

The influence of recent developments in tin on present and future tantalum supply

The vast majority (perhaps over 95%) of tantalum is currently produced in association with tin, and so the continuing "crisis" in this industry has important implications for tantalum supply, in terms of both current production and future availability. On the very anniversary of the suspension in 1985 of tin trading on the LME, the T.I.C. held a panel discussion which attempted to provide a realistic assessment of these implications. This was on the occasion of the Twenty-sixth T.I.C. General Assembly in Brussels last October. Sitting on the panel were experts on tin and tantalum production in the significant regions of the world. Questions and comments were invited — and received — from the assembled delegates and guests. This article summarises the replies offered by the panel, as well as attempting to inform further on this subject.

Speaking on the situation in **Africa**, Mr Michael Herzfeld (Sominki) estimated that production of tin-in-concentrates had declined from about 10 000 tpy to 5500 tpy with the result that the associated Ta_2O_5 production in all materials had almost been halved from 80-90 tpy to 40-50 tpy. However, this reduction had been under way well before the outset of the tin crisis. In Zaire, there had historically been three major producers: Somika (BRGM), Sominki and Zairetain (Geomines). Production of Ta_2O_5 had declined from about $36\frac{1}{2}$ tpy in previous years to about $12\frac{1}{2}$ tpy currently. Most Zairean mining operations were of a small, high-cost nature. Geomines were in liquidation, and so little production was taking place at the Zairetain smelter. Similarly in Rwanda, Somirwa (also Geomines-owned) had closed, previously producing about 12 tpy Ta_2O_5 . In Nigeria, Makeri Smelting's production of tin (and hence of tin slag) was now only nominal, and that, together with a fall in the mining of other tantalum raw materials, meant a fall in output from $12\frac{1}{2}$ tpy Ta_2O_5 to $2\frac{1}{2}$ tpy. In South Africa and Zimbabwe, however, Mr Herzfeld reported that production was being sustained at previous levels. The South African-owned Iscor smelter was continuing to produce about 8 tpy Ta_2O_5 although this quantity would decline in the longer term. Grades in the slag were 5-7 % Ta_2O_5 . At Kamativi Tin Mines in Zimbabwe, there was also no immediate reduction in output envisaged, about 25 tpy being produced. Mr Herzfeld omitted to mention tantalum production at Minas Gerais de Mozambique which has no tin association, and so the events of the past year will have no direct influence there.

Mr Rod Tolley (Datuk Keramat Smelting) described **Malaysia** as a "marginal producer" of tantalum, this being contained in low-grade tin slag, typically 2-3 % Ta_2O_5 unless special measures were taken. At the current low prices for tantalite, a grade of 3 % Ta_2O_5 had little value. It was not economic for the smelters to maintain stocks and segregate higher Ta-content ore batches in order to produce higher-grade slag material. Past combined production at the two Penang smelters had been about 90 tpy Ta_2O_5 : this quantity was currently down to about 50 tpy. Tin production in Malaysia would be 28-29 000 t of tin-in-concentrates (newly mined) in 1986 and could fall as low as 18-20 000 t in 1987, according to the States of Malaya Chamber of Mines. The Singapore smelter (Kimetal), which in the past had produced quantities of Ta_2O_5 -containing slag (produced from Thai tin concentrates) had closed.

Tin production in **Thailand** in 1987 was estimated to fall to 15-18 000 t, according to Mr Jaap Langenberg (Thaisarco). This would be half of the 1982 level just before ITC export controls were in place. If this reduction was spread equally over all the tin-producing provinces, it would mean that the quantity of Ta_2O_5 produced in slags would experience the same overall decline. Most of this tantalum came from concentrates originating from a specific tin belt spread over several provinces. Grades of Ta_2O_5 in Thaisarco slag are high, normally over 10 %.

Mr Noel Cook (Wogen Resources) spoke of the situation in **China** which has certainly been affected by the tin crisis, although the impact has been softened by a major devaluation of the currency. Figures are difficult to obtain on domestic consumption, but their self-sufficiency in tin is demonstrated by large exports of tin concentrates in recent months. Little is known of their tantalum production, but again they would appear to be self-sufficient. There would not appear to be

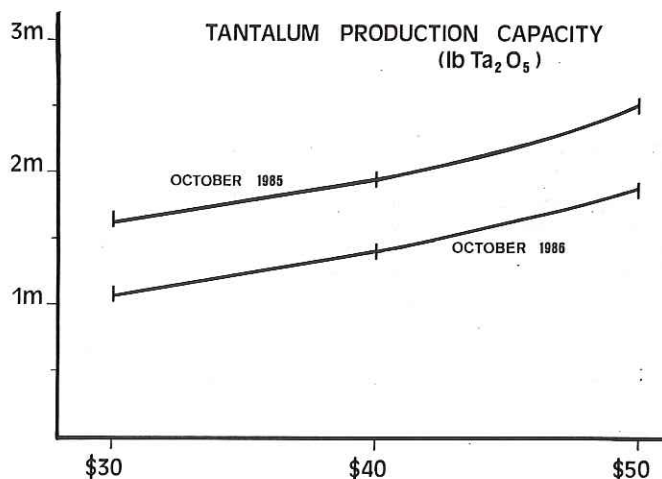
any commercial amounts of tantalum associated with their tin concentrates.

Mr Egberto Silva Filho (Mamoré Mineração e Metalurgia) said that the existing tin-mining regions of **Brazil** would experience a long-term decline in output as a result of the crisis. The Ta_2O_5 grades in the slag from the Mamoré smelter were normally 1-2 %, not saleable at current tantalite prices. However, the Pitinga primary deposit in the Amazon held huge reserves of tin at a higher grade than other deposits in Brazil. The Paranapanema Group were planning to operate a pilot plant at Pitinga in 1987 producing tin concentrates and 100 t/month of by-product columbite with a $Nb_2O_5 : Ta_2O_5$ ratio of 10 : 1. If this plant proved feasible to operate, this columbite would become commercially available. Brazilian tin production in 1987 would experience a slight increase over 1986, said Mr Silva.

In **Australia**, reported Mr John Linden (Greenbushes), only tin deposits in the western half of the continent contained tantalum. Operations in the Pilbara region and Northern Territory had closed in the past year, leaving only the Greenbushes field still in production. Here, mining was being concentrated on high-grade tin deposits to produce more tin and so increase cash-flow. Almost 1000 tpy were currently being produced of which practically all went to domestic buyers. Due exclusively to the poor state of the tantalum market, 1986 tantalite production was significantly down on the previous year's level.

