PROCESSING OF COLUMBITE-TANTALITE ORES AND CONCENTRATES FOR NIOBIUM AND NIOBIUM COMPOUNDS IN ELECTRONIC APPLICATIONS

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Abstract

A small percentage of Niobium and Niobium compounds produced in the World is being used in sofisticated electronic components and systems, such as capacitors, piezoelectric devices and optical circuits. This paper briefly describes the outline of the production process of these materials and their main characteristics.

Niobium: From Ore to Sophisticated Products

The Niobium Market

In 1999, about 87,60% of the total worldwide requirements (50,6 Mlb of contained Nb) for niobium was marketed in the form of ferroniobium for the high strength low alloy (HSLA) steel and stainless steel industries (1). About 2% of niobium was converted into special alloys like NbTi, NbZr, NbCu and roughly 10% took the form of chemical compounds like Nb_2O_5, $NbCl_5$ and vacuum grade FeNb, NiNb.

Table I Illustrates the application and niobium product shipments from 1996-1999 (1)

Niobium Products Shipments, 1996-1999 Mlb contained niobium				
	1996	**1997**	**1998**	**1999**
Chemicals & unwrought forms:				
Nb_2O_5, $NbCl_5$, Vac. Grade FeNb, NiNb	3.45	6.02	4.87	4.91
Wrought Nb, Nb alloys, mill products:				
Powder, ingot, and scrap	0.24	0.25	0.38	0.33
Niobium alloys, NbTi, NbZr, NbCu	0.34	0.3 1	0.85	1.02
HSLA- grade FeNb	3 1.53	37.72	53.06	4.36
Total	*35.56*	*44.30*	*59.16*	*50.62*

Fabrication of Niobium Alloys and Compounds

Niobium alloys like FeNb for the steel and stainless Steel industry are mainly based on pyrochlore concentrates, whereas niobium compounds for nonferrous applications are exclusively produced from ores like columbites, tantalites, struverites or tin slag as byproducts for their tantalum content.

Obtaining and Processing of Pyrochlore Concentrates. Concentrates containing 50-60 % Nb_2O_5 are obtained from pyrochlore-containing carbonatites or weathered ores by conventional beneficiation processes such as crushing, grinding, magnetic separation, and flotation. Whereas pyrochlore from Araxa can be converted directly to ferroniobium, most pyrochlore concentrates are first chemically pretreated before niobium can be obtained. Usually**,** even in Araxa concentrates, lead, phosphorus, and sulfur have to be removed (2).

Processing of Ferroniobium. The production of FeNb in the past was based on the aluminothermic reduction of pyrochlores (3). Since 1944, the production of ferroniobium was modified to include an electronic arc furnace in the process. This achieved improvements in process control, enhanced control of gaseous effluents, increased production capacity and significantly reduced the consumption of aluminum (4).

Processing of Columbites and Tantalites for Niobium Compounds and Alloys for the Nonferrous Market

Niobium compounds and alloys for nonferrous applications can be produced either by chlorination or hydrometallurgical processing.

Chlorination. The chlorination process is an alternative to the extraction process. Today it is mainly applied to the chlorination of the niobium scrap or FeNb alloys. The reductive chlorination of ores or concentrate has been abandon because the hydrometallurgical processing of the alloys is much simpler and more economical (5).

As shown in Figure 1, niobium containing scrap or ferroniobium is comminuted and fed together with sodium chloride into a $NaCl$-$FeCl_3$ melt. The chlorinating agent is $NaFeC1_4$. The complete reaction is described by:

$$FeNb + NaC1 + 7NaFeCl_4 \rightarrow NbC1_5 + 8\ NaFeCl_3 \qquad (1)$$

$$8\ NaFeCl_3 + 4\ C1_2 \rightarrow 8\ Na\ FeC1_4 \qquad (2)$$

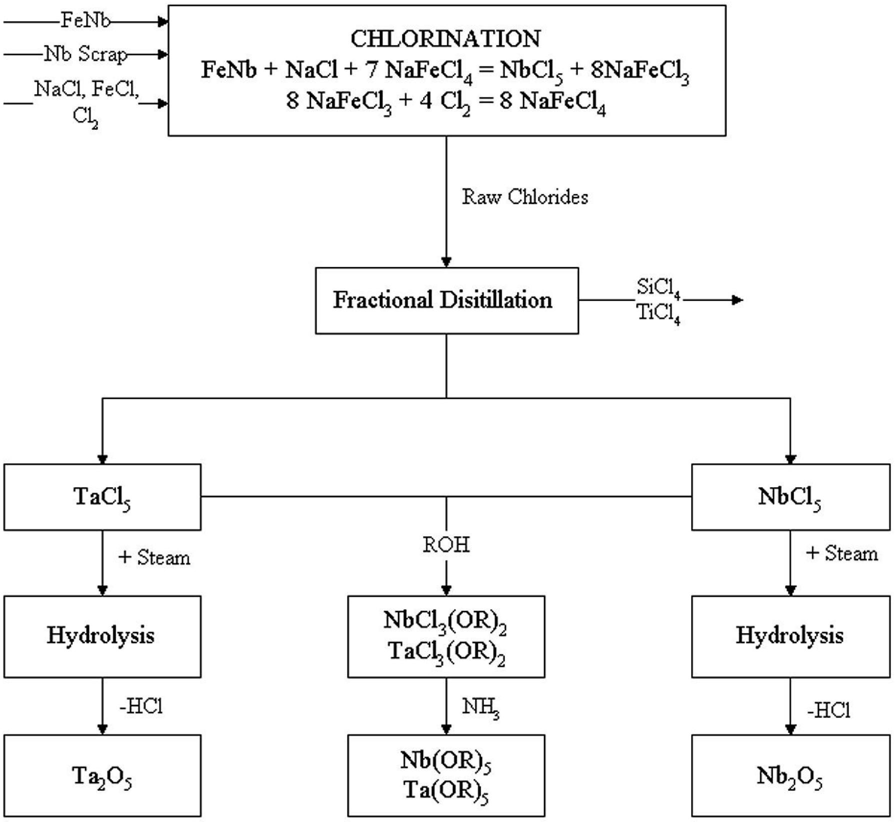


Figure 1: Processing of Nb compounds by chlorination.

