

## Japanese Tantalum production 1974 and 1975

The latest reports received from the Japanese New Metals Association and the Ministry of Finance provide a comparison of the tantalum market in Japan:

PRODUCT (Unit : kg.)	1974 Actual	1975 Actual	% Change
CONSUMPTION :			
Capacitors — Powder	76,515	34,778	(54.5)
Wire	13,566	5,843	(56.9)
Foil	833	711	(14.6)
Other	2,806	2,377	(15.3)
Total	93,720	43,709	(53.4)
Industrial — Powder	4,950	601	(87.9)
Mill Prod.	8,663	2,564	(70.4)
Carbide	34,508	14,284	(58.6)
Oxide	10,540	9,340	(11.4)
Total	58,661	26,789	(54.3)
Grand Total	152,381	70,498	(53.7)

### SOURCE OF PRODUCTS :

Imports	58,651	25,507	(56.5)
Produced	93,730	44,991	(52.0)
Grand Total	152,381	70,498	(53.7)

The proportion of total consumption used by the electronics industry increased to 66.5 % in 1975 from 61.5 % in 1974. However, the proportion domestically produced for the electronics industry decreased from 58.1 % in 1974 to 51.3 % in 1975.

A comparison of the consumption pattern for all segments of the market during recent years shows that, even with the extreme recession in total tantalum use, the proportion used by the electronics industry continued to increase :

MARKET SEGMENT	% of total consumption			
	1972	1973	1974	1975
Electronics	48.2	54.3	61.5	66.5
Industrial	11.4	9.3	8.9	4.5
Carbide Tools	31.7	28.7	22.7	20.3
Ceramics	8.7	7.7	6.9	13.2
Consumption (m.t.)	83.7	144.5	152.4	70.5
Growth rate — %	13.9	73.0	5.2	(53.7)

Imports of source materials for 1974 and 1975 compare as follows :

SOURCE (Unit : m.t.)	1974	1975
Ores and Concentrates	109	62
Potassium fluotantalite	137	22
Tantalum scrap	22	1
Approx. tantalum content	116	36

Sources of ores in 1974 were widespread with 39 % from Australia, but in 1975 the sources were limited to fewer countries with 68 % from Australia. In both of the years, all of the fluotantalite and most of the scrap originated in the United States. The approximate tantalum content of the source materials amounted to 124 % of the finished weight of domestically produced tantalum products in 1974 indicating a slight increase in inventory after allowing for unrecoverable losses during processing. But in 1975, the approximate content amounted to only 51 % of the weight of tantalum products indicating a sizeable reduction in source material inventories.

The New Metal Association has forecast that in 1976 domestic production of tantalum products will be 62 m.t., about a 38 % increase over 1975. Imports are forecast at 28 m.t., 10 % above 1975. Thus the total expected consumption of 90 m.t. will be 28 % above 1975.

### T.I.C. SIXTH GENERAL ASSEMBLY

On October 12, 1976 at 10.00 a.m., the Sixth General Assembly of the T.I.C. will convene at the offices of Compagnie Geomines at Chaussée de la Hulpe 154, Brussels. All members will be represented and prospective members have been invited.

The Agenda for the meeting will be :

1. Approval of minutes.
2. Report of Committees :
  - a. Executive and membership
  - b. T.I.C. Bulletin
  - c. Technical Advisor
3. Status of Statistics.
4. T.I.C. Study - Phase II
5. Continuing T.I.C. Program.
6. Seventh General Assembly - Location and date
7. Other Matters.

The principle portion of the meeting will be devoted to items 4, 5, and 6. Mr. Emory Ayers and Mr. Tom Barron will personally report the results of the Phase II study. A preview shows that it will be the most comprehensive work available to date dealing with the tantalum industry. It will include production and consumption statistics as well as forecast through 1980.

The further activities of the T.I.C. will partly evolve from this study. They might include a survey of undeveloped world resources of tantalite and columbite, an investigation of secondary tantalum use and improvement of recycling, and consideration of a columbium supply/demand study.

