# MANUFACTURING OF SPECIAL NIOBIUM OXIDES FOR OPTICAL AND CERAMIC APPLICATIONS

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## Abstract

The main applications of high-purity niobium pentoxide (>99.9%) are optical glass, ceramics and single crystal lithium niobate. It is a very important material for electronics. This paper describes the brief outlines of high-purity niobium pentoxide, i.e. raw materials, processes, specifications and the market in Japan.

## Introduction

More than 90% of the total niobium production is used in the steel industry in the form of ferroalloy (ferroniobium). The market for high-purity niobium pentoxide (>99.9%) is very small, however, it is a very important material in high tech areas.

About 400-500t of high-purity niobium pentoxide were used worldwide in 2000. Of this total, Japan accounted for approximately 40-50% of the consumption and the rest of the world 50-60%.

It has many applications. An important one is in optical glass: when the silica in glass is replaced by niobium oxide, the refractive index is much greater, so thinner and lighter lenses can be used for the same focal length. This is already in use in many camera lenses and for eyeglasses. Also it is used in capacitors, and as single crystal lithium niobate in surface acoustic wave filters for television sets and similar equipment.

## Production of Niobium Oxide

Raw Materials

The main niobium source in the world in the early sixties was columbite/tantalite [$(Fe,Mn)(Nb,Ta)_2O_6$], but now the major source of niobium is pyrochlore [$(Na,Ca)_2Nb_2O_6F$]. More than 90% of all niobium is recovered as ferroniobium from the smelting of pyrochlore. A small part is recovered during the treatment of tin slag and columbite/tantalite mined in Australia, Africa, Brazil and South East Asia. Table I shows the typical analyses of niobium sources.

Table I Typical analyses of niobium sources

| Constituent | Tantalite/Columbite | | Tin Slag | Ferroniobium |
|---|---|---|---|---|
| | ? | ? | | |
| Nb2O5/Nb | 15.3 | 55.3 | 7.3 | 65.7 |
| Ta2O5/Ta | 63.6 | 6.5 | 1.5 | 0.2 |
| Fe2O3/Fe | 6.4 | 22.0 | 6.8 | 32.6 |
| Al2O3/Al | 0.9 | 0.3 | 10.4 | 0.4 |
| SiO2/Si | 1.9 | 0.3 | 34.8 | 3.3 |
| TiO2/Ti | 3.2 | 7.7 | 7.2 | 0.1 |
| Mn3O4/Mn | 4.5 | 1.7 | 1.2 | 0.2 |
| SnO2/Sn | 1.6 | 2.4 | 7.9 | 0.1 |

- Analysis in weight%
- Ferro-niobium is metal content.

Processing of Niobium Oxide

The industrial separation of niobium from tantalum was previously carried out using the Marignac process. This method separates niobium and tantalum by the fractional crystallization of their potassium double fluoride salts, employing conditions which produce the normal double fluoride of tantalum, $K_2TaF_7$, and the oxyfluoride of niobium, $K_2NbOF_5$ ($K_2NbF_7$ is stable only in strong hydrofluoric acid.). The two salts are not isomorphous and their solubilities are very different.

The Marignac process had been used very satisfactorily for the production of tantalum, however it was not satisfactory for producing high purity niobium because of the titanium.

After the development of the solvent extraction process in the U.S. Bureau of Mines and Ames Laboratory of Iowa State University in the 1950's, the Marignac process was abandoned in favor of the solvent extraction process because the solvent extraction process lends itself readily to large-scale operations and satisfactorily to the production of pure niobium compounds.

Solvent Extraction Process (MIBK-HF/H2SO4 system)

Ferro-niobium, tantalite/columbite concentrates and tin slag, with high tantalum content, are directly treated by a wet chemical process. Low-tantalum tin slag, on the other hand, is first melted in an electric-arc furnace with the addition of a flux material, and the tantalum/niobium content is collected as a ferroalloy.

