# PRODUCTION OF NIOBIUM METAL AND COMPOUNDS FROM TANTALITE-COLUMBITE NATURAL ORES AND SYNTHETIC TANTALUM-NIOBIUM CONCENTRATES

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## Summary

The present paper discusses methods for breaking down tantalum-niobium ores and synthetic tantalum-niobium concentrates and for separating tantalum from niobium. For the production of niobium compounds such as chloride, oxide, metal and carbide a variety of different processes have been developed. Among those, the liquid - liquid extraction, chlorination of ores and ferro-alloys, the aluminothermic and carbothermic reduction are the most important ones.

## Introduction

In addition to the true niobium minerals such as pyrochlore and columbite, tantalum minerals and tin slags are important raw materials for the production of niobium and its compounds.

In 1980 the world's tantalum consumption (tantalum metal and tantalum compounds) was approximately 3.3 million lbs. $Ta_2O_5$ content. During the processing of the corresponding raw materials approximately 2.3 million lbs. $Nb_2O_5$ were produced as a by-product.

More than one-third of the world's tantalum demand is filled by means of tin slags, which will continue to be an important source of tantalum in the future (1). Tin slags also contain niobium. The average ratio of $Ta_2O_5$ : $Nb_2O_5$ is approximately 1:0.85.

Niobium and tantalum ores as well as tin slags with a high tantalum content (exceeding 12% $Ta_2O_5$) are directly dressed, in most cases by a wet chemical process. However, tin slags having a low tantalum content (1 - 6% $Ta_2O_5$) have to be pretreated with an enrichment process.

Several companies and research institutes have been involved with these wet-chemical and pyrometallurgical enrichment processes (2, 3, 4, 5, 6, 7). Hermann C. Starck (Berlin) started producing synthetic tantalum-niobium concentrates from tin slags 25 years ago. Today it possesses the world's largest plant of this kind, able to treat 18,000 tpy tin slags.

## Production of Synthetic Tantalum-Niobium Concentrates

After a long period of research and development Hermann C. Starck (Berlin) succeeded in developing a process using chloro- and pyrometallurgical methods to upgrade tin slags (8).

Tin slags are melted in an electric arc furnace together with a flux material; the tantalum-niobium content is collected in the resulting ferroalloy and the tantalum-niobium free slag is poured off. After crushing and dressing, this ferroalloy is converted to a tantalum-niobium concentrate either by means of a second pyrometallurgical process, or by means of a chemical process, such as:

- dissolution of the material in mineral acids to produce a tantalum-niobium concentrate.

- Chlorination of the alloy and separation of the tantalum-niobium chlorides by fractional distillation.

Table I shows the composition of some important tin slags; while Figure 1 shows the primary steps in the processing of tin slag.

The analyses of the alloy and the concentrate produced thereof by a pyrometallurgical process, based on two different kinds of tin slags of Malayan provenance, are shown in Table II.

Figure 2 shows a part of H. C. Starck's plant for the production of synthentic tantalum-niobium concentrates.

Table I. Tantalum-Containing Tin Slags

| | Source | % $Ta_2O_5$ | % $Nb_2O_5$ | %$TiO_2$ | % FeO |
|---|---|---|---|---|---|
| High grade | Australian | 10 | 5.5 | 9 | 10 |
| | Zaire | 11 | 10 | 2 | 9 |
| | Thailand | 12 | 9 | 13 | 10 |
| Medium grade | South Africa | 5 | 7 | 2 | 14 |
| | Nigeria | 4 | 12 | 7 | 13 |
| | Malaysia | 4 | 4 | 11 | 15 |
| | Thailand | 5 | 4 | 18 | 11 |
| Low grade | Malaysia | 0.8-2 | 0.8-2 | 5-9 | 18 |
| | Thailand | 0.3-1 | 0.2-1 | 1-5 | 20 |
| | Brazil | 1-2 | 2-4 | 20 | 8 |
| | Singapore | 1-2 | 1-2 | 15 | 19 |