The immediate outlook for tin is not encouraging: current production is being depressed by the old ITC buffer stock which has still to be consumed, and the future trend of demand for the metal is downwards. Available smelting capacity is nearly three times world demand. It is noticeable that two tin-mining areas of the world which are committed to increasing production are non-tantaliferous: Indonesia and Renison in Tasmania (Australia). In 1985, production of tantalum in slags totalled about 1.1m lb Ta_2O_5 : this is set to fall to about 0.9m lb in 1986 and 0.6m lb this year. The actual quantities may be less but will almost certainly not be greater. If prices for tin do not improve significantly within the foreseeable future, tin miners in S.E. Asia, especially those operating high-cost gravel pump mines, will probably walk away from the business for good. In Nigeria, Rwanda and Zaire, the decline in the mining sector was well in progress before the tin crisis occurred.

Current tantalum production is depressed not only due to the crisis in tin but also because of the depressed tantalum market. It is therefore maybe more meaningful to examine the effect on production capacity rather than looking only at current output. This can be done by contrasting the T.I.C. production estimates for the year ahead made in October 1986 with those from October 1985, immediately before the crisis broke. World capacity is being under-utilised at present due to the inventories of raw material being held by processors.



It can be deduced that about 0.5m lb Ta_2O_5 of capacity has been "lost" at \$30, \$40 and \$50 MB price quotations. Taking into account unrecoverable processing losses and scrap recycling, current demand by processors can be estimated to be about 2.1-2.2m lb Ta_2O_5 . The above estimates indicate that whereas previously this

demand could be met by a price of about \$40/lb Ta₂O₅, now a price of over \$50 would be required.

It should be noted that most major tantalite producers are either relatively small in terms of tin (Cia. de Estanho Minas Brasil, Greenbushes) and so have greater flexibility in the marketing of their tin output or are not tin producers (Minas Gerais de Mozambique, Tanco). Kamativi Tin Mines plan to commence tantalite concentrate production this year. And at Coframines (France), although the deposit is tin- as well as tantalum-bearing, the major product is kaolin. The envisaged future annual output is approximately 100 000 lb Ta₂O₅. Processors of tin-mining waste in S.E. Asia can provide swing capacity by producing struverite and tantalite, although their capability is obviously limited by the availability of suitable raw material.

These sources of supply will need higher tantalite prices to bring them into large-scale operation because of their higher costs of production.

Andrew Jones
Technical Officer

President's letter

The recent panel discussion in Brussels brought out very clearly the strong interdependence of tin and tantalum, and I am sure I was not alone in remarking how consistent the relationship was in the very different parts of the world described by the panellists. The recent histories of the two metals have much in common: a run-up of price to the point where substitution occurred, "new" sources of supply attracted to the market (the Brazilian and other tin fields for tin; the slag from under the streets of Penang for tantalum) and great technical advances so that very much less of the metal was required for a particular application (higher CV powders for tantalum capacitors; thinner tinplate coatings on a smaller throughput).

Even the second metal in our new title, niobium, was caught up to some extent in the tin turmoil, because:

- there is at least as much of it as tantalum in the average tin slag, and it is recovered from it and then used for high-purity applications;
- commercial deposits of columbite are worked in tin-mining areas, and mining is liable to be cut back generally when the market for the major metal falls.

It is curious that within two days of our Twenty-fourth Assembly in Brussels the Tin Council ran out of money, with all the consequences we discussed, and that over the period of the Twenty-sixth Assembly there appeared the first significant rise in the price of tin from the depths. This rise has continued since we met, and I hope for all our sakes that we can now look forward to the tin industry again contributing annually the one million pounds or so of recoverable Ta₂O₅ to provide the bedrock of the world's supplies of the metal.

I cannot conclude this, my first letter for the Bulletin, without expressing the warm thanks of all of us to Dr Hayashi for the work he did during his year of office as President (including organising the highly successful meeting in Kobe), and to Dr Korinek for stepping in at short notice and so admirably running the recent meeting in Brussels.

Yours sincerely,
R.J. Tolley
President

Twenty-sixth General Assembly

The Assembly was held at the Ramada Hotel, Brussels, on October 24th 1986. The meeting was chaired by Dr George Korinek, NRC Inc., who commenced the proceedings by giving a brief summary of the present state of the tantalum industry.

Nava Bharat Enterprises Ltd, manufacturers of capacitor anodes in India, were re-instated as a T.I.C. member. Resignations accepted by the Assembly brought the total number of members to sixty-nine.

Mr Rod Tolley, Datuk Keramat Smelting, was elected President for the coming year.

The Technical Officer exhibited data which showed that world tantalum capacitor shipments had risen by an average of 9 %/quarter from 4th quarter 1985 to 2nd quarter 1986: this was, however, merely attributed to re-stocking by manufacturers following the previous year's draw-down of component inventories. It was also shown that following the outset of the tin crisis in October 1985 about 0.5m lb Ta₂O₅ had been lost from tantalum raw material production capacity as a result. This subject — the effect of the crisis on tantalum

production — formed the central theme to the afternoon's panel discussion: an account of those discussions is included in this issue of the Bulletin.

Two presentations formed the remainder of the meeting:

"Ultrapure refractory metals - facts and fiction" by Prof. Hugo Ortner, Metallwerk Plansee;

"Production, characterization and applications of ultrapure niobium" by Dr Klaus Schulze, Max-Planck-Institut für Metallforschung.

It was announced that the Twenty-seventh General Assembly would be held in Rio de Janeiro, Brazil, in June 1987, and would include visits to the mines of CBMM and Cia. de Estanho Minas Brasil.

MEMBERSHIP

The following company was re-instated as a member of the association, by decision of the Twenty-sixth General Assembly:

Nava Bharat Enterprises Limited
(Electronics Division),
Navabharat House,
6-3-654, Somajiguda,
Hyderabad 500 482, India.

The General Assembly accepted the resignations of:

Bhuket Union Thai Minerals
Kennametal
Alfred H. Knight International
Centro Minero Penouta
Reading Alloys
Willan-Wogen Alloys

Twenty-seventh General Assembly

The next meeting of the T.I.C. will be held from June 1st to 3rd 1987, including the Twenty-seventh General Assembly on June 2nd, at the Sheraton Hotel, Rio de Janeiro. Further information on the programme will be available from the Secretary General of the T.I.C.