Raw materials are ground and dissolved with hydrofluoric acid, then adjusted to the desired acidity with $H_2SO_4$ (>8mol/l). The accompanying elements, such as iron, manganese, titanium, etc., are dissolved along with the tantalum and niobium. After removal of the insoluble materials (Al, Si, Ca, rare earth metals, etc.) by filtration, the acid solution is extracted with an organic solvent (methyl isobutyl ketone: MIBK).

At first, niobium and tantalum are extracted together in the organic phase, and most of the impurities (iron, manganese, titanium, etc.) remain in the aqueous phase. Next, by bringing into contact the organic solution of tantalum and niobium with an aqueous solution, the niobium is back extracted into the aqueous phase with tantalum remaining in the organic. The aqueous niobium solution is re-extracted with MIBK to remove traces of tantalum. Then, ammonia is added to the aqueous niobium solution to precipitate niobium oxide hydrate. This process is designed for operation in mixer-settlers but a similar process has been performed in columns.

Finally, the oxide hydrates are collected by filtration, dried and calcined at 800-1100? in heated chambers or rotary furnaces. Variations in the conditions of precipitation, drying and calcinations produce different particle sizes for various applications. Figure 1 shows the flow diagram for the processing of niobium oxide in the MIBK-HF/H2SO4 system.