Table II, Enrichment of Tantalum in the Starck Tin Slag Process

| Composition of slag (Malaysia) | Alloy | synth Concentrate |
|---|---|---|
| Higher Grade Slag: | | |
| 4 % $Ta_2O_5$ | 15 % $Ta_2O_5$ | 26.9 % $Ta_2O_5$ |
| 4.3 % $Nb_2O_5$ | 17 % $Nb_2O_5$ | 30.9 % $Nb_2O_5$ |
| 10.5 % Ti $O_2$ | (as metal) | 18.6 % $TiO_2$ |
| 1.5 % Sn $O_2$ | | 0.1 % $SnO_2$ |
| 2 % $WO_3$ | | 0.1 % $WO_3$ |
| 1.2 % $P_2O_5$ | | 0.1 % $P_2O_5$ |
| 15 % Fe O | | 8 % FeO |
| CaO, MgO, $Al_2O_3$, $SiO_2$ | | |
| Low Grade Slag: | | |
| 2 % $Ta_2O_5$ | 8 % $Ta_2O_5$ | 20.8 % $Ta_2O_5$ |
| 2.2 % $Nb_2O_5$ | 10 % Nb | 25.6 % $Nb_2O_5$ |
| 10.5 % Ti $O_2$ | (as metal) | 25 % Ti $O_2$ |
| 1.2 % Sn $O_2$ | | 0.1 % Sn $O_2$ |
| 2.6 % $WO_3$ | | 0.1 % $P_2O_5$ |
| 15 % Fe O | | 8 % Fe O |
| CaO, MgO, $Al_2O_3$, $SiO_2$ | | |

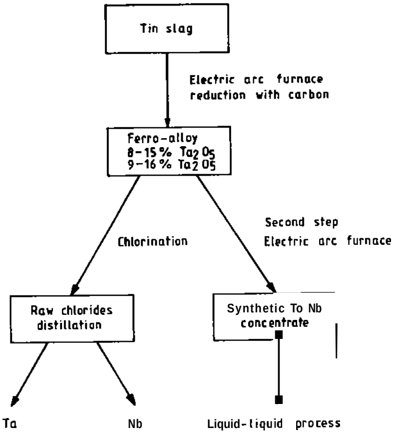


Figure 1. Flow sheet Tin Slag processing.

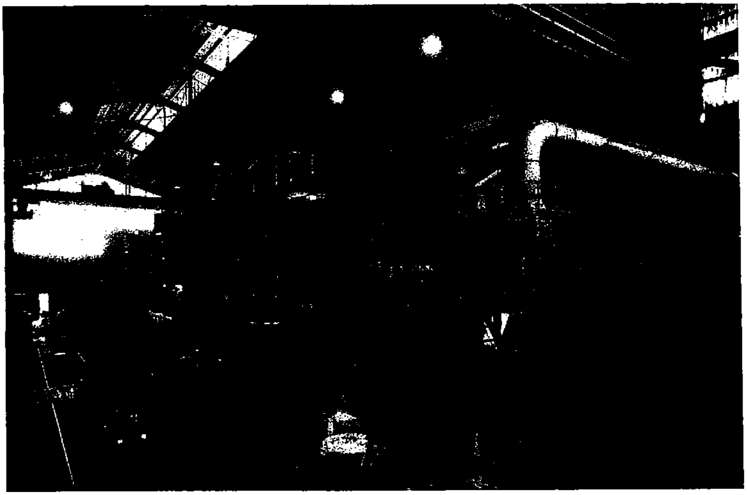


Figure 2. A part of HCST's plant for the production of synthetic TaNb concentrates.

## Separation of Tantalum from Niobium

Methods for separating niobium from tantalum have been described by Schäfer (9). Previous processes such as fractional crystallization of the K2 double fluorides (Marignac process) or separation by means of ion exchange are no longer used. Today only two processes are applied:

Decomposition of the ores and the synthetic concentrates by means of acids, mostly HF or HF + $H_2SO_4$, and separation of tantalum and niobium by liquid-liquid extraction with methyl-isobutyl ketone (10, 11, 12).

Figure 3 illustrates the simplified flow sheet of a tantalum-niobium separation process by liquid-liquid extraction. Niobium is precipitated by means of $NH_3$ as niobium hydroxide. After filtration, drying and calcining takes place. The analysis of this oxide is presented in Table III.

