	1	1	1	1	1	1
N	128	59	45	28	26	20
Total	812	196	107	71	50	39

A mass-spectrometric determination of the residual gas components (partial pressures) was performed during the maximum degassing of the fifth remelt cycle.

The degassing behaviour of niobium at high temperatures has been thoroughly investigated. The final contents that can be achieved are largely determined by the residual gas partial pressures during the last melting cycle. In the temperature ranges quoted, thermodynamic equilibria are established for the gases H₂, N₂ and CO and stationary states for O₂ and H₂O. The corresponding P-T-C relationships for solid solutions are known.

The gas contents of niobium were calculated from the partial pressures with the aid of these relationships; these approximated to the values determined by gas analysis, especially for oxygen and nitrogen. Thus, with the aid of continuous mass-spectrometric measurements during the melting process, a qualitative control of the final contents is possible.

Hardness vs degree of deformation

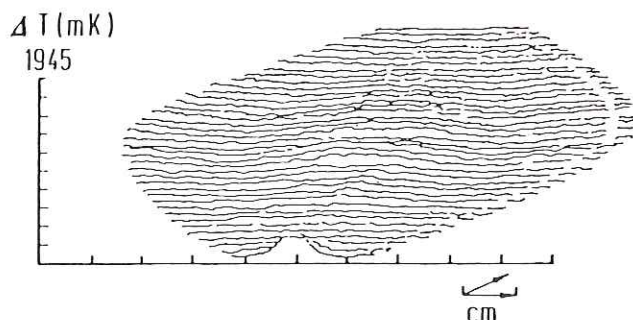


The mechanical properties of these high-purity niobium qualities are of interest with regard to the deep drawability for producing cavities.

The individual hardness curves show almost the same characteristic shape but are displaced parallel to each other; the low degree of final work hardening represents an advantage for the deep drawability of this material.

Microscopic surface defects, such as scratches, inclusions of foreign material and rolling defects, have a negative effect on the quality of cavities, because they represent sensitive areas of disturbance for the high-frequency superconductivity leading to local overheating.

Temperature maps ΔT vs cavity surface



Mechanical parameters of niobium sheets with high thermal conductivity

	Tensile strength R_m (N/mm ²)	Yield strength $R_p 0.2$ (N/mm ²)	Elongation $A_L 30$ (%)	Grain size ASTM
longitudinal	183	80	59	6-7
transverse	180	83	59	6-7

SUMMARY

The test results and the accelerating voltages achieved are shown for cavities manufactured at the most important worldwide research centres from the new niobium qualities. The data represent a breakthrough in the fields of high-frequency superconductivity.

Cavity performances

Laboratory	CERN		Cornell	DESY	KEK	Darmstadt/Wuppertal
Material	Nb	Nb	Nb	Nb	Nb	Nb
f (MHz)	350	500	1500	1000	508	3000
Operat. temp. (K)	4.2	4.2	1.8	4.2	4.2	1.8
Single cell cavities						
E_{acc} (MV/m)	10.8	13.5	22.8	5.5	7.6	23.1
Q_0 at low field	3.8	3.5	-	-	(4)	7
Q_0 at E_{max}	1.9	0.7	2.5	0.5	0.6	1.2
Multicell cavities						
Number of cells	4	5	5	9	3	5
E_{acc} (MV/m)	7.5	5	15.3	5.5	5.8	12.3
Q_0 at low field	6	1	-	0.7	(2)	-
Q_0 at E_{max}	2.4	0.7	2.2	0.5	0.6	3.5

Since the introduction of 'Nb 100', W.C. Heraeus have constantly developed better qualities with enhanced properties and corresponding mechanical parameters for the different cavity applications. As a result of the use of the new niobium qualities, an increase in the high-frequency field strength is often no longer limited by materials but by electron field-emission phenomena.

For this reason, better surface qualities have to be developed in competition to copper cavities with sputtered Nb layers in the future. Additionally, critical mechanical parameters of so-called national pressure vessel codes are coming more and more into account, and niobium becomes, therefore, an actual construction material. Major efforts are in progress to achieve a number of specialised properties, especially on a large scale for big projects.

T.I.C. statistics

PRODUCTION AND SHIPMENTS

(quoted in lb Ta₂O₅ contained)

2nd quarter 1987

Material grade	Production	Shipments
Tin slag (over 2 % Ta ₂ O ₅)	121 307	124 086
Tantalite (all grades)	49 740	49 916
Other materials	0	0
Total	171 047	174 002

Note : The response from the companies asked to report was 14/16 and included these producers :

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

PROCESSORS' SHIPMENTS

2nd quarter 1987

Product category	lb Ta contained	lb Ta ₂ O ₅ equivalent
Tantalum oxide/K ₂ TaF ₇	30 860	41 661
Carbide	125 318	169 179
Powder/anodes	213 442	288 147
Mill products	72 449	97 806
Alloy additive, scrap, ingot, unworked metal and other	43 076	58 153
Total	485 145	654 946

Notes :

1. The response from the companies asked to report was 18/19 and included these processors :

Cabot Specialty Metals - Electronics
Fansteel
W.C. Heraeus
Kennametal
Metallurg Group
Mitsui Mining and Smelting
NRC
Showa Cabot Supermetals
Hermann C. Starck Berlin
Treibacher Chemische Werke
Vacuum Metallurgical Company

2. Reports were made in lb tantalum contained.

Capacitor statistics

EUROPEAN TANTALUM CAPACITOR SHIPMENTS

(thousands of units)

2nd quarter 1987

138 542

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

JAPANESE TANTALUM CAPACITOR PRODUCTION AND EXPORTS

(thousands of units)

2nd quarter 1987

Production 684 124
Of this exports 196 223

(Data from JEIDA)

U.S. TANTALUM CAPACITOR SALES

(thousands of units)

1st quarter 1987

	<i>U.S. shipments</i>	<i>Exports</i>	<i>Total</i>
Foil	284	18	302
Metal-cased	25 939	8 811	34 750
Molded	80 407	15 070	95 477
Dipped	70 844	13 093	83 937
Chips	27 073	1 888	28 961
Wet slug	2 352	298	2 650
Total	<u>206 899</u>	<u>39 178</u>	<u>246 077</u>

2nd quarter 1987

	<i>U.S. shipments</i>	<i>Exports</i>	<i>Total</i>
Foil/wet slug	2 455	216	2 671
Metal-cased	31 675	10 183	41 858
Nonmetal-cased	157 487	30 519	188 006
Chips	22 922	1 800	24 722
Total	<u>214 539</u>	<u>42 718</u>	<u>257 257</u>

(Data from EIA)