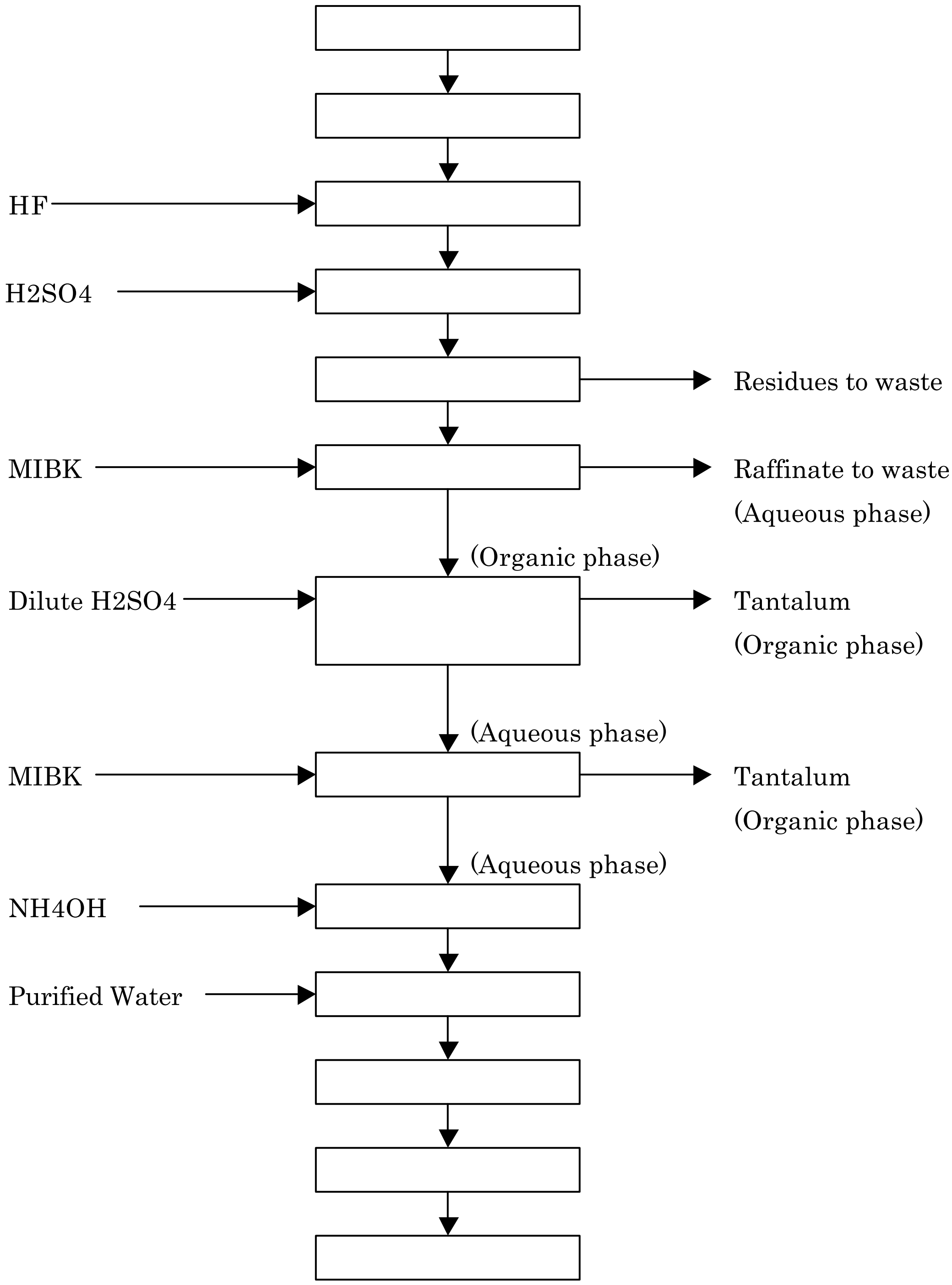


Figure1: Flow Diagram for the processing of niobium oxide in MIBK-HF/H2SO4 system.

Organic Solvents

There are a lot of potential organic solvents and many ways to examine them. Ketones are the most promising and of all of them, MIBK is the best for industry. Table II shows the properties of the principal organic solvents.

Table II The properties of the principal organic solvents

| | MIBK | TBP | cyclohexanone |
|---|---|---|---|
| Boiling Point (? ) | 116 | 178 | 155 |
| Density ($g/cm^3$) | 0.80 (20? ) | 0.97 (25? ) | 0.95 (20? ) |
| Solubility in water (vol%) | 2 | 0.5 | 16 |
| Price | Low | High | Low |

The disadvantage of cyclohexanone is its high solubility in water, and this brings a large consumption of solvent. TBP has the advantages of a high boiling point and low solubility, however, it is difficult to separate the solvent and water because of the high density (close to water). Therefore, MIBK is the most popular solvent used in industry.

MIBK is best carried out with the hydrofluoric acid / sulfuric acid system. The extractability of niobium and tantalum in MIBK is found to be a function of $H_2SO_4$ acidity. In short, both niobium and tantalum extract in high $H_2SO_4$ acidity (>8N), but only tantalum extracts in lower $H_2SO_4$ acidity (3N-8N). Figure 2 shows the effect of $H_2SO_4$ acidity on niobium and tantalum in the MIBK-HF/$H_2SO_4$ system.