Table III. Typical Analysis of Niobium Chloride and Oxide-ppm

| | $NbCl_5$ High Purity (Metal in Chloride) | $Nb_2O_5$ Special Pure Grade (Oxide in Oxide) | $Nb_2O_5$ Liquid/Liquid (Oxide in Oxide) |
|---|---|---|---|
| Al | < 1 | < 1 | < 10 |
| Au | < 0.1 | < 0.1 | |
| Ag | < 1 | < | |
| B | < 0.1 | < 0.1 | |
| Be | < 0.1 | < 0.1 | |
| Bi | < 1 | < 1 | |
| Ca | < 1 | < 1 | < 10 |
| Cl | | < 10 | |
| Cd | < 0.1 | < 0.1 | |
| Cr | < 0.2 | < 0.2 | < 1 |
| cu | < 0.1 | < 0.1 | |
| co | < 0.1 | < 0.1 | < 1 |
| F | < 1 | < 1 | < 50 |
| Fe | < 0.1 | < 1 | 100 |
| K | < 1 | < 1 | |
| Li | < 0.1 | < 0.1 | |
| Mg | < 1 | < 3 | < 15 |
| Mo | < 3 | < 3 | < 15 |
| Mn | < 0.3 | < 0.3 | < 3 |
| Ma | < 1 | < 1 | |
| Ni | < 0.2 | < 0.2 | < 2 |
| P | < 10 | < 10 | |
| Pb | < 1 | < 1 | |
| S | < 1 | < 1 | |
| si | < 2 | < 2 | < 120 |
| Sn | < 1 | < 1 | < 3 |
| rare earth} total | < 2 | < 2 | |
| Ta | < 10 | < 20 | < 200 |
| Ti | < 3 | < 3 | < 10 |
| V | < 2 | < 2 | |
| W | < 3 | < 3 | < 30 |
| Zr | < 3 | < 3 | |
| Θ | < 100 | | |

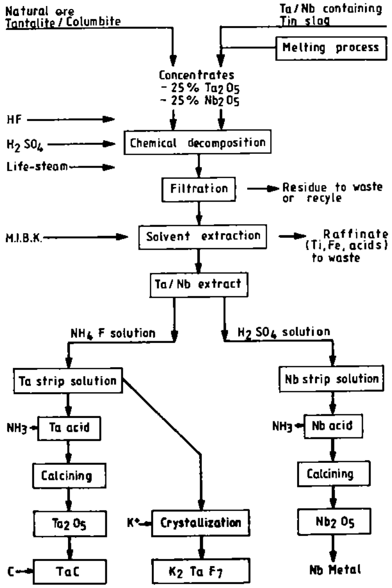


Figure 3. HCST's Ta/Nb Chemistry.

### Chlorination of ores or of ferroalloys and separation of the raw chloride mixture by distillation (13)

The ores and concentrates are chlorinated as follows:

- Finely ground ores are mixed with carbon in a fluidized bed. This process is mainly used for titanium chlorination. However, it is also used for niobium (14).

- After pelletizing the finely ground ores with carbon–coke and pitch, coking takes place. Porous pelletes are very important (15, 16, 17).

- After preliminary reduction with carbon carbides are formed (15).

In the case of niobium, the chlorine reacts with niobium oxide and carbon according to the formula:

$$Nb_2O_5 + 5\ Cl_2 + 5\ C \rightarrow 2\ NbCl_5 + 5\ CO \qquad (1)$$

Chlorination takes place at temperatures of approximately 800°. Chlorination additives such as NaCl or $CaF_2$ are used. The highly volatile chlorides such as $TiCl_4$, $SnCl_4$, $SiCl_4$, $WOCl_4$, $TaCl_5$, $NbOCl_3$, $NbCl_5$ and $FeCl_3$ are distilled and condensed (fractionated). Chlorides which are difficult to volatilize e.g. $CaCl_2$, $MnCl_2$, etc. remain in the residue. For the separation of tantalum from niobium by distillation it is absolutely necessary that niobium be present in the form of $NbCl_5$. The $NbOCl_3$ is directed over a charcoal layer in a secondary chlorinator with chlorine and is chlorinated. The waste gases of the chlorination process consist largely of phosgene together with $Cl_2$ and gaseous chlorides.

The flow sheet for ore chlorination is presented in Figures 4 and 5. The equipment for this process is very expensive, since special construction materials such as quartz and Inconel are required. Compared to the chlorination of ferroalloys it is too expensive.