Production, characterization and application of ultrapure niobium

This paper was presented at the T.I.C. meeting in Brussels on October 24th 1986 by Dr Klaus Schulze, Max-Planck-Institut für Metallforschung.

The efforts directed to the preparation of ultra-high-purity (UHP) niobium are described. The first step in production of UHP niobium is understanding the goals: the degree of purity necessary, the impurities which are especially intolerable and, finally, what the experimental constraints are (i.e. size and shape of samples, temperature, gases, etc.). The major importance of purity is due to the influence that the interstitial impurities C, N, O and H have on electrical and thermal conductivity, as well as on superconducting and mechanical properties of Nb.

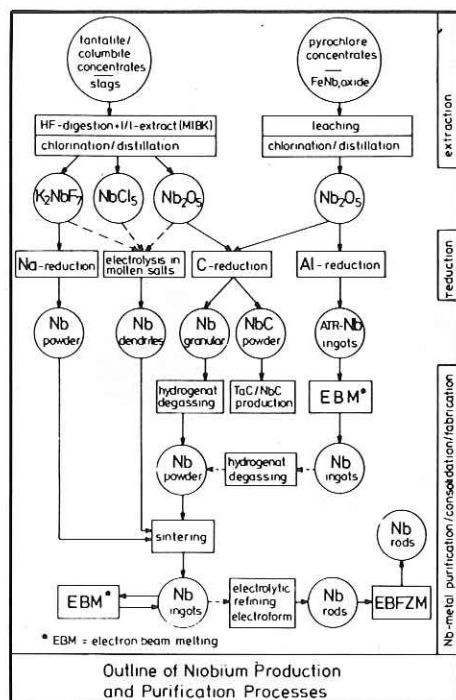
The major metallic impurities are reduced by chemical and electrochemical methods and EB melting. The highest degree of purity has to be attained by EB melting, because during subsequent fabrication and application an irreversible uptake of non-metallic impurities occurs, unless high-temperature UHV annealings are performed. The application of pure Nb and Nb-based alloys is discussed.

EXTRACTION AND PRODUCTION

At first view, processing raw materials, reduction, refining by EB melting and fabrication routes have remained unchanged; on a nearer view, considerable improvement in Nb quality has been achieved due to purer oxide production, a better understanding of ATR processes and EB refining, the availability of new EB production plants and the application of modern analytical methods with high detection sensitivities.

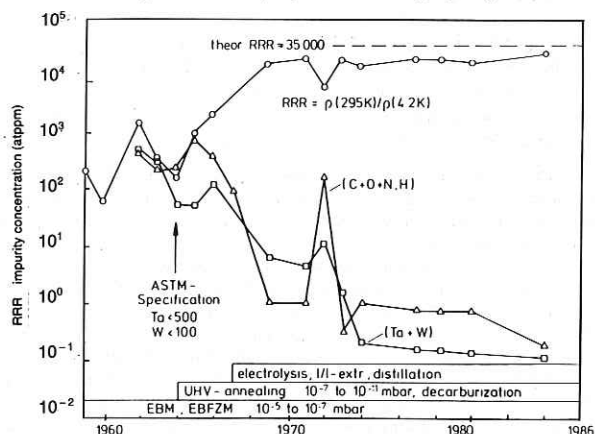
Nb metal production, previously from columbite/tantalite processing, was extended by the increasing importance of the pyrochlore route branch: today about 95% of Nb consumed comes from pyrochlore as the source material. Therefore the aluminothermic reduction (ATR) of Nb₂O₅ from pyrochlore processing, followed by EBM, was applied on a larger scale. However, the problems of purification shifted from extraction metallurgy to metal refining during EBM. The separation

of volatile metals (like Al) from ATR-Nb ingots can easily be performed by EBM. Small concentrations of less volatile elements, mainly Ta and W, must be separated either during extraction or after EBM, e.g. by electrolytic refining.



A short review of the results of Nb ultrapurification on a laboratory scale indicates the future development of purification processes on an industrial scale. A brief survey of the efforts directed to preparing high-purity Nb is given below. The maximum electrical residual resistivity ratios (RRR values) published each year and the corresponding Ta, W and interstitial concentrations are plotted against the year. Measuring the electrical resistivity of metals at low temperatures is an excellent tool in determining impurity concentrations. The upper curve shows that RRR values have steadily increased by more than two orders of magnitude over the last two decades and approach the theoretical value. The best results from large-scale production of Nb are comparable with those achieved 20 years ago on a laboratory scale.

Progress in the preparation of high-purity Nb



During earlier years, electron-beam melting techniques (EBM, EBFZM) were applied with moderate results. Neither the thermodynamics or kinetics of the reactions between Nb and the residual reactive gases in high vacuum nor the behavior of metallic impurities during EBM and EBFZM were well known. The simultaneous application of consecutive refining steps for three groups of impurities — volatile metallic elements (Al, Fe, alkalis, Cr, etc.), non-volatile metallic elements (Ta, Mo, W) and non-metallic elements (C, O, N, H) — lead to a further increase in purity.

PREPARATION OF ULTRAPURE NIOBIUM

Based on the results of known purification processes and by consequently applying knowledge about niobium-gas reactions, an improved method has been developed for the preparation of ultrapure niobium, consisting of :

- a double electrolytic refining in an alkali-fluoride melt containing fluoro-potassium niobate (K₂NbF₇);
- electron-beam float-zone melting (EBFZM) in UHV; and
- UHV annealing and decarburization.

Starting with EBFZM Nb of commercial quality (140 wt-ppm Ta, 35 wt-ppm W), the Ta and W contents were reduced by a first electrolysis to approximately 4 and 0.04 ppm. Before secondary electrolytic refining using a salt bath with extremely low Ta and W contents, this material was subjected to an additional EBFZM process. The material produced by the second electrolysis was further EBFZM-refined three times. Material produced by this technique has impurity concentrations below 0.4 wt-ppm Ta and 0.01 wt-ppm W. The concentrations of volatile metallic elements range from sub-ppm to sub-ppb levels. A further reduction of the interstitials by annealing in UHV results in an impurity content far below 1 µg/g (1 wt-ppm) or 99.99999 % Nb.