The reaction temperature is as low as 500-600^{0}C. The volatile chlorides like $TiC1_4$ and $SiC1_4$ evolve from the molten salt bath. The boiling points of $NbC1_5$, $TaC1_5$ and $WOC1_4$ lie between 228 ^{0}C and 248 ^{0}C, and these compounds must therefore be separated by means of a distillation column. The chlorination of the ferroalloy produces very pure niobium pentachloride in large quantities. The pure chloride can easily be converted into high purity niobium pentoxide by hydrolysis with steam or further processed to metal organic compounds like alkoxides. The $NbCl_5$ contains less then 5-ppm tantalum and l to 2-ppm of other metallic impurities.

Hydrometallurgical Processing of Niobium Compounds (6). Today niobium and tantalum compounds are processed in large tonnage by the fluoride process including the solvent extraction process as described by the flow chart given in Figure 2.

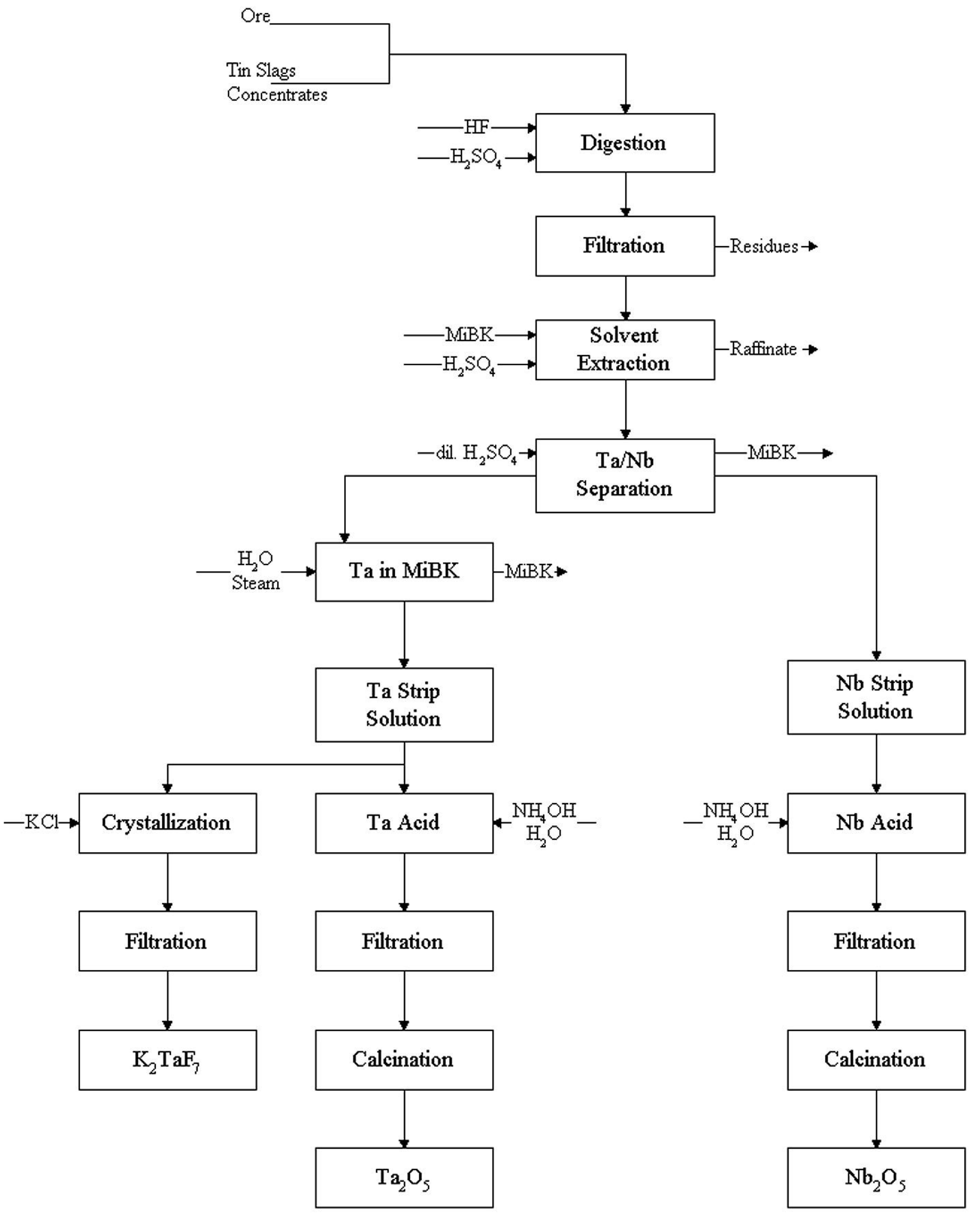


Figure 2: Hydrometallurgical Processing of Niobium and Tantalum.

Columbite and tantalite, either naturally occurring or synthetically produced as concentrates from tin slag, are digested with hydrofluoric acid at elevated temperatures. The accompanying elements are dissolved along with the niobium and tantalum, which form the complex heptafluorides H_2NbF_7 and H_2TaF_7. After filtering the insoluble residue (fluorides of alkaline-earth and rare earth metals), the aqueous solution of tantalum-niobium in hydrofluoric acid is extracted in several continuous mixer-settlers or columns with the organic solvent, like methylisobutylketone (MIBK). The complex fluorides of niobium and tantalum are extracted by the organic phase and the impurities like iron, manganese, titanium, etc., remain in the aqueous phase, the raffinate.

In practice, concentrations equivalent to 150-200 g/l $Nb_2O_5 + Ta_2O_5$ in the organic phase are maintained. The organic phase is commonly washed or scrubbed with *6-15* N sulfuric acid and then extracted with water or dilute sulfuric acid to obtain niobium by selective extraction or stripping. The aqueous phase takes up the complex fluoroniobate and free hydrofluoric acid, while the complex fluorotantalate remains dissolved in the organic phase. The aqueous niobium solution is contacted with a small amount of MIBK to remove traces of co-extracted tantalum.