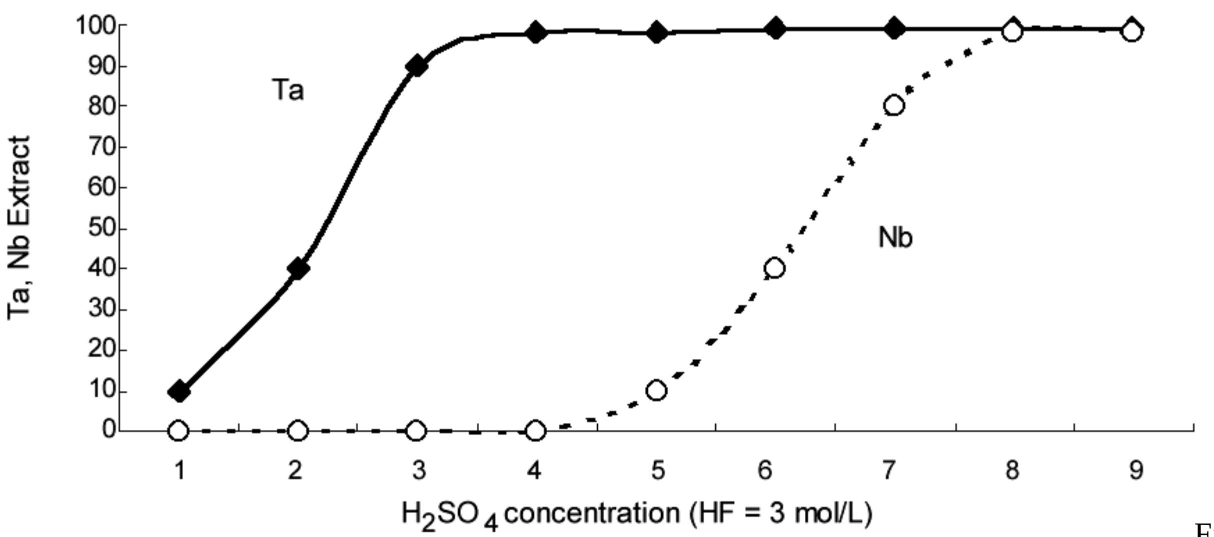


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Figure 2: Effect of $H_2SO_4$ acidity on Nb and Ta extraction in MIBK-HF/$H_2SO_4$ system.

In the MIBK-HF/$H_2SO_4$ system, satisfactory separation is obtained from impurities, such as iron, manganese, titanium and tin, because there is a big difference between the distribution coefficient of niobium, tantalum and impurities. Table III shows the distribution coefficient of niobium, tantalum and other impurities.

Table III Ta, Nb and impurities distribution coefficient in MIBK-HF/H2SO4 system

| | Distribution coefficient |
|---|---|
| Ta | 215 |
| Nb | 25 |
| W | 0.35 |
| Mo | 0.1 |
| Ti | 0.01 |
| Zr | 0.008 |
| U | 0.007 |
| Fe | 0.007 |
| Sn | 0.007 |
| Mn | 0.004 |
| Ga | 0.002 |
| Al | 0.002 |

* HF-10N, $H_2SO_4$-6N

Qualities of Niobium Oxide

Various applications require different qualities of niobium oxide. In optical glass, niobium oxide is used as an additive to molten glass. Optical grade niobium oxide must be free of color impurities such as chromium, nickel, iron, manganese, etc. and with a purity of >99.9%. Ceramics grade niobium oxide requires a special particle size distribution.

For lithium-niobate single crystal, very high-purity niobium oxide is required (>99.99%). Table IV shows the details on the qualities of niobium oxide.

## Niobium Oxide Market in Japan

The demand of high purity niobium oxide in Japan has increased over the last decade along with the expansion of the electronic industry, and reached a record level of 200t in 2000. Figure 3 shows the consumption in Japan. The annual growth rate is 6.4% from 1990 to 2000.

Table IV Specification of niobium pentoxide

| Specification | Ceramics Grade | Optical Grade | High Purity Grade |
|---|---|---|---|
| Composition[*1] | | | |
| Nb2O5 | >99.9 | >99.9 | >99.99 |
| Ta | <0.02 | <0.02 | <0.002 |
| Al | <0.0005 | <0.0005 | <0.0003 |
| Ca | | <0.001 | <0.0002 |
| Co | | <0.0005 | <0.0002 |
| Cr | <0.0005 | <0.0005 | <0.0003 |
| Cu | | <0.0005 | <0.0003 |
| F | | <0.03 | <0.0005 |
| Fe | <0.0005 | <0.0005 | <0.0003 |
| Mn | <0.0005 | <0.0005 | <0.0003 |
| Na | | | <0.001 |
| Ni | <0.0005 | <0.0005 | <0.0003 |
| Sb | | | <0.0003 |
| Si | <0.005 | <0.005 | <0.001 |
| Ti | <0.0005 | <0.0005 | <0.0003 |
| Loss on ignition | <0.4 | <0.2 | <0.1 |
| Average particle Size[*2] | 0.6-1.0 μm | 1.0-1.6 μm | 1.0-3.0 μm |

[*1] L.O.I. not included

[*2] By Blained Method

Optical Glass

Optical glass containing up to 30% of niobium oxide has high refractive indices, which allow lenses to be thinner and lighter than ordinary ones. Also, from the environmental point of view, niobium glass is used as one of the lead free glasses. An example of the composition is $B_2O_3$: 23%, ZnO: 5%, $La_2O_3$: 40%, $TiO_2$: 5%, $ZrO_2$: 5%, $Nb_2O_5$: 17%, and $Ta_2O_5$: 5%.