The behavior of metallic impurities dissolved in Nb during electrolytic refining is shown below. In the first column the composition of the starting material is shown; in the other columns are the analyses of samples purified by electrolysis (Nb-R-1) and by EBFZM (Nb-R-2).

Impurity concentration in Nb

Element	Nb(TWCA) ^a	Nb-R-1 ^b	Nb-R-2 ^b
Ta	83 ppm	0.05-3 ppm	0.05-3 ppm
W	3.8 ppm	1 - 30 ppb	1 - 50 ppb
Mo	1.2 ppm	96 ppb	75 ppb
Cr	3 ppb	6 - 28 ppb	17 - 44 ppt
Fe	26 ppb	1 - 3 ppm	3 - 11 ppb
Co	85 ppt	0.3-2.5 ppb	6.3-30 ppt
Cu	95 ppb	44 ppb	<20 ppb
V	5 ppb	0.4 ppb	0.3 ppb
Ti	0.3 ppm	<0.1 ppm	<0.1 ppm
Al	90 ppb	110 ppb	20 ppb

* in atomfraction, (a) averages from three determinations, (b) content ranges of separately purified samples

The most difficult reactions to control are those between niobium and gases and so these reactions are treated in more detail.

NIOBIUM-GAS REACTIONS

One of the most significant characteristics of Nb is its ability to react readily with gases (H₂, N₂, O₂, H₂O, CO, CO₂, NH₃, hydrocarbons, etc.) and elementary C. The interaction of Nb with the elements H, N, O and C is not only responsible for undesirable changes in physical and mechanical properties of the solid metal but also plays an important role during refining in the liquid and solid states and during fabrication processes. Purification can only be achieved by melting or annealing at temperatures above 2000 °C under high vacuum. Annealing at lower temperatures, even under high vacuum or in inert gas, leads to a continuous uptake of interstitials.

When Nb reacts with gases a particular mechanism is involved. Gas molecules striking the surface are decomposed, they penetrate the surface and finally are dissolved. Absorption and desorption of H₂ and N₂ follow these reaction steps. Under certain conditions of low gas pressure and high temperature, the rates of gassing and degassing reactions become equal, resulting in thermodynamic equilibria.

In the Nb-oxygen system, the equilibrium oxygen pressure is negligibly small and below the residual gas pressure of ultra-high vacuum systems, and no O₂ desorption is possible, only absorption. However, the removal of oxygen can be accomplished by the evaporation of the volatile monoxide at temperatures greater than 1900 °C. The formation of volatile oxide leads to a continuous metal loss during melting and annealing of O-containing metal or in O-containing environments. At low O₂ pressures and high temperatures, the rate of NbO evaporation can become equal to the rate of O₂ uptake which results in so-called steady states, where the concentration of dissolved oxygen is a function of O₂ pressure for a given temperature. When water vapour reacts with Nb, the same steady states are observed, but at these high temperatures H₂ desorbs from the surface. In a flowing NH₃ atmosphere, another type of steady state reaction occurs : NH₃ is completely decomposed and H₂ and N₂ molecules are absorbed and desorbed. At high temperatures, the N concentration in Nb is determined by the rate of N uptake from the NH₃ atmosphere. During the reaction with CO, true thermodynamic equilibria can be established between CO gas and C and O atoms dissolved in liquid or solid Nb. In contrast, a steady uptake of carbon is observed when Nb is annealed in hydrocarbon atmospheres.

DEGASSING, DEOXIDATION AND DECARBURIZATION

The conditions for optimizing the degassing treatments of Nb are not completely described by the equilibrium reactions and steady states :

the kinetics of the processes are also of great importance. In general a high degassing rate can be established when the difference between the state of supersaturation and the partial pressure is high. Large amounts of gases can be freed from the ingot only at high equilibrium partial pressures. In other words, if high equilibrium partial pressures cannot be achieved by using the appropriate degassing temperatures, the amount of gas evolved at the surface is too low to guarantee a reasonable degassing rate. For low concentrations and low equilibrium pressures, UHV techniques must be applied even for degassing in the liquid state: this is the situation for nitrogen in niobium.

The lowest possible concentration of nitrogen which can be achieved is determined by the ultimate partial pressures in the reaction chamber. From this it can be deduced that the time necessary to achieve this final state and the condition of partial pressure is not only given by the kinetics, i.e. reaction rate, diffusion, melting time, etc., but also by the practical constraints, such as pumping speed, leakages and composition of the residual atmosphere.

A complete degassing of oxygen by oxide formation at temperatures above 1900 °C can easily be achieved by annealing or melting niobium under high-vacuum conditions.

Carbon desorbs only through a mixed channel in the form of CO. The equilibrium pressure of CO over niobium is relatively high and so the carbon content of oxygen-containing niobium is rapidly reduced at high O and C concentrations. Depending on the relative concentrations of oxygen and carbon, either decarburization via CO and simultaneous deoxidation via NbO formation for high O concentrations, or only volatile NbO formation for low O concentrations at the surface may occur. Therefore two ways of decarburization are possible:

- CO degassing of ingots with excess oxygen concentration in the bulk, leading to a critical carbon concentration of about 6 wt-ppm which cannot be removed further due to the by-pass NbO evaporation;
- CO degassing by increasing the oxygen partial pressure to establish an excess oxygen concentration at the surface.

When Nb is annealed in hydrocarbon atmospheres, deoxidation can be accomplished either by the formation of volatile oxide or via the formation of carbon monoxide. As with decarburization, deoxidation depends on the oxygen surface concentration. After longer reaction periods, carbon is present in excess and dissolves into Nb.

FINAL INTERSTITIAL CONCENTRATIONS

The final concentrations of the interstitially-dissolved elements (O, N, C, H) which can be achieved during annealing Nb in typical HV and UHV environments are shown below.