The resulting organic phase is returned to the combined tantalum/niobium extraction stage. Gaseous or aqueous ammonia is added to the aqueous niobium solution to precipitate niobium oxide hydrate. Tantalum is extracted or stripped from the organic phase with steam, water or dilute ammonia hydroxide. Tantalum oxide hydrate is precipitated by ammonia, or alternatively potassium salts are added to produce the potassium salt, K_2TaF_7.

The precipitation of the oxides can be done in a batch process or in a continuously operated facility. The oxide hydrates are collected by filtration, dried and calcined at up to 1100 ^{0}C. The conditions of precipitation, drying and calcination are varied to produce different particle size distributions needed for oxides for various applications. Depending on quality requirements, the calcination is carried out in a directly or indirectly heated chamber or rotary furnace. The nature of the furnace lining has considerable influence on the purity of the oxide. For example, a lining made with Inconel will elevate the Ni and Cr impurities. Sophisticated process control and optimization enable niobium and tantalum to be produced with high yield (>95 %) and purity (> 99.9 %). These improvements have been achieved by:

a) improved process understanding,
b) precise control and monitoring of process parameters like concentrations, acidity and flow rates,
c) improved equipment like flow rate meters, special construction materials like fiber reinforced plastics or with special ceramic clad drying and calcining equipment,
d) sophisticated analytical tools like GDMS (Glow Discharge Mass Spectroscopy).

Niobium Compounds

Niobium compounds represent only about ten percent of the total niobium market (1). A variety of different applications have been commercialized for applications in the electronic market. The use in catalysts (7), optical glass (8) and pigments (9) are important as well as the upcoming use of niobium metal powder for capacitor applications.

Niobium in electronics can be subdivided into the production of single crystals (10), dielectric ceramics (11), piezoelectric ceramics (12) and ferrite's (13).

Niobium oxide, available in different qualities, is generally used as a starting material whereas other commercially available compounds like niobium chloride or niobium ethoxide play only a minor role in the niobium market.

Applications of Niobium Compounds

Lithium Niobate. For the production of lithium niobate single crystals (LN), a special quality niobium oxide (minimum 99.99 % purity) is demanded. Although this quality can easily be achieved by the chlorination process, constant improvements of the hydrometallurgical process combined with cost advantages have made niobium oxide derived from the hydrometallurgical processing the material of choice.

Two commercial applications for both integrated optical circuits (IOC´s) and surface acoustic wave (SAW) devices are dominating the LN market.

Production of Lithium Niobate Single Crystals. LN single crystals are produced by the Czochralski method (14). Niobium oxide and lithium carbonate are mixed and prereacted to form LN-pellets. In order to pull homogeneous crystals, a congruent composition is chosen slightly away from stoichiometric $LiNbO_3$.

The pellets are fed into a platinum crucible surrounded by a refractory housing and melted (at 1253°C) by radio frequency induction heating (see Figure 3). A rotating seed crystal with a given orientation is lowered into the molten lithium niobate bath and then slowly withdrawn to produce a single crystal boule. The crystal boule is then sliced into wafers, polished and sectioned into the desired shape.

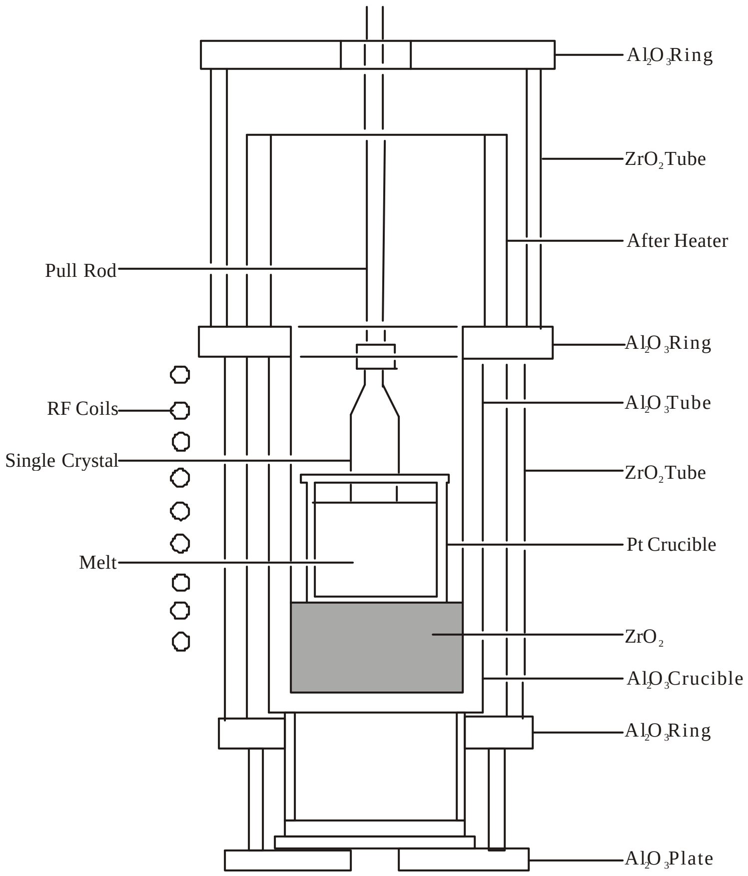


Figure 3: The Czochralski method for producing LN and LT single crystals.

Surface Acoustic Wave Devices. A series of metal (e.g Aluminum) electrodes is built on top of a polished wafer by vapor deposition to form a surface acoustic wave filter. They serve as input and output electrodes for the surface wave. The signal, while passing through the filter, is manipulated in various ways.

SAW devices are used in consumer electronics like TV sets, video games, video recorders and military applications such as encoders/decoders (15). In recent years mobile phones have contributed to the LN market growth, although lithium tantalate (LT) is gaining market share due to the demand for increased bandwidths at higher frequencies.

Integrated Optical Circuits (16, 17). Integrated optical circuits consist of one or more optical devices such as optical waveguides. An optical waveguide is able to direct light in a desired direction. LN is also used in other applications such as multipliers, wavelength filters, switches, and modulators. In contrast to electrical integrated circuits the signal is transmitted by light.

Signal transmission by light has the advantages of reduced weight, multiplexing (different wavelengths can travel simultaneously and independent), no crosstalk (no interaction as electromagnetic coupling), high reliability, higher speed than electrons in a wire and larger bandwidth (18). The greatest advantages, however, are the low loss and the ability to make the simultaneous transmission of millions of calls through one glass fiber.