Niobium glass is used widely in lenses for cameras, copying machines, eyeglasses and other optical instruments. The demand for the use in digital cameras is increasing rapidly. Optical glass use accounts for about 50% of the total niobium oxide consumption in Japan.

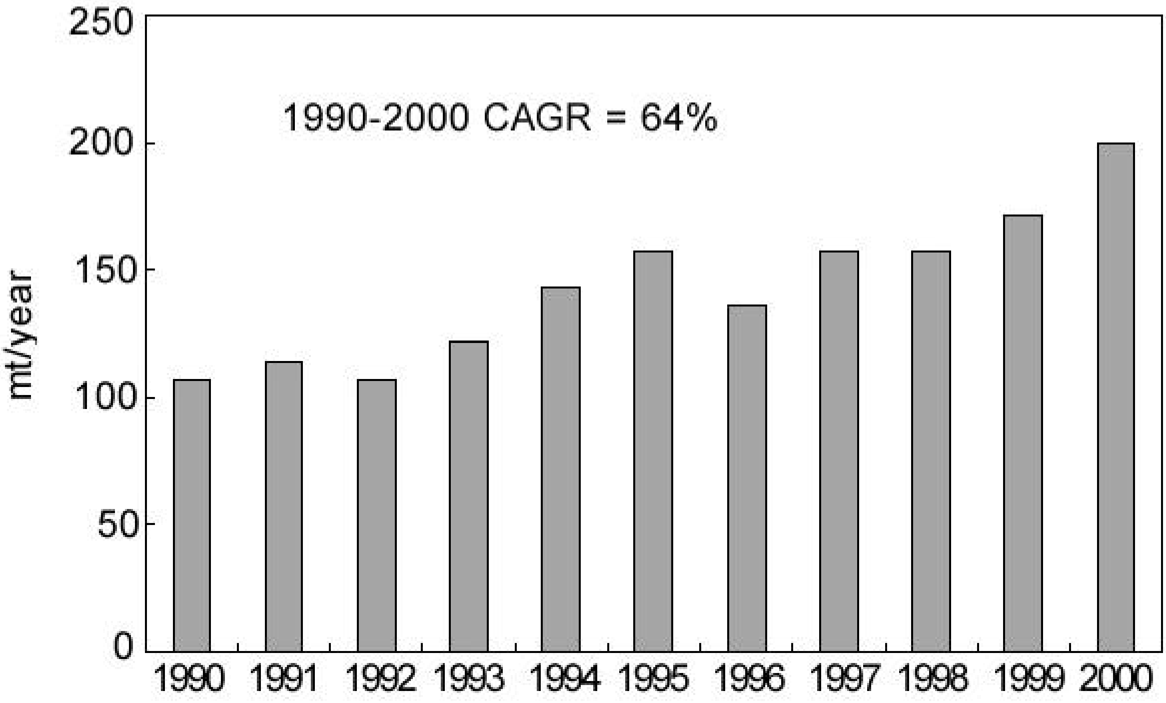


Figure 3: High-purity niobium oxide consumption in Japan.

Ceramics

Niobium oxide is increasingly being used in the field of electro ceramics. Niobium based perovskites are expected to overtake traditional titanate/zirconate based ceramics because of their lower sintering temperature, their higher dielectric constant, and the possibility of adjusting the temperature characteristics of the dielectric constant by changing the combination of B-Site ions. Typical examples of niobium-containing ceramics are $Pb_3MgNb_2O_9$, $Pb_2FeNbO_6$, and $Pb_3NiNb_2O_9$. Ceramics` use accounts for about 40-45% of the total.

Lithium Niobate

Single crystals of lithium niobate (LN) are suitable for surface acoustic wave filters because they exhibit large electromechanical coupling factors, have low high-frequency losses, and can convert electrical energy into acoustic waves with efficiency. LN is used in radar, communication systems, and television receivers.

LN is also suitable for electro-optical applications. Electro-optical modulators are used for modulating or encoding information for laser beams in communication systems. High purity niobium oxide used in LN accounts for about 5-10% of the total.

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