Compared with oxide chlorination, the <u>chlorination of ferroalloys</u> is simpler. Several processes are known and have been described among others in the following literature (18, 19, 20). Concerning the chlorination of ferroalloys in melts (20), a mixture of ferroalloy and NaCl is continuously fed into a melt of sodium iron chloride ($NaFeCl_4$) and converted with chlorine.

Under certain conditions intermediate products from the tin slag process can be used as ferroalloys. As a general rule, alloys from tantalite, columbite or pyrochlore produced by aluminothermic or electrothermic processes are used. The conversion of the ferroalloy takes place according to the following formulas:

$$FeNb + NaCl + 7\ NaFeCl_4 \rightarrow NbCl_5 + 8\ NaFeCl_3 \qquad (2)$$

$$8\ NaFeCl_3 + 4\ Cl_3 \rightarrow 8\ NaFeCl_4 \qquad (3)$$

$NaFeCl_4$ is used as a chlorinating agent. The plan of such a plant is indicated in Figure 6.

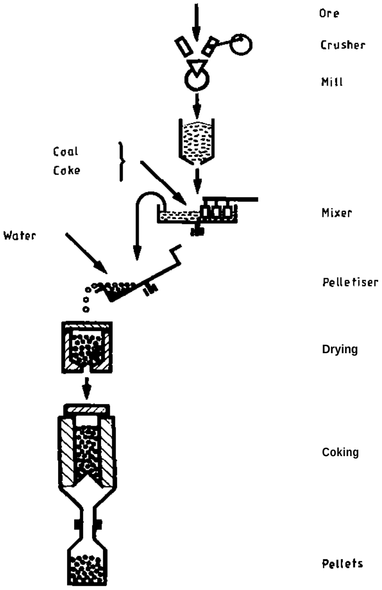


Figure 4. Ore Pellets Preparation.

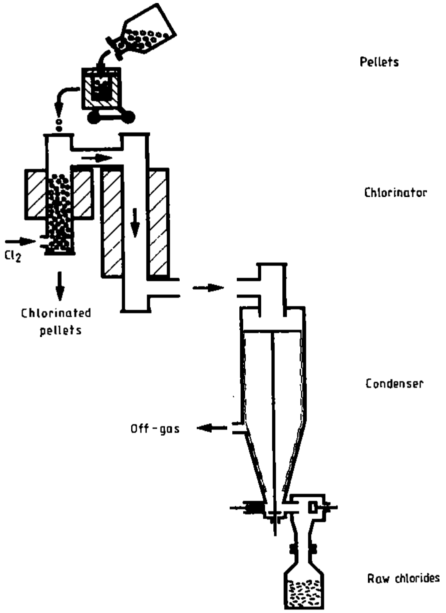


Figure 5. Chlorination.

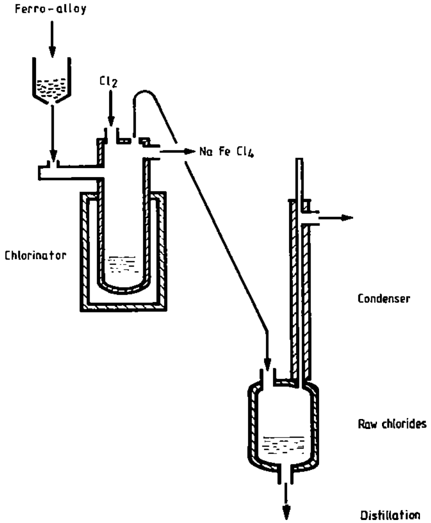


Figure 6. Ferro-Chlorination.

The chloride mixtures from both processes are treated by fractional distillation (21, 22). The boiling points of the chlorides contained in the raw chloride mixture are given in Table IV.

Table IV. Boiling Points of Chlorides

| | | |
|---|---|---|
| $SiCl_4$ | - | 58 C |
| $SnCl_4$ | = | 114 C |
| $TiCl_4$ | - | 136 C |
| $WOCl_4$ | - | 228 C |
| $TaCl_5$ | - | 234 C |
| $NbCl_5$ | - | 248 C |
| $WCl_6$ | - | 347 C |

The flow sheet of a distillation plant is shown in Figure 7. By this process very pure niobium pentachloride is produced; this is used for CVD applications as well as for manufacturing very pure niobium oxide and niobium metal.