To encode transmitted signals, internal or external optical modulation is necessary. Internal (direct) modulation means to switch a laser on and off. This leads to wavelength instability and results in a reduced transmission distance. To avoid this problem, LN-modulators interrupt the laser signal externally to ensure a good quality, long-distance transmission as needed for WDM (wavelength division multiplexing) and TDM (time domain multiplexing) applications (19).

Dielectric ceramics: In general, a capacitor is used to store electrical energy. It consists of two plates separated by space. The amount of electrical energy stored by a capacitor is given by the following equation:

$$C = K\frac{A}{d} \tag{3}$$

The capacitance (C) depends on the surface area of the plates (A), the dielectric layer thickness (d) and the dielectric constant (K). Due to limitations in space, attempts to increase the capacitance are made by reducing the dielectric layer thickness or by using a material with a higher dielectric constant. Table II gives a selection of dielectric constants for different materials:

Multilayer ceramic capacitors (MLCC´s) commonly use barium titanate (BT) as dielectric material. Lead magnesium niobate (PMN) as a dielectric material is playing a minor role, but in terms of quantity, PMN is already an important market for Nb-compounds. Barium titanate, however, must be doped to achieve the desired temperature characteristic. The X7R-type MLCC´s may vary ± 15 % in capacitance between –55 °C and 125 °C. The temperature characteristic is the capacitance variation as a function of temperature (20,21). Because pure barium titanate cannot stay within the capacitance range at lower temperatures it needs to be doped with a compound such as niobium oxide, oxalate or chloride (21).

Table II Dielectric constants of different materials

Material	**Dielectric Constant (K)**
Air	1
Alumina	10
Water	81
Titanium dioxide	100
Potassium niobate	700
Barium titanate	4000
Modified barium titanate	˜ 10000
Lead magnesium niobate	20000

What distinguishes PMN from BT is the higher dielectric constant the lower sintering temperature. A sintering temperature below 1000 °C allows the use of cheaper, silver-rich palladium electrodes instead of using pure palladium.

Unfortunately, the production of PMN is difficult, because during sintering a so called “pyrochlore phase” with inferior dielectric properties instead of the desired “perowskite-phase” is formed. Therefore H.C. Starck has developed a modified process for the production of PMN (22), which inhibits the formation of the undesired phase.

Nevertheless, the use of niobium compounds in MLCC´s may diminish in the future. One reason is the change of the inner electrode material in MLCC´s from pure palladium or Ag/Pd to nickel (base metal MLCC´s). Nickel electrodes require a reducing atmosphere upon sintering, which prohibits the use of niobium oxide as an additive. Instead, rare earth oxides are used. Also, lead containing materials like PMN may be banned due to environmental reasons.

Piezoelectric ceramics. When subjected to an electric field, piezoelectric ceramics undergo a change in dimension. Conversely, when subjected to pressure they exhibit electric polarization. Thus, piezoceramics convert electrical energy into mechanical energy and vice versa. Therefore they can be used for a) the generation of charge at high voltages, b) the detection of mechanical vibrations, c) applying pressure control by voltage, d) frequency control and e) the generation of acoustic or ultrasonic sound. Common applications range from buzzers, filters, igniters, and ultrasonic cleaners to sonar arrays, ultrasonic imaging systems, shutters and positioners for optical systems. Recently, the automotive industry has applied piezoelectric actuators for fuel injection systems and sensors for antilock braking systems (23).

PMN shows excellent electrostrictive properties, but because of its high cost, its use is restricted to applications where high precision is needed. The optical performance of the Hubble space telescope was enhanced by using PMN actuators (24). Lead zircon titanate (PZT) is most commonly used nowadays and has superseded BT which was used for b), c) and e) in former times. PZT is an effective and relatively cheap material for piezoelectric applications. Nevertheless, the piezoelectric properties have to be adjusted according to the application. Therefore a doping is necessary. As PZT has a perowskite-type structure ABO_3, A ions as well as B ions can be partially replaced by higher (donor) or lower (acceptor) charged ions. Nb^{5+} is typically used to replace Ti^{4+} (soft doping, higher DK and dielectric loss) whereas for example alkalines replace Pb^{2+} (hard doping, lower DK and low loss) (21). A typical example for a niobium doped PZT ceramic application is sensor arrays for ultrasonic diagnostic machines. Next to pure niobium oxide or oxalate, several niobates produced by H.C. Starck as potassium niobate, nickel niobate, cobalt niobate etc. can be used as dopants.

Ferrites. Ferrites are ceramic materials having magnetic properties. Depending on their magnetic properties they can be generally categorized as hard (permanent magnetization) or soft (nonpermanent magnetization). Soft ferrite’s are mainly based on the material groups MnZn and NiZn. Major applications for ferrites include transformers and inductors used in telecommunications, power conversion and interference suppression (25). In these areas, modern ferrites have to fulfill high demands with respect to efficiency. Additives like niobium oxide or oxalate are needed to improve significantly the magnetic properties of ferrites like power loss, electric resistance and permeability by influencing the grain growth and grain density (13). Thus, the addition of niobium compounds to soft ferrites ensures the high quality needed. However, the fundamentals of the effects observed upon niobium addition are not fully understood.

Catalysts. Various catalytic reactions are promoted by niobium oxide due to its acid and oxidizing properties. In recent times numerous patents and publications about the catalytic properties of niobium compounds, e.g. the oxidation of propylene to acrolein (26), have been published. The relative molar ratio of niobium in such mixed metal oxide catalysts is around 0.1; the main component is Mo. To achieve a homogenous mixture of all elements, soluble compounds are required. Thus, H.C. Starck has developed a niobium oxalate quality, which can be used instead of niobium oxide.

At present, the use of niobium compounds in the catalyst industry is small. However, remarkable activities can be observed for academic and applied research as well as for industrial development (27). Therefore, catalytic applications of niobium compounds are expected to grow significantly in future.