Calculated Interstitial Concentrations and RRR-Values for Niobium after High-Vacuum Annealing at 2200°C		
Reactions	Percent of Total Pressure	
	UHV	HV
(1) $H_2 \rightleftharpoons 2 H$	90	8
(2) $H_2O \rightarrow O + 2 H$	<1	20
(3) $O_2 \rightarrow 2 O \rightarrow 2 NbO$	<1	20
(4) $CO \rightleftharpoons C + O$	9	8
(5) $N_2 \rightleftharpoons 2 N$	<1	40
(6) $C_m H_n \rightarrow mC + n/2 H_2$	<1	4

However, the final concentrations are additionally determined by:

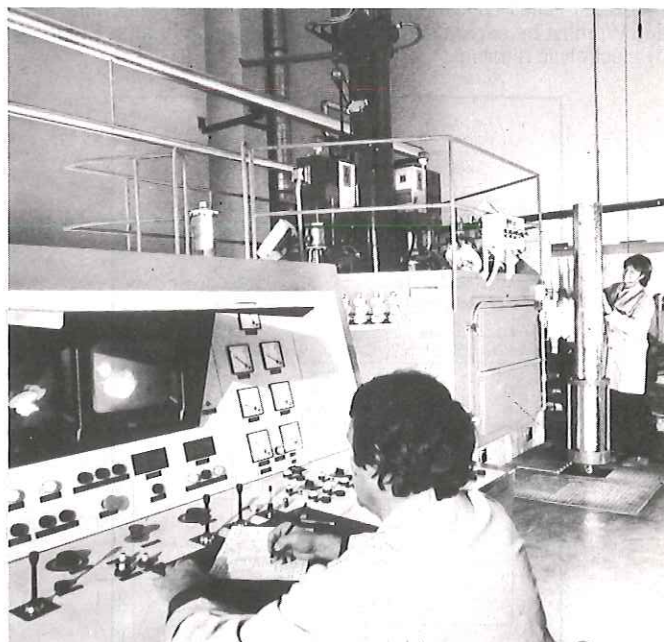
- the rate constants for the reaction and the activation energies;
- the attainable end pressures of the equipment during annealing or melting;
- the distribution of the element between liquid and solid state.

ELECTRON-BEAM MELTING

Because of the increasing demand for IVa, Va and VIa metals over the last decade, the electron-beam furnace has been developed to a reliable, efficient apparatus for melting, purification and alloying.

EBM is particularly suited to the production of niobium ingots. A furnace with a capacity of 450 kW which was built for purifying ATR niobium is shown below. The installed EB power is sufficient for the production of Nb ingots with 225 mm diameter and 2300 mm length. The material is fed horizontally in the first melt and vertically in the following melts.

EBM plant at Leybold Heraeus



The main process data differ from plant to plant with ingot diameter, EB power and pump speed. A typical example for non-metals is shown with the chemical analyses of C, O, N, H after each melt.

Concentration of non-metals after each melting cycle (µg/g)

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

From these and similar results, the following conclusions can be drawn:

- due to the low solubility of hydrogen at elevated temperatures, H_2 is easily eliminated;
- the C concentration is nearly constant with the number of melts and practically no decarburization occurs, although — at first sight — sufficient oxygen is available. This effect is due to the strong NbO evaporation and low O surface concentrations;
- the N concentration decreases slowly until it approaches the final value determined by the N_2 partial pressure.

From a rough evaluation of the scarce reliable data and analyses of refined niobium ingots, it can be summarized that the Al content in niobium, starting with ATR ingots with 3-6wt% Al, can be reduced quantitatively during the first two melts. Therefore, refining niobium by EB melting is a question of the O, N and C removal. Differences in chemical composition of the top and bottom parts of the ingots are often reported, indicating that the final gas pressure has a greater effect than the time that the metal is in the liquid state. Therefore, it is desirable to improve the vacuum system with respect to pumping speed and final pressure. Modern EB furnaces are equipped with melt-chamber valves, which allow loading and unloading of drip-melt electrodes without breaking the vacuum, and with dynamically-pumped sealings at feedthroughs and doors. With these improvements, a pressure of 10^{-5} to 10^{-6} mbar can be maintained during melting, thus providing better ingots and reducing the number of melts.

FABRICATION

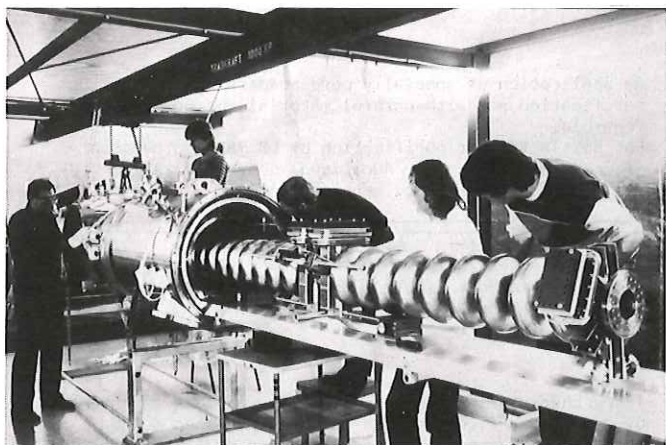
The fabrication of niobium is complicated by the fact that at elevated temperatures it reacts with gases and so all heat treatments must be carried out in high vacuum or under a pure inert gas atmosphere. The amounts of gases and carbon absorbed even at room temperature are considerable.

The thickness and the quality of the absorbed oxide layers depend on the purity of the niobium. The thickness of the absorbed oxide layers determined by angle-resolved X-ray photon spectrometry (ARXPS) show that high-purity samples have better surface behavior due to a very thin NbO layer below Nb_2O_5 . These smoother oxide layers are defect-free, thus reducing serration of the surface.

APPLICATION OF HIGH-PURITY NIOBIUM

Niobium has the highest critical temperature for superconductivity of any element (T_c of 9.2K). Pure niobium is used for the fabrication of superconducting high-field, high-frequency accelerating cavities in particle accelerators. Quenching of the superconducting state caused by small area defects and electron loading are today the prime field limitations encountered in superconducting rf cavities. Any fabrication step and cleaning procedure will leave defects in the micron range which produce thermal instabilities on the surface of the cavity.

Superconducting cavity structure



Niobium can be considered to be the "working horse" in superconductivity: nearly all alloys and compounds used and tested have niobium as a base material, e.g. NbTi, Nb₃Sn, Nb₃Ge and finally Nb₃Al. One of the promising compounds for high magnetic fields ($H_c > 20T$) is Nb₃Al, but unfortunately multifilament structures made from Nb₃Al must be produced by the powder-metallurgical route. The amount of absorbed gases in the Nb powder particles has to be carefully controlled, a considerable challenge to production.