The membership must discuss and decide upon the program of the Seventh General Assembly in accordance with the decision to rotate the location. Consideration will also be given to T.I.C. sponsorship of a World Congress on Tantalum to be held in Europe following the Eighth General Assembly in Brussels during the fall of 1977.

Non-members wishing to attend the Sixth General Assembly should contact Mr. H. Becker-Fluegel, President of T.I.C. care of National Resources Trading Corp., Inc., 576 Fifth Avenue, New York, N.Y. 10036, U.S.A., area code 212, 765-2680, telex 420213/12-6668.



# U. S. Shipments of Tantalum and Columbium products

The Bureau of Mines, U.S. Department of Commerce, reports that the shipments of tantalum and columbium products during 1975 were (1,000 lb. units) :

Product	1974	1975	% Change
Tantalum (Ta content)			
Oxides & Salts	226.1	127.4	(43.7)
Alloy Additive	24.8	8.5	(65.7)
Carbide	163.4	106.5	(34.8)
Powder & Anodes	929.4	436.6	(53.0)
Ingot	1.7	1.0	(41.2)
Mill Products	288.8	172.0	(40.4)
Scrap	45.6	13.0	(71.5)
Other	1.3	0.0	—
Total	1,681.1	865.0	(48.5)
Columbium (Cb content)			
Compounds	1,520.5	930.8	(38.8)
Metal	133.4	112.7	(15.5)
Misc.	34.0	21.2	(37.6)
Total	1,687.9	1,064.7	(36.9)

The tantalum shipments were the lowest since 1968 and were 10.0 % below the last recession year of 1971. Powder and anodes, primarily electronic product material, however, was 50.5 % of the total in 1975 and only 41.4 % in 1971.

During the year, processors product inventories were reduced in total by 9,400 lb. contained tantalum making net production at about 855,600 lb. Allowing for recoverable losses in processing and scrap purchased by processors for recycling, the ores and slags consumed by U.S. processors contained about 1,140,500 lb.  $Ta_2O_5$ . Tin slag inventories remained almost constant, but tantalite inventories increased by 1,543 tons. At an assumed average content of 33 %  $Ta_2O_5$ , the increase amounted to 306,000 lb. The G.S.A. sold 79,000 lb.  $Ta_2O_5$  in tantalite in 1975. By calculation, the imports of tin slags and tantalites would have contained about 1,370,000 lb.  $Ta_2O_5$ .

## Reduction of Tantalum

Tantalum is easily embrittled by contaminants such as oxygen, nitrogen, and carbon. Unless the content of these elements is kept to a very low level in parts per million, the tantalum metal has no ductility and is useless as a practical material. Production of pure tantalum is difficult as it is very reactive when heated and the embrittling elements are easily absorbed during processing. Efforts to develop a suitable reduction process have been made in the laboratory since the early 1800's without too much success until about 1905 when vacuum techniques were first applied. The methods developed then were not applicable to commercial production and it was not until 1920 that a feasible process evolved. Limited amounts of pure tantalum were produced until the demands during World War II led to further development. By the end of the 1950 decade, three processes were being used on a commercial scale :

1. **Sodium Reduction** - During the 1930's, Siemens & Halske in Germany developed a « bomb » process for sodium reduction of the potassium double salt ( $K_2TaF_7$ , k-salt) and produced tantalum metal at a rate of 300-350 kg. per month. Introduction of a « retort » process, described below, greatly improved the volume capability of sodium reduction.

2. **Electrolysis** - As early as 1922, Fansteel Metallurgical Corp. (now Fansteel Inc.) produced tantalum metal by electro-

lysis of fused k-salt. The pure k-salt formed the electrolyte in an iron pot which served as a cathode with a carbon rod in the center as the anode. At a temperature of 700°C a direct current passed through the cell causes tantalum metal crystals to form on the lining of the pot and the electrolysis proceeds until polarization brings it to a halt when about one-half of the tantalum in the salt has been reduced. After cooling, the contents of the pot are removed, pulverized, and washed to separate the tantalum from the remaining salt.