Pigments. Yellow pigments based on titanium are nickel antimony titanate and chromium antimony titanate. These colors are in competition with cadmium yellow pigments as well as lead based yellow pigments. However, the use of all of them may suffer from environmental and health aspects because lead, cadmium and antimony may be harmful. One solution might be changing the antimony for niobium leads to nickel niobium titanate and chromium niobium titanate as an alternative. So far, the potential for niobium oxide in this market is hard to predict.

Optical glass. For special lenses as in cameras and photocopiers, a high refractive index combined with low weight is desired. High purity niobium oxide and tantalum oxide is added up to 30 % to achieve a high refractive index and, in addition, gives a good chemical resistance against environmental influences. For niobium oxide glasses the weight increase is moderate compared to tantalum oxide, which is important with respect to the competition against plastic lenses. However, the tendency to color the glasses slightly yellow poses certain restrictions for glass applications.

Niobium Metal and Niobium Based Alloys

Only 2.5% of the total niobium output is marketed in the form of pure niobium metal and niobium based alloys. The increase in shipments in the late 90`s is due, at least in part, to the requirements for a new particle accelerator, the Large Hadron Collider project at Cern (near Geneva, Switzerland), which demands in total 400 t of niobium titanium alloy and 23 t of pure niobium metal (15, 28, 29).

Table III Shipment of niobium and niobium based alloys (t contained Nb)

	1989	**1990**	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**
pure Nb	-	-	-	-	-	108	108	114	113	172	150
Nb alloys	-	-	-	-	-	127	130	154	141	386	463
Total	211	261	264	277	186	235	238	268	254	558	613

Applications of Niobium Metal. Most niobium metal is used for the production of niobium based alloys and high purity niobium oxide. Other uses for pure niobium metal are (15, 30):

- corrosion resistance (e.g. impressed current cathodic protection anodes ICCP);
- high temperature parts (e.g. furnace hardware);
- medical applications (e.g. surgical implants);
- Sputtering targets (e.g. glass & electronic industry, razor blades);
- electronic applications (e.g. electrolytic capacitors, permanent magnets);
- nuclear components (fast neutron reactor).

Production of Niobium Metal. There are many niobium production processes described in the literature, however, most are not used on an industrial scale because they are not economical, yield low purity products, etc. The most important starting materials for these production processes are:

- Niobium oxide Nb_2O_5
- Potassium heptafluoro niobate K_2NbF_7
- Niobium chlorides $NbCl_5$
- Niobium alkoxides $Nb(OR)_5$

Reduction of Niobium Oxide

Aluminothermic/Magnesiothermic Reduction. Most niobium metal (> 90%) is produced by the alumothermic reduction of niobium oxide.

$$3\ Nb_2O_5 + 10\ Al \rightarrow 6\ Nb + 5\ Al_2O_3 \qquad (4)$$

High purity niobium oxide (> 99.5%) and aluminum metal powder are mixed and reduced after ignition in a vertical arrangement. In general, an excess of aluminum is used to produce a niobium aluminum alloy (31, 32). The ATR (Aluminothermic reduction) bars are then used as feedstock in electric arc, vacuum or electron-beam furnaces to produce high-purity niobium.(33). The amount of excess aluminum determines the yield of niobium and its oxygen content (34).

The reduction with alkaline-earth metals like magnesium is done in a similar manner.

$$Nb_2O_5 + 5\ Mg \rightarrow 2\ Nb + 5\ MgO \qquad (5)$$

However, although the reduction of niobium oxide with alkaline-earth metals or –hydrides is in principal well known (35-37), none of these processes are used on an industrial scale yet.

Carbothermic Reduction. Several multi-stage processes can be used for the reduction of niobium oxide with carbon.

$$Nb_2O_5 + 5\ C \rightarrow 2\ Nb + 5\ CO \qquad (6)$$

Niobium metal is made when Nb_2O_5 and carbon black are mixed, pressed into pellets and reduced in a two-step process to niobium metal in a vacuum furnace (direct reduction). During the first stage the oxide is present in a stoichiometric excess up to 15% over the stoichiometric proportions**.** In the second stage the prereduced material is treated with further reducing agents and the reduction is completed by heating the mixtures in a vacuum furnace to high temperatures (~ 2000 °C) (38-40).

In another process (indirect reduction) very pure niobium carbide is formed in the first stage of the reduction by heating pelletized mixtures of Nb_2O_5 with carbon black or graphite in a vacuum furnace. In the second stage this NbC is mixed with pure Nb_2O_5, pelletized and heated in a vacuum to high temperatures (~ 1950 °C) to form niobium blanks (41-43).

$$Nb_2O_5 + 7\ C \rightarrow 2\ NbC + 5\ CO \qquad (7)$$

$$5\ NbC + Nb_2O_5 \rightarrow 7\ Nb + 5\ CO \qquad (8)$$

In general, by starting with a very pure niobium oxide the resulting Nb metal is only contaminated with carbon and oxygen (e.g. NbC, Nb_2C, NbO_2, NbO) and can be refined in further high temperature processes (e.g. by electron beam melting).

A variation of this process is the combined carbonitrothermic reduction of Nb_2O_5: In the first stage, NbN is formed by reaction of a pelletized mixture of Nb_2O_5 and carbon black with ammonia at approx. 1570 °C in an induction furnace. The mixture is then thermally decomposed at higher temperatures (~ 2100 °C). A major advantage of this process is that the nitriding and denitriding can be carried out in a single sequential step without any intermediate operation. In spite of the fact that this process was carried out successfully on a pilot scale, it does not yet appear to have been used on an industrial scale (44, 45).

Nitrothermic Reduction. Niobium metal can be also produced by reduction of Nb_2O_5 with ammonia in a three-stage process. In the first step the niobium oxide is treated with ammonia at temperatures between 650 - 850 °C to form a oxynitride phase which is further reacted with ammonia at elevated temperatures (1100 - 1500 °C) to a niobium nitride phase. In the last stage this niobium nitride is decomposed to niobium metal at high temperatures (~ 2000 °C) in a vacuum furnace (46).

Reduction of Halides and Alkoxides

Reduction with Hydrogen. According to (32), niobium metal was originally prepared by hydrogen reduction of $NbCl_5$. Today, a variety of methods are described for the reduction of $NbCl_5$ by means of hydrogen (47-55). In spite of the fact that niobium metal of highest purity is obtained, none of these methods are used today on a large scale. Due to very high costs, hydrogen reduction of niobium halides or alkoxides is limited to specific applications, e.g. preparation of thin niobium layers by chemical vapor deposition (CVD) (56).