The chlorination and distillation plant of Hermann C. Starck (Berlin) is shown in Figure 8. The chemical analysis of niobium chloride is presented in Table III.

## Production of Niobium Oxide

The production of pure niobium oxide with a liquid–liquid extraction process has already been described. A typical analysis is given in Table III.

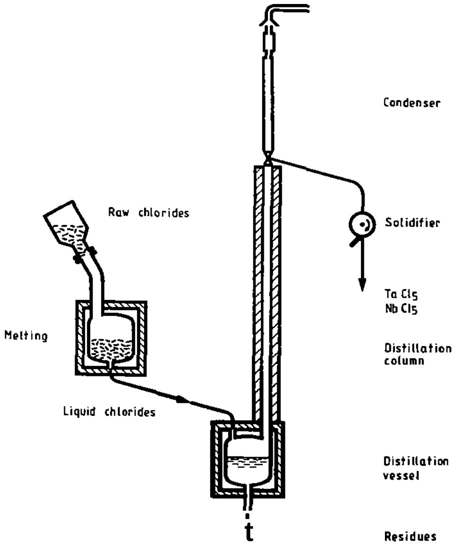
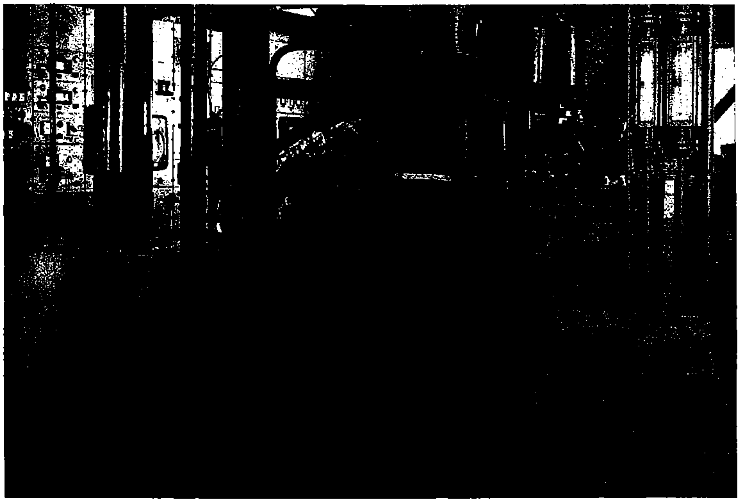


Figure 7. Distillation.