3. **Carbon Reduction** - The simplest reduction process is the reduction of tantalum oxide by carbon. A mixture of the oxide and fine carbon, usually lamp black, is placed in a retort within a vacuum furnace. At 2100°C, the reduction reaction takes place with the evolution of carbon dioxide, the latter carried off by the vacuum system. After cooling in the vacuum to ambient temperature, the metal can be removed in chunks for further processing. Union Carbide Corp. practiced this method to provide feed stock for subsequent purification by electron-beam melting.

Each of the above processes as practiced in the 1950 and 1960 decades had limitations, particularly as a source of metal to provide powder suitable for the production of pressed anode capacitors. The « bomb » method of sodium reduction was limited to small batches and was too

costly. Although electrolysis provided most of the tantalum used until 1960, the particle size and quality left much to be desired for capacitor powder. The balance of carbon against oxide was difficult to control in the carbon reduction process and the tantalum almost always contained excessive levels of either element.

## SODIUM REDUCTION

The first breakthrough in a viable process using sodium reduction was made by National Research Corporation (now NRC Inc.) in the late 1950's. Gradually the entire industry adopted the process and since 1970 almost all tantalum metal has been produced by sodium reduction. Up to this time sodium reduction of tantalum had been effected in « bombs », but the development of the Kroll process for the reduction of titanium demonstrated a technique that could be applied to the reduction of tantalum by sodium in larger retorts. The process has gradually developed to that used today but the hardware involved is essentially the same as designed at the beginning. The only significant change has been the increase in size of the reduction retorts to some in use now which reduce as high as 3,000 lb. per batch.

The general type of hardware in use illustrated in the sketch consists of the following parts :

1. **Retort** : The retort is a thimble shaped vessel with a pressure tight lid made of nickel-base alloy to resist the corrosiveness of the salts.

2. **Agitator** : An agitator is used to keep the fused salts moving in the retort providing homogeneity during the reduction cycle.

3. **Sodium feed** : The sodium is liquified external to the retort in a heating chamber and is pumped into the retort at a controlled rate.

4. **Furnace** : A pit type furnace is used into which the retort is placed during the reduction cycle. The furnace has the capability to heat the retort and its contents to 1,000°C. It is an air furnace lined with refractory.

## SODIUM REDUCTION

Potassium fluotantalate (k-salt) is reduced by metallic sodium in the following manner :



The reduction is seemingly independent of temperature as long as both the k-salt and the sodium are in the liquid state. Since k-salt melts at 650°C and sodium melts at 97.9°C, the reaction should be initiated at a temperature above 650°C. However, as the reduction progresses, the evolved two parts KF and five parts NaF has a melting temperature in the range of 875 to 880°C. Thus the temperature must be allowed to rise during reaction to maintain a liquid condition. Such is easy as the reaction is exothermic but the rate of sodium addition must be controlled to prevent runaway.

As originally practiced, the salt charge consisted entirely of k-salt. When the sodium was fed into the top surface of the molten charge, the KF and NaF immediately formed at the top surface.



Since the density of these salts is considerably lower than that of the k-salt, they floated on the surface and, as a result of their higher melting temperature, formed a crust which prevented the sodium from penetrating to the k-salt underneath. Although the temperature could be increased to melt the crust, the result was a considerable loss of sodium as it vaporizes at 880°C. An agitator was introduced which kept the salt mass moving from top to bottom, preventing the formation of the crust and keeping unreduced k-salt at the top surface to react with the sodium. Thus the temperature could be kept below the vaporization temperature of the sodium and loss was minimized.

Subsequently, it was found that mixing a fluxing salt, NaCl, with the initial charge of k-salt made it possible to operate at still lower temperatures. This resulted in improved quality. It has been demonstrated that with sufficient fluxing salt addition, reduction could be carried out at temperatures as low as 300°C. However, the yield in recoverable tantalum drops as the reaction temperature is reduced. Thus today the reaction temperatures are maintained in practice somewhat above 800°C, low enough to prevent sodium loss but high enough to produce recoverable yields above 95 %.