Metallothermic Reduction. The reduction of fluoroniobate K_2NbF_7 has not gained industrial significance, as it did in the case of tantalum production. The two reasons for this are the low production yields for the K_2 salt and its strong hygroscopic nature, resulting in the formation of very aggressive oxyfluorides (e.g. K_2NbOF_5).

The metallothermic reduction of $NbCl_5$ with sodium (57, 58), magnesium (59) and zinc (60) have been reported as well, however, these methods have not become industrially significant.

Electrochemical Reduction. Very pure niobium can be also obtained by electrochemical reduction of $NbCl_5$ or K_2NbF_7 from oxygen-free molten salt systems (e.g. KCl-NaCl, KCl-KF etc.), however, current efficiencies are low and these systems are very corrosive (61). Therefore, and to the best of our knowledge, these methods are not used on an industrial scale today. Nevertheless, the level of academic interest and research activities in the electro-obtaining of niobium remains high (62-66).

Process for the Production of Capacitor-Grade Niobium Powder. A solid electrolytic capacitor consist of a porous sintered pellet of tantalum metal (anode) with an embedded Ta wire and an amorphous, dielectric layer of Ta_2O_5 which is anodically formed on the surface of the pellet. The anodized porous body is then impregnated with a cathode material (e.g. MnO_2, conductive polymers), connected to a cathode lead wire and encapsulated in epoxy resin. Figure 4 shows the general design of a tantalum chip type capacitor.

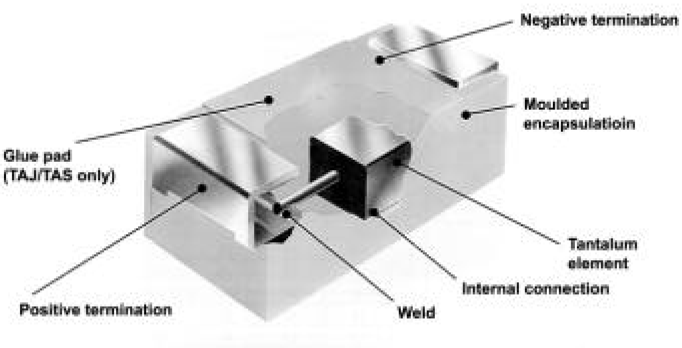


Figure 4: Design of a chip type capacitor.

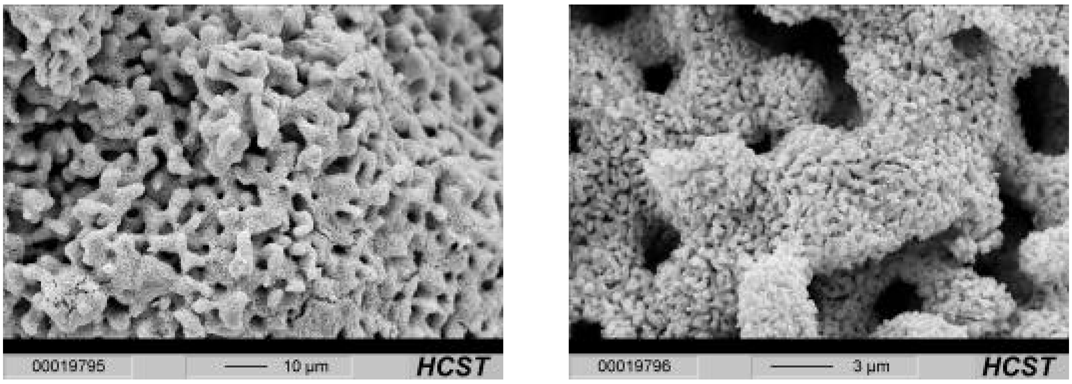
Many times in the last forty years it has been the goal of various researchers to find a substitute for tantalum in electrolytic capacitors (67-71). The logical substitute for tantalum has always been niobium because of its similar chemical properties. In addition, amorphous niobium pentoxide has a significantly higher dielectric constant ($\varepsilon \sim 42$) compared with Ta_2O_5 ($\varepsilon \sim 27$), although this is partially neglected by a higher oxide growth rate per volt ($Nb_2O_5 \sim 2.9$ nm/V, $Ta_2O_5 \sim 1.9$ nm/V).

Niobium capacitor production for military applications was started in the late fifties in the former Soviet Union because of the shortage of tantalum. However, the lack of a sophisticated process gave niobium powders with non-ideal morphology, poor purity, and low specific surface areas. This prevented a broader use of niobium as capacitor material in the world market. A niobium powder suitable for production of solid electrolytic capacitors must fulfill very complex requirements:

- high chemical purity (> 99.9%), especially with respect to "harmful" elements like C, Fe, Cr, Ni, Al, Na, K.
- a high specific surface area for storage of high capacitance.
- open pore structure which allows good impregnation with counter-electrode precursor.
- a narrow particle size distribution and a good flowability which allows use in fully automatic high speed presses.
- strong agglomerates resulting in high crush strength of anode pellets.
- a high sinter activity for a good bonding of the particles to the wire.

Using magnesiothermic reduction, the main problem is the strong exothermic nature, which is hard to control. After igniting a mixture of the niobium oxide and the reduction metal, the reaction proceeds very fast and reaches high temperatures (> 1000 °C) in a few seconds. The reduction is difficult to control because of the increasing high pressures and temperature. This also places extreme requirements on the reactor material, e.g. because of the demand of a good heat removal. In particular, the batch-to-batch reproducibility, *e.g.* with respect to particle size distribution of the powder, is poor. For this reason, none of these mentioned processes will yield high purity niobium powder combined with a high specific surface area suitable for capacitor applications.

In contrast, the heat management of the reduction of Nb_2O_5 with magnesium vapor is much easier to control. This is one of the key steps of a new process recently developed at H. C. Starck (72) which allows the production of very pure niobium powders (purity with respect to metallic impurities > 99.9%) with high specific surface areas combined with a unique, sponge like morphology (see Figures 5 + 6).