Low Ta-content niobium is of primary interest in reactor technology because of its low thermal neutron cross-section and so is used as a cladding material for fuel elements. Furthermore, Nb is well suited as a monitoring material for fast neutrons, so reactor safety and surveillance programs, as well as material testing programs, are using Ta-free niobium. Ta contents below 1 ppm are necessary.

SUMMARY

Ultra-high-purity niobium (7N-5N) can be produced on a laboratory scale with Ta below 0.3 wt-ppm. If this material is annealed in UHV, RRR values of 25 000 are attained, i.e. the theoretical value is approximated (0.1 ppm residual impurities). Starting from high-purity oxide, ATR of the oxide and EBM, volatile metallic elements are reduced to the sub-ppm level, even on an industrial scale. The production of niobium ingots with low gas and carbon contents has to be improved, because during further fabrication impurities are always introduced.

There is sufficient room to improve the quality of Nb ingots, mill products and powders if known thermodynamic and kinetic results on niobium-gas reactions are applied carefully.

The number of melts can be reduced to four by using better vacuum conditions, resulting in a quality with RRR ~ 500.

Bayer acquire Hermann C. Starck Berlin

Bayer issued the following press release during October 1986:

"Bayer AG, Leverkusen, have bought an interest of over 90 per cent in Hermann C. Starck Berlin KG, the chemical and metallurgical company. The acquisition has been approved by the Federal Cartels Office.

The company will continue to operate in its present form as a separate legal entity. Starck's existing activities will not only be maintained but are also to be further developed and expanded in partnership with Bayer and supplemented by moving into new areas.

In addition to the parent company with plants at Goslar and Laufenburg employing a total of about 2500 people, the Starck group

also includes the joint ventures NRC Inc. (USA) and Hermann C. Starck Berlin Werk Rhina in Laufenburg, and sales companies in New York and Tokyo. Group sales in 1985 were about DM 800m, with foreign business accounting for over 60 per cent.

With the acquisition of Starck, one of the world's major producers of special metals and their compounds, Bayer AG are expanding their activities in inorganic chemistry and opening up further future-oriented fields, such as high-performance materials — including hard metals and engineering ceramics — and electronics.

In this way, Bayer are continuing to pursue their strategy of rounding out existing activities and opening up important new areas of technology to the company through acquisitions. In January 1986, Bayer acquired a majority interest in Cremer-Forschungs-Institut GmbH of Roedental near Coburg, thus gaining a foothold in the development-intensive and highly promising field of engineering ceramic components.

Starck's business centres on the manufacture and marketing of tantalum and niobium compounds, and also tungsten, molybdenum, cobalt and their compounds. These are used in the manufacture of hard metals, catalysts, chemical raw materials and special alloys, as well as in a number of other applications. The company also markets a variety of specialties, such as raw materials for engineering ceramics and special powders for flame and plasma spraying.

Bayer expect their co-operation with Starck in inorganic research to be of benefit to both companies."

Since 1984, Bayer have been co-operating with Greenbushes in a joint exploration venture at the Bynoe tin-tantalum project, Northern Territory of Australia. This is through their wholly-owned subsidiary, Barbara Mining, which funds 100 per cent of exploration costs while earning a 50 per cent interest. A pilot plant was constructed in 1985.

Ultrapur refractory metals - facts and fiction

This paper is by Prof. Hugo Ortner and Dr Peter Wilhartitz of Metallwerk Plansee and Prof. Manfred Grasserbauer of the Institute for Analytical Chemistry, Technical University of Vienna. It was presented at the T.I.C. meeting in Brussels on October 24th 1986 by Prof. Ortner.

Ultrapur is becoming an increasingly common term in the field of refractory metals. Applications in electronics, superconductors and the nuclear industry require materials of very high purity. The greatest influence on ultrapur of refractory metals at present comes from electronics for VLSI applications. Essentially, VLSI (Very Large Scale Integration) means miniaturization, the goal of VLSI development being to pack as many tiny electronic components as possible into the smallest possible space. Smaller circuits operate faster and so ultimately reduce the cost of computation, creating new possibilities for application.

Refractory metal silicides are being increasingly employed as gate materials and diffusion barriers for MOS-LSI technology (Metal Oxide Semiconductor - Large Scale Integration). Materials presently in use comprise WTi, Mo, MoSi₂, TaSi₂ and TiSi₂. The different components are normally deposited on the silicon substrate by PVD (Physical Vapour Deposition) and have to be ultrapur, especially with respect to mobile ions. With increasing miniaturization, intrinsic radioactivity also has harmful effects, and so components have to be free of uranium and thorium. Non-metals (O, N, H and C) are detrimental too, as are impurities of Fe, Co, Ni and Cu for certain applications. The quality of PVD-deposited components depends to a high degree on the properties of the target used for PVD deposition. Usually, refractory metals and silicon are co-sputtered due to the shortage of ultrapur refractory metal silicides. An increasing number of companies is offering ultrapur refractory metal materials for PVD sputter targets, but information on analytical methods used for chemical characterization of such materials is often scarce and sometimes misleading. This is not surprising since it is only gradually being realized that the preparation of ultrapur refractory metals might be easier than reliable trace chemical characterization.

FACTORS LEADING TO FICTION IN CHARACTERIZATION OF ULTRATRACES

Results of ultratrace analysis are frequently misinterpreted, not only by commercial colleagues with little technological background but also by technical staff, simply because it is not realized what is being discussed. Scientific managers want simple analytical answers so as not to further complicate already complex questions about material properties. But simple answers are sometimes wrong answers.