## PROCESSING PRACTICE

In general, processing is practiced as follows :

1. The k-salt and fluxing salt mixture is loaded into the retort to a level which leaves adequate room for the sodium and the increased volume of salt resulting from the reaction.
2. The lid is secured in place and the retort is first evacuated and then back-filled with an inert gas, which prevents contamination from the air as the salt is brought up in temperature to the molten state.
3. The retort is placed in the furnace and the sodium feed system, gas system, control wires, etc., are connected.
4. The temperature is elevated to the melting point of the salt and held there long enough to be sure that all of the salt is in the molten state.
5. Liquid sodium is fed into the retort at a controlled rate to maintain a constant temperature. During the reduction cycle, the external heat of the furnace is cut off as the process generates its own heat. The agitator is operated to keep the molten mass of salt circulating so that all of the salt is exposed to the sodium.
6. After the reduction is complete, ascertained by the quantity of sodium introduced to effect complete reduction of the k-salt charged, the temperature is maintained to keep the salt liquid for an extended time of three to four hours. After a short time, agitation is stopped so that as many of the dispersed tantalum particles as possible will settle to the bottom of the retort. Most of it collects in a friable lump at the bottom, but the very fine particles remain suspended in the salt.
7. The heat source is removed and the retort is allowed to cool to ambient temperature, maintaining a vacuum so that no air contamination will result. When ambient is reached, the retort, which has been removed from the furnace, is opened.

8. The spalt is either dug or flushed out of the retort. It is completely dissolved to recover all of the tantalum suspended in the spalt although 90 % or more is usually in the chunk in the bottom.

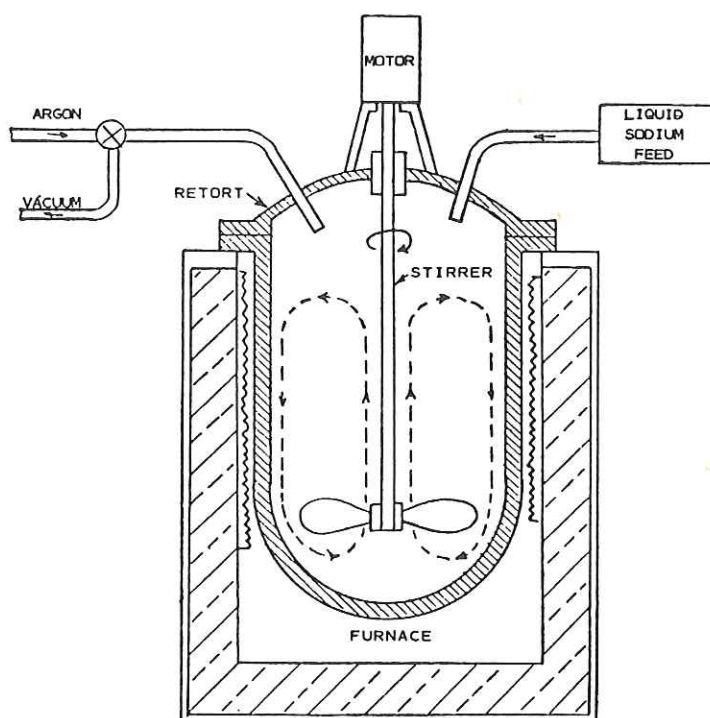
9. A series of steps washing and leaching are performed to remove all of the spalt from the tantalum.

Due to some k-salt not being reduced and the loss of some very fine particles in washing, the overall yield is generally about 95 %.

## RECENT DEVELOPMENTS

The literature, particularly issued patents, indicates that efforts are continuing to improve the sodium reduction process in the search for techniques that will lead to higher capacitance powders for elec-

tronic capacitors. Since particle size, particle shape, size distribution, and contamination all affect the quality of capacitor powder, means are being developed to optimize these characteristics. The effect of the ratio of k-salt to fluxing salt on the particle size and the reaction temperature has been explored. Increased use of fluxing salt results in lower reaction temperatures and, as a result, less contamination and smaller particle size. But in view of lower yields at the lower temperatures, NCR, Inc. has developed a method of pre-coating the k-salt particles with sodium so that an intimate association of the two materials is obtained. Thus reduction begins at a temperature as low as 300°C and, although the ultimate temperature might reach 1000°C, the benefits of low temperature are obtained for at least part of the reduction. By this means, NRC, Inc. claims to be able to produce capacitor powder with much higher capacitance levels than previously attained.