Figures 5 + 6: Morphology of niobium powder from magnesium vapor reduction.

In addition, this new process may be carried out in many different types of equipment, including tube furnaces, fluidized bed reactors, rotary kilns etc.

As shown in Figure 7 the reduction of Nb_2O_5 to niobium metal can be carried out in one, two (via NbO_2) or three steps (via NbO_2 and NbO), depending on the desired powder properties (purity, physical properties etc.).

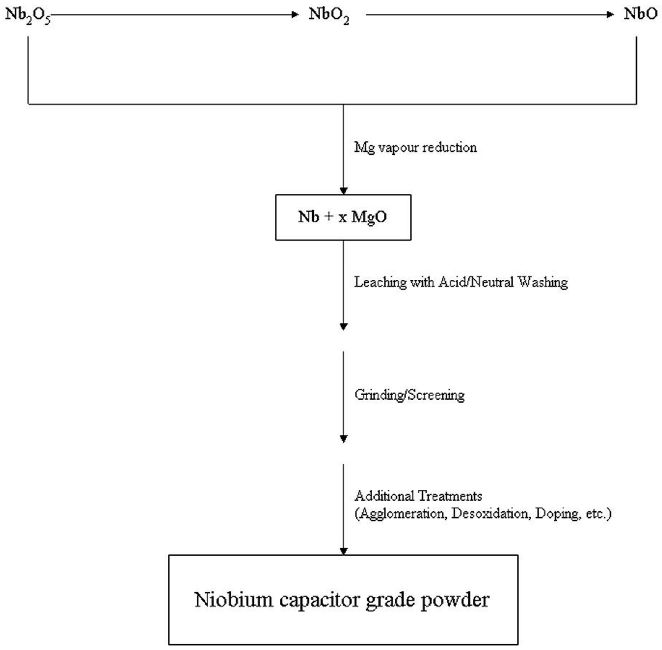


Figure 7: Flow chart for the production of niobium capacitor grade powder.

This process will produce a niobium powder with a wide range of specific surface areas, which correlate to the specific capacitance of the powder. The physical characteristics of these new niobium powders are quite comparable to capacitor grade tantalum powder (flowability, bulk density etc.). For this reason they can be processed with nearly the same equipment and processes used for the production of tantalum capacitors. Typical properties of new niobium powders are given in Table IV.

These powders have been recently evaluated by many capacitor manufacturers and the feasibility of good solid electrolyte niobium capacitors with very high capacitance and low leakage currents have been demonstrated. These niobium chip-capacitors will have better volumetric efficiency than aluminum electrolytic capacitors. An application for surface mounted niobium capacitors would be a substitute for those wishing to replace OS-CON-type aluminum capacitors with a more reliable and smaller capacitor.

Table IV Typical properties of niobium powders via magnesium vapor reduction

Oxygen/Surface Area (ppm/m^2)	[ppm/m^2]	≤ 4000
Metallic impurities	[ppm]	≤ 1000
FSSS	[µm]	3 – 8
Bulk Density (Scott)	[g/inch^3]	12 – 18
Flowability (Hall)	[sec/25g]	≤ 28 without vibration
Surface Area (BET)	[m^2/g]	0.5 – 10
Particle size (Mastersizer) D50	[µm]	≤ 210
Particle size (Mastersizer) D90	[µm]	≤ 320
Specific Capacitance CV/g	[µFV/g]	40.000 - 170.000
Leakage Current I_r/CV	[nA/µFV]	< 0.5
Wire Pull Strength (72 mg Anode)	[kg]	≥ 2.0
Crush Strength (72 mg Anode)	[kg]	≥ 2.5

Two major improvements of the new niobium powders were recently achieved at H. C. Starck labs. First, anodic niobium oxide films were doped with vanadium, demonstrating improved properties of the dielectric layer in comparison to oxide films on pure niobium. In particular, it has been found, with the aid of impedance spectroscopy and evaluation of Schottky-Mott diagrams, that the concentration of oxygen vacancies in anodically produced oxide layers on vanadium doped niobium is significantly reduced and similarly low as in corresponding Ta_2O_5 layers. For this reason, anodized pellets of vanadium doped niobium show, as in the case of tantalum, no BIAS dependence of capacitance (see Figure 8).

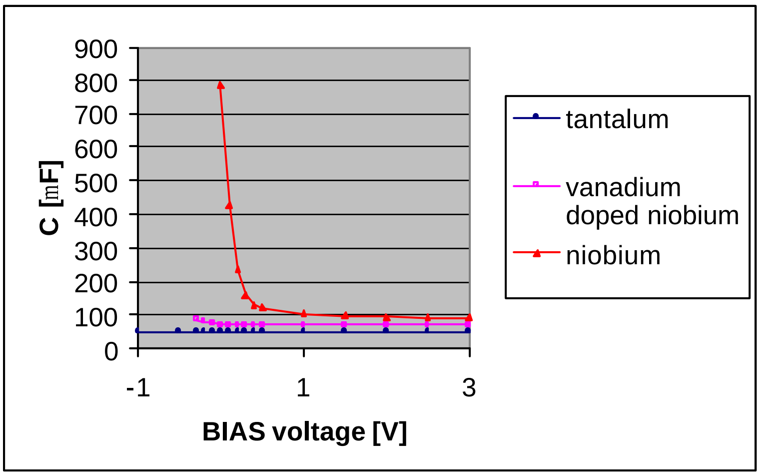


Figure 8: BIAS dependence of capacitance of Nb, Ta and V- doped Nb anodes.

The second observation was that the alloying of the new niobium powders with tantalum results in a dramatic increase in capacitance. For example, an Nb-25Ta alloy powder, produced by co-reduction of Nb_2O_5/Ta_2O_5 mixtures with gaseous magnesium, shows a specific capacitance two times higher than that of pure niobium powder with a comparable surface area. It was found that the growth rate of 2.4 nm/V of the dielectric oxide layer of these alloys lies between those of Ta_2O_5 and Nb_2O_5. In addition, there is evidence that the dielectric constant of the mixed oxide Nb_2O_5 / Ta_2O_5 (ε approx. 65) is even higher than that of pure Nb_2O_5.