Pure and ultrapure refractory metals and analytical limitations - present situation and specifications of Metallwerk Plansee (MP) products

Purity (m/m) products				Normal MP Specifications		Necessary Analytical Installations/Remarks	
Purity % (m/m)	Common Abbreviation	Sum of Trace Impurities (µg/g)	Matrix Metal	Guaranteed Purity % (m/m)	Typical Purity % (m/m)		
99,9	3N	Pure	1000	Nb	99,80	99,90	Trace characterization in well-equipped industrial laboratories feasible with highly-experienced personnel. Detection limits in the order Of 0,1 to 1 µg/g. Main methods of analysis: GFAAS and ICP-OES
99,95	3N5	RM	500	Ta	99,83	99,92	
99,98	3N8		200	Ta (+Nb)	99,88	99,93	
				Ta K, KS	99,95	99,98	
				Mo	99,95	99,97	
				W	99,95	99,98	
↓							
MP Ultrapure RM							
99,99	4N	Ultra-	100	Mo, W }	99,99	99,995	By application of specially pure powders without further purification and with careful material characterization feasible.
99,995	4N5	pure RM	50	Nb, Ta }	99,995	99,990	
				Gases O, N, H and other re- fractory metal traces are usually excluded.			For Nb, Ta further purification by EB melting necessary if gases should be low. Additional characterization by NAA, SIMS, SSMS, etc. very advisable.
↓							
99,999	5N	If RM	10	Ultratrace analysis (bulk		Trace characterization only feasible with highly in- strumental methods (NAA, SIMS, etc.). Hence not feasible in ordinary industrial laboratories.	
99,9995	5N5	available, 5 true purity very questionable to be 5N, 6N		contents ≤ 1 to < 0,001 µg/g)			
				Usually, gases and other re- fractory metal impurities are excluded.			
99,9999	6N		1	Even surface impurities are in the same order as relevant bulk contents. Therefore, such purities exclude also surface contents.		Trace characterization only feasible in clean rooms and by use of purified reagents and multiple-step methods (trace-matrix separation mandatory) or by SIMS (ultra- sensitive, ultraclean method, UHV).	

Analytical results at the ppb-level are difficult to obtain, and inter-laboratory comparisons exhibit a scatter of values which is inversely proportional to the concentration level. This is a natural phenomenon symbolizing the state of the art of analytical characterization of materials and should not be interpreted — as it often is — as due to incompetency of the analytical laboratories involved. Results are frequently misinterpreted due to a lack of understanding of the terms generally used in analytical chemistry — especially those for the ultratrace characterization of solid materials. The most important definitions are according to IUPAC recommendations.

A **typical analysis** for a trace component in a metal matrix should be derived from a long-term inspection of a metal production and is the mean of cumulative measurements taken over a period of production. The following information should also be available :

- the number of independent measurements from which the mean was derived;
- the standard deviation;
- the time period of observation together with any observed trends;
- the method of analysis with respective figures of merit.

Typical analysis data for a trace contaminant give an impression of the general impurity level for this element and also any observable trends. Such data are, however, no guarantee for the actual trace content of a specific lot. For ultratrace levels, such data are frequently obtained with methods, such as NAA and SIMS, which are not easily adaptable to routine production control.

The **actual analysis** is carried out for a specific production batch, samples usually being taken according to a fixed schedule.

The **guaranteed analysis** is the maximum impurity level which the supplier guarantees his customer in a particular product. Such guarantee levels are derived from a long-term characterization of the product, also taking into account any trends in the respective concentration level. Difficulties arise in this context with heterogeneously-distributed impurities.

Certificates of analysis for ultrapure materials often exhibit a number of features which might mislead the user who is not an expert in ultratrace characterization. Some specific examples follow :

- If only typical analyses are given with no further information, this gives no guarantee that the trace contents in the delivered material are similar to the values in the certificate.
- Typical and guaranteed analyses are frequently mixed up in analysis certificates. If this is so, the elements for which guaranteed analyses are provided should be clearly indicated, and the same additional information as was outlined for typical analyses is highly desirable for guaranteed analyses also.

— The "analytical volume" of the method used must be considered. This is the volume or quantity of the material to be used for the analysis. For classical methods, it is usually in the order of one to ten grams which are dissolved and so homogenized prior to end determination. For SIMS, SSMS or OES, this is not the case, and the amount of material actually used might be in the order of a few milligrams (OES) or even micrograms (SIMS, SSMS). With these small quantities, heterogeneous distribution, especially of ultratrace components, is often observed. Hence it is necessary either to take measurements at many locations or to do a depth profile to give further information on ultratrace distribution. Only on the basis of such information is it possible to come to an unequivocal bulk value for an ultratrace component using minute samples.

— Since it became common use for total purities to be given according to the number-of-nines concept, hardly an ultrapure material can be found where this concept is applied without exceptions. For refractory metals, other refractory metal traces and gases (O, N, H), as well as carbon, are usually excluded. Therefore, even materials declared as 6N-purity are in fact 4N or at best 4N5 if all traces are considered. The number-of-nines concept, although easily understood, has lost much of its relevance. It would be technologically more meaningful to tabulate the trace components with their actual contents which are important or harmful for the particular application of the material.

ULTRATRACE CHARACTERIZATION OF REFRACTORY METALS - FACTS

Those trace analytical methods which are widely applied for routine control are generally capable of bulk analysis down to the µg/g-level without tedious matrix separation procedures. Generally, analysis down to a level of about 0.1 µg/g can also be handled without special precautions. The most sensitive methods for metallic trace components in refractory metals are presently GFAAS, ICP-OES and DCP-OES. For non-metallic components, such as O, N, H, C and S, fusion extraction and combustion analysis are the only methods used throughout industrial laboratories, again with detection limits in the µg/g-range. Purities of 4N and 4N5 for refractory metals can be verified only by a combination of all these methods and experienced personnel. Additional characterization and cross-checking by methods such as NAA, SIMS, GD-MS or SSMS and extensive "round-robin" tests are necessary to assess the accuracy of such results.

Materials of 5N-purity or better can only be characterized by highly-instrumental methods, mainly by AA and mass spectrometry, exhibiting detection limits in the ng/g- or even pg/g-range. Both groups of methods frequently exhibit the additional advantage of

being able to distinguish between bulk and surface trace contents. Intensive development, especially for SIMS, led to fascinating results in the field of ultratrace and topochemical analysis of refractory metals. In the following, the results obtained for bulk ultratrace analysis are summarized for tantalum and niobium.

SIMS was used for the determination of about 40 elements in **tantalum**. Calibration is, however, only accomplished for some elements by use of ion-implanted standards, since no doped tantalum powder is presently available. A comparison of relative sensitivity factors of tungsten and tantalum shows that relevant factors are similar, and so results for tantalum samples were calculated by use of RSF's for tungsten. The results, which are summarized below, were obtained from two EB-melted sheet-bar materials.