## Niobium - Processing and use

Niobium (called « columbium » in the United States) is a sister element of tantalum. Comparable physical characteristics are as follows :

	Niobium	Tantalum
Atomic Number	41	73
Atomic Weight	92.91	180.948
Specific Gravity	8.57	16.6
Melting Point °C	2,415	2,996

The mechanical characteristics of the two metals are so similar that they can be used almost interchangeably for many applications. Tantalum is used for capacitors as its oxide has preferable dielectric quality, but the use of niobium has been evaluated. In high temperature structural applications, niobium is frequently used instead of tantalum because of weight and price advantage. The carbides provide similar benefits to cutting tools and the present trend is away from exclusive use

of tantalum carbide to a mixture of the two carbides. As alloying additions to steels and superalloys, niobium is favored because of cost.

## SOURCES OF NIOBIUM

There are four sources of niobium : pyrochlor, columbite, tantalite, and tin slags. Pyrochlor is used almost exclusively to make the common grades of ferroniobium



used by the steel industry in applications which can tolerate a fair amount of contaminating elements not removed in processing. But when purity is required, niobium alloying additions and niobium metal must be derived from high purity niobium oxide produced as a by-product of tantalum processing.

All tantalites with the exception of micro-lites and the Bernic Lake materials contain significant amounts of niobium. So do the tin slags used as sources of tantalum. The columbites from Nigeria, Brazil, and Malaysia usually contain enough tantalum that they are processed for the tantalum content with the niobium becoming available as the refined oxide. Beyond these materials, however, there are no sources which provide high purity niobium. Economic ways have not been developed to produce such from pyrochlor. Direct refinement is too expensive and, until the demand for high purity niobium exceeds the supply from tantalum processing, there will be no incentive to develop economic pyrochlor processing.

## PROCESSING HIGH PURITY NIOBIUM

In the chemical process used to digest and extract tantalum from raw materials, high purity fluoniobic acid is separated from the fluotantallic acid. Then, by precipitation with ammonium hydroxide, pure niobium oxide is formed. After filtering the precipitate from the solution, it is calcined to produce a stable oxide. This white powder can then be exothermically reduced by either aluminum or carbon to produce ferroniobium, nickel-niobium, niobium metal, or niobium carbide.

To produce either master alloys or pure metal, the oxide is mixed with aluminum powder and placed in a shaft furnace lined with alumina refractory. The mixture is ignited and a violent exothermic reaction takes place generating tremendous heat and a great volume of aluminum oxide smoke. The entire mixture becomes molten and the niobium, being heavier than the aluminum oxide slag, sinks to the bottom of the furnace and collects into a large mass of metal. Upon cooling, the metal chunk can be extracted from the furnace and separated from the slag. Since an excess of aluminum is preferred to incomplete reduction, the mass includes some entrapped aluminum as well as some slag. For alloying addition purposes, the slag is mechanically cleaned away from the metal by hand and by shot-blasting.

For metal applications, however, more sophisticated cleaning is required. Niobium, like tantalum, is ductile only in a highly purified state. With the included aluminum and slag, it could never be worked into useful shapes. To further refine it, electron-beam melting is required. The reduced metal is broken into small enough pieces that it can be charged into the electron-beam furnace in aluminum boats. The metal melts slowly and the aluminum (in the metal and in the boats) and other impurities vaporize. Because of the dirty condition of the reduced metal, more than one melt is

required to clean it up, as many as four or five melts are sometimes required.

Once a ductile ingot has been obtained, the niobium can be readily processed by forging and rolling. Since most applications require characteristics not available from pure niobium, alloys are produced. These are generally made by using the electron-beam melted ingot as an electrode for remelting in a vacuum arc furnace of the consumable electrode type. The alloying elements are welded to the outside of the electrode in the proper weight to produce the desired analysis. Sometimes two melts are required to obtain large ingots, complete homogeneity, and to make a final correction in composition.