Refining of Niobium. For most applications, the crude niobium metal, produced by one of the reduction methods described earlier, must be refined in order to remove impurities introduced either from the raw materials or during the treatment stages. Usually, this is done by high-temperature treatments since the high melting point of niobium allows the removal of most impurities by vaporization. Melting must always be carried out in a vacuum or in a very pure inert gas atmosphere due to the extreme reactivity of niobium with oxygen, nitrogen etc. The two most common methods are electron beam melting (EBM) and plasma melting.

In the EB melting furnace, electrons, agitated by a high voltage, are aimed at the niobium electrode. Part of this energy is converted into heat, which is needed to melt the electrode and keep the bath in a liquid state while impurities evaporate. The liquid metal solidifies in a cooled crucible and the resulting ingots can be removed from the furnace on a continuous basis. The current standard EB furnace uses a "Drip-Melting" method, however, in the future, hearth melting may eventually become more efficient as higher power furnaces are developed (73). Sufficient refinement cannot be achieved with a single melting cycle; in practice, the produced ingots must be remelted several times. The melting rate (kg Niob/h) for the first melt (main refining step) depends strongly on the feed material and is lower for ATR niobium due to the high concentrations of aluminum and oxygen (vaporizes as NbO), which must be evaporated. With the current state-of-the-art-technology, the crude ATR ingot has to be remelted 2 - 3 times before reaching high purity niobium. The EB melting and remelting technique generates niobium metal with less than 50 ppm of interstitial and metallic impurities below 500 ppm (main impurities are Ta and W).

Due to their high energy density, plasma furnaces can also be used for refining niobium. In this case, the crude metal is melted by several portable plasma guns. The resulting melt is then refined with another plasma gun. A disadvantage of this method is that only impurities with a vapor pressure higher than the furnace pressure can evaporate.

Ultra-high purity niobium (which is primarily of scientific interest) can be prepared from EB melted metal by several sophisticated methods. Refractory impurity metals (e.g. Ta, W), having a similar vapor pressure to Nb, cannot be removed by EB or plasma melting. Their removal requires the usage of special chemical or physical methods, which take advantage of the different thermodynamic and kinetic properties of the impurity and of the host metal and its compounds. For the purification of niobium metal from tantalum the most powerful methods are based on fused salt electrolysis and iodination (74).

The electrolyte in the electro-refining process is usually a eutectic LiF-NaF-KF melt containing very pure K_2NbF_7 (75). The molten salt electrolysis method requires several conditions, such as the pre-purification of the niobium metal (by EB melting) and of the electrolyte (by an initial electrolysis), as well as the strict avoidance of oxygen or water vapor traces in the electrolyte.

Ultra high purity niobium, especially with regard to tantalum, can be produced by a modified van Arkel de Boer process as well (76). In this process, crude niobium metal is first iodized to a higher niobium iodide, which is then reduced in an inert gas or hydrogen atmosphere to a lower niobium iodide. After thermal decomposition of the iodides at temperatures > 700 °C, very high purity niobium metal is obtained.

By using these methods, niobium metal with metallic impurities in the parts per billion range and with interstitial impurities below one ppm can be achieved (77).

Niobium Based Alloys. Commercial niobium alloys are relatively low in strength and extremely ductile and can be cold-worked over 70% before annealing becomes necessary. The resulting ease of fabrication into complex parts, combined with the relatively low density, frequently favors the selection of niobium alloys over other refractory metals such as molybdenum, tantalum or tungsten (78).

Many high temperature niobium alloys were developed in the 1960's, mainly for nuclear and aerospace applications; however, further development has been limited since the early 1970's (79). Today, niobium alloys are also used in human body imaging equipment, communication satellites and a wide range of high-temperature components. However, their susceptibility to oxidation and to long-term creep at higher temperatures have prevented a broader use of these alloys for other applications.

In most cases, alloying of niobium produces immediate and severe complexities for fabrication, with the exception of tantalum, titanium and vanadium based alloys. Although alloying with these elements increases hardness and strength, toughness, malleability and fabricability are equal to, or even superior to pure niobium. All other alloying elements reduce toughness, malleability and fabricability in varying degrees (80).

In general, niobium alloys are less tolerant to impurity pickup than other reactive metals (e.g. Zr, Ti), since these impurities often drastically reduce tensile elongation, primarily at the grain boundaries. For example, the mechanical properties of such alloys can significantly deteriorate by introducing copper (e.g. during welding).

In order to increase the oxidation resistance at high temperatures, niobium alloys are often extensively coated in special processes, for instance with silicides, (78, 81).

Most niobium alloys are prepared by EB, plasma and vacuum-arc remelting with the appropriate additions of elements. For large ingots, two melts may be required to produce a homogenous ingot with the desired composition. Nowadays, the most common alloy additions are titanium, zirconium, tungsten, tantalum and hafnium, which readily go into solution during melting.

Another promising approach for the production of niobium based alloys could be joint electro-deposition from salt melts (82-84), e.g. from the $KCl-KF-K_2ZrF_6-K_2NbF_7$ system (85).

Niobium based alloys can be prepared by powder metallurgy processes as well. Several methods have been evaluated for the preparation of niobium alloy powders, including gas-atomization, hammer quenching, mechanical alloying (86), diffusion at high temperature or the hydride-dehydride process (87, 88). However, when applying these methods, oxidation, the introduction of impurities, as well as high costs, are difficult to avoid.

The most important applications for niobium based alloys are:
- precision support members for sodium vapor lamps (Nb-1Zr)
- superconductors for MRI (Magnetic Resonance Imaging), NMR (Nuclear Magnetic Resonance), SMES (Superconducting Magnetic Energy Storage), SQUID (Superconducting Quantum Energy Device), Particle accelerators (e.g. Nb-50Ti, Nb_3Sn) (89)
- rocket thrusters and nozzles in aerospace applications (e.g. Nb-10Hf-1Ti)
- construction material in nuclear industry (Nb-Zr)
- corrosion resistance (e.g. Nb-40Ta)

Intermetallic compounds like Nb_3Al are gaining interest as promising A-15 superconductors candidates, showing higher transition temperatures and withstanding higher electrical fields than niobium titanium alloys (90-93). In addition, they are expected to be used as ultra-high temperature structure materials due to a high melting point and superior specific strength.

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