Summary of trace levels for impurities in EB-melted Ta sheet-bar material:

< 1 ppb : B Mg Mn Sr V Y
 < 10 ppb : Al Ca Cr Ga La Na Ti Zr
 < 100 ppb : As Ba Br Cs Fe K Ni Th
 0.1 - 1 ppm
 and < 1 ppm : Ag Ce Cl I P U
 Major impurities,
 10 - 1 ppm : Cu Mo Nb S Si

The use of SIMS for the ultratrace characterization of EB-melted **niobium** for superconductors and nuclear applications is planned. However, niobium is an ideal matrix for activation analytical methods due to its low cross-section of absorption, especially for thermal neutrons. The preparation of ultra-high-purity niobium has been extensively described by Dr Klaus Schulze, Max-Planck-Institut für Metallforschung. By a combination of processes such as molten-salt electrolysis, electron-beam float-zone melting and ultra-high vacuum annealing, niobium with a residual electrical resistivity ratio of less than 10^4 can be produced. Less than 1 ppm of interstitial impurities (except for H) has also been achieved.

CONCLUSION

Ultrapure refractory metals are becoming increasingly important for micro-electronic applications (Mo, W, Ta and their silicides) or for superconducting and nuclear applications (Nb). Materials of at least 4N- and at best 6N-purity are presently in use and on the market. However, rather than considering total purity, it would be technologically more meaningful to specify for harmful trace elements for particular applications. Concentrations of certain trace impurities below 1 ppm down to 1 ppb are found critical, e.g. U and Th traces in the ever finer structured VLSI-MOS chips of 1 mega-bit and more capacity.

In a systematic survey of trace analytical methods which can be applied to ultratrace characterization of refractory metals, it became obvious that only mass spectrometric and activation analytical methods are applicable with a broader scope, i.e. for multi-element characterization at the ppb-level.

The application of high-performance SIMS to EB-melted tantalum is superior to any other ultratrace analytical approach. It could be shown that the inspected tantalum was very pure with only five traces above the 1 ppm limit.

SIMS usage for the ultratrace characterization of EB-melted niobium for superconducting and nuclear applications is under way. However, niobium can also be excellently characterized by AA methods. The purest available technically-prepared EB-melted Nb materials usually exhibit RRR values of 110 to 150. Japanese brochures claim RRR values of up to 3500 for 5N-niobium (Toyo Soda Mfg. Co.). This material is purified by thermal decomposition of Nb-halogen compounds prior to EB-melting.

The ultratrace characterization of refractory metals is feasible with sufficient sensitivity by mass spectrometric and activation analytical methods. SIMS has the unique additional advantage of offering topochemical information on ultratrace distribution in refractory metals. An intensive application of SIMS to ultratrace characterization of refractory metals will greatly enhance our knowledge of refractory metal ultrapurity, related effects and behaviour of these materials in the most advanced fields of high technology.

ABBREVIATIONS USED IN THE TEXT

AA Activation Analysis
 DCP-OES Direct Current Plasma - Optical Emission Spectrometry
 EB Electron Beam
 GD-MS Glow Discharge - Mass Spectrometry
 GFAAS Graphite Furnace Atomic Absorption Spectrometry
 ICP-OES Inductively Coupled Plasma - Optical Emission Spectrometry
 NAA Neutron Activation Analysis
 RM Refractory Metal
 RRR Residual Resistivity Ratio

RSF Relative Sensitivity Factor
 SIMS Secondary Ion Mass Spectrometry
 SSMS Spark Source Mass Spectrometry
 UHV Ultra High Vacuum

T.I.C. statistics

Price Waterhouse report the following collected statistics :

QUARTERLY PRODUCTION ESTIMATES

(quoted in lb Ta₂O₅ contained)

LMB quotation :	\$30	\$40	\$50
4th quarter 1986	262 350	332 100	446 850
1st quarter 1987	272 350	347 100	461 850
2nd quarter 1987	272 350	357 100	461 850
3rd quarter 1987	272 350	357 100	491 850
4th quarter 1987	272 350	357 100	491 850

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

PRODUCTION AND SHIPMENTS

(quoted in lb Ta₂O₅ contained)

3rd quarter 1986

Material grade	Production	Shipments
Tin slag (over 2 % Ta ₂ O ₅)	177 121	70 060
Tantalite under over 25 % Ta ₂ O ₅	32 789	25 486
Other materials	0	0
	209 910	95 546

Notes :

- The response from the companies asked to report was 15/18 and included these producers :
 Datuk Keramat Smelting
 Greenbushes
 Malaysia Smelting
 Metallurg Group
 Tantalum Mining Corporation of Canada
 Thailand Smelting and Refining
- Taking into account unrecoverable processing losses, it can be estimated that the above raw material shipments are equivalent to 70 775 lb tantalum (after processing).

PROCESSORS' SHIPMENTS

3rd quarter 1986

Product category	lb Ta contained	lb Ta ₂ O ₅ equivalent
Tantalum oxide/K ₂ TaF ₇	49 279	66 527
Alloy additive	53 351	72 024
Carbide	140 739	189 998
Powder/anodes	176 353	238 077
Mill products	70 622	95 340
Scrap, ingot, unworked metal and other	57 140	77 139
Total	547 484	739 105

Notes :

- The response from the companies asked to report was 17/18 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
- Reports were made in lb tantalum contained.

T.I.C. data for the years 1981-1983 (lb tantalum) :

<i>Product category</i>	<i>1981</i>	<i>1982</i>	<i>1983</i>
Carbide	610 814	445 019	472 865
Powder/anodes	687 301	623 529	728 893
Mill products	229 118	190 261	248 329
Oxide/K ₂ TaF ₇ , alloy additive, scrap, ingot, unworked metal, other	227 906	205 041	458 447
Total	1 755 139	1 463 850	1 908 534

Capacitor statistics

EUROPEAN TANTALUM CAPACITOR SHIPMENTS

(thousands of units)

3rd quarter 1986 130 284

(Data from ECTSP)

JAPANESE TANTALUM CAPACITOR PRODUCTION AND EXPORTS

(thousands of units)

	<i>Production</i>	<i>Of this, exports</i>
3rd quarter 1986	602 237	144 969
(Data from JEIDA)		

U.S. TANTALUM CAPACITOR SALES

(thousands of units)

3rd quarter 1986

	<i>U.S. sales</i>	<i>Exports</i>	<i>Total</i>
Foil	307	15	322
Metal cased	27 008	8 794	35 802
Non-metal cased	133 387	27 245	160 632
Chips	17 043	1 602	18 645
Wet slug	2 089	193	2 282
Total	179 834	37 849	217 683

(Data from EIA)