## HIGH PURITY NIOBIUM USES

The uses of high purity niobium result from its unique properties, singly available in other metals, but generally not in the unique combination offered by niobium. Some applications are:

1. **Superalloys** : Many of the superalloys used in the manufacture of jet engines, gas turbines, and missiles contain up to 5 % niobium as an alloying constituent. The addition of niobium to these nickel-base alloys increases the resistance to thermal shock and improves the hot ductility and strength. Additions are made to the superalloy melt by use of a nickel-niobium master alloy produced by exothermic reduction of the refined niobium oxide with nickel addition similar to the production of the pure metal.

2. **Cutting tools** : Tantalum carbide is added to tungsten carbide in cemented carbide cutting tools, particularly those used for machining steel, to improve the transverse rupture strength of the tool. In order to reduce cost, some producers are using tantalum-niobium carbide which provides similar benefits.

3. **Superconductors** : Some materials, particularly niobium-base alloys containing titanium, tin, and zirconium, have zero electric resistance at cryogenic temperatures. Such allows high electric current flow with no energy loss. By using these alloys to make electromagnets, very strong magnetic fields can be generated. To the present, such magnets have been used principally for physical research and medical equipment, but research is being carried out to apply the superconductive principle to power transmission lines, alternating current generators, magnetically suspended trains, particle filtration, fusion reactors, etc.

4. **Nuclear energy reactors** : Because of the low neutron absorption characteristic of niobium, it is a good structural material in nuclear power reactors. Although most reactors use zirconium as fuel cladding, there are several operating reactors using alloys containing niobium. Such alloys can usually operate at higher temperatures than those using zirconium cladding. The combination of high-temperature strength, low neutron absorption, and inertness to liquid sodium and potassium makes niobium the prime candidate for use in the

next generation of power reactors operating at higher temperatures with liquid metal coolants.

5. **Gas turbines** : In addition to the super-alloy use in gas turbines and jet engines, niobium-base alloys provide even higher temperature operation capability in the combustion zones of gas turbines. Although use at present in production turbines is small, the trend toward higher temperature operation to attain greater efficiency indicates an increase in the use of niobium metal and alloys.

6. **Nuclear fuel reprocessing** : Neither tantalum nor niobium react with plutonium, a major constituent of spent nuclear fuel. Because of its lower cost, niobium is being used in equipment for reprocessing nuclear fuel to salvage from it the residual energy containing elements. With continued growth of nuclear power generation, the amount of fuel reprocessing will greatly increase providing a growing market for niobium components of the processing equipment.

Free world production of refined niobium oxide is estimated to have grown from about two million pounds in 1972 to somewhat over three million pounds in 1974. During this period a sizeable portion of the source material was the columbite sold by the U. S. National Stockpile. That source is now exhausted and future supply must come from currently produced tantalite, columbite, and tin slag. In 1975, due to the general recession and low production of tantalum, the newly produced refined niobium oxide probably dropped again to the two million pound level. However, in 1975 the market did not decline to this extent and accumulated inventories were used. Although tantalum production is expected to be higher in 1976 than in 1975, the production of refined niobium oxide will be inadequate to meet the market demand. These assumptions are supported by the increase in price from about \$3.10 per kilogram in 1972 to \$10.25 per kilogram at present.

## FUTURE POTENTIAL

Although rapid escalation of the demand for high purity niobium products has been forecast at regular intervals for the past twenty years, such has never materialized. Instead, there has been a gradual spread of applications as technologies have developed which require higher performance materials. Commercial application of several new products resulting from this technical development could result in significantly greater demand at any time. If a significant proportion of the potential superconductivity applications are realized, demand could possibly increase by several thousand tons per year by the end of the century. Since, at present, the supply of high purity niobium is limited by the availability and processing of tantalum source materials, even a small increase in the demand rate could create a very tight supply situation. The trend for greater use of niobium products is upward in almost every application. It can be expected that a tight supply-demand condition will continue.