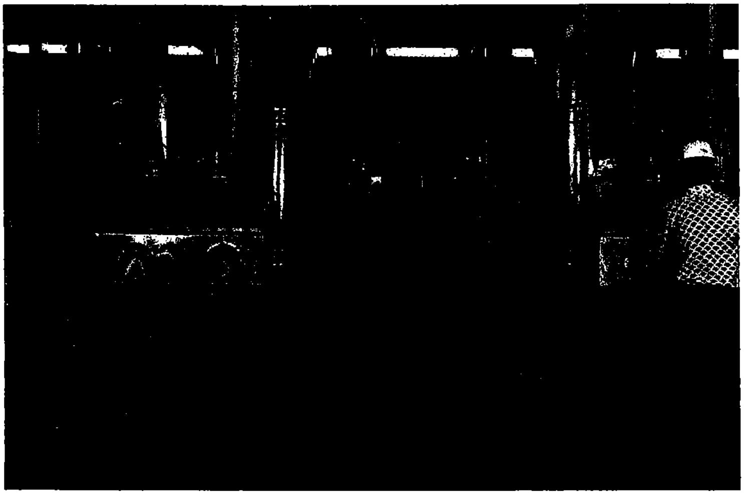


**Figure 8.** Views of H. C. Starck chlorination and distillation plant in Berlin.

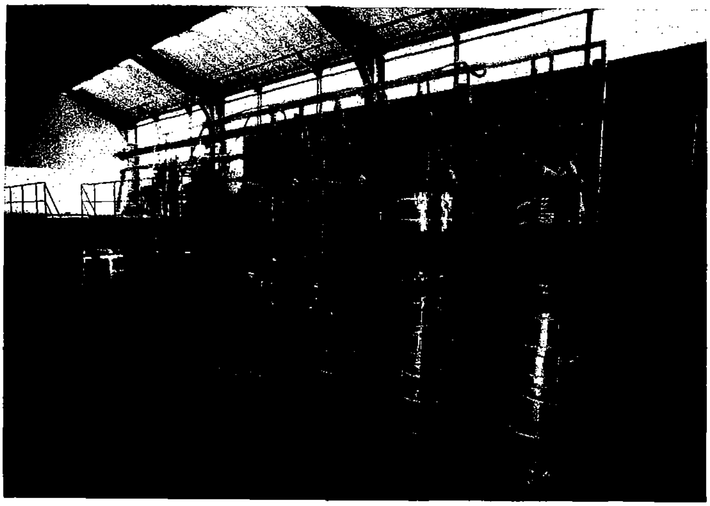


Figure 8. View of H. C. Starck chlorination and distillation plant in Berlin.

Hermann C. Starck Berlin also produces niobium oxide of the highest purity for optical and electronic applications. This is accomplished by fluidized bed hydrolysis using finely ground $NbCl_5$ and subsequently calcining it (23, 24). The composition of this special quality niobium oxide is seen in Table III. Figure 9 indicates the flow-sheet of this process.

## Production of Niobium Metal

Niobium metal can be produced from 3 different compounds:

- Niobium oxide
- $K_2NbF_7$
- Chlorides $NbCl_5$ and $NbCl_3$

Niobium oxide can be reduced as follows:

### Metallothermic reduction.

Here the most widely used method is reduction by means of aluminum. Niobium oxide and aluminum ate mixed and reduced to a raw niobium ingot in special vessels. This ingot, free of slag and surface impurities, is purified by melting 2–3 times in an electron beam furnace. Wilhelm (25) described this process.

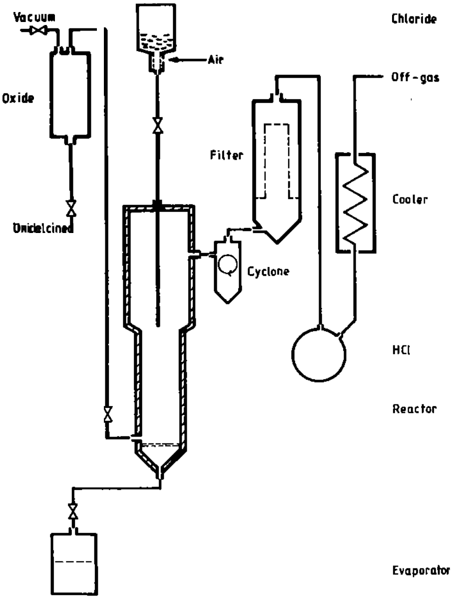


Figure 9. High purity Niobium Oxide.

## The carbothermic reduction.

Niobium oxide and carbon are mixed, pelletized and converted to niobium metal by means of a two-step process in a vacuum furnace. The main reaction takes place during the first step; during the second step the C/O stoichiometry is corrected by adding further reducing agents or by treating the pellets with oxygen. After a second vacuum treatment very pure niobium metal pellets are obtained; the main impurities are gases and carbon. By hydriding, crushing and milling the pellets, coarse material and fine powders can be obtained. A typical analysis is shown in Table V. Based on a very pure oxide, niobium metal with high purity can be obtained (26, 27, 28, 29, 30).

Table V. Typical analysis of Niobium Pellets via Carbothermic Reduction

| | | (ppm) |
|---|---|---|
| $O_2$ | | 300-500 |
| $M_2$ | < | 50 |
| C | | 20-30 |
| Ta | < | 100 |
| Fe | < | 7 |
| Cr | < | 2 |
| Ni | < | 2 |
| Mn | < | 1 |
| cu | < | 1 |
| T | < | 10 |
| Zr | < | 10 |
| Sn | < | 10 |
| Ca | < | 10 |
| Mg | < | 1 |
| Al | < | 10 |
| Si | < | 10 |

## Reduction of $K_2NbF_7$

Niobium metal is produced by reduction of $K_2NbF_7$ with sodium in a manner analogous to the corresponding tantalum process (31, 32). However, since in most cases $K_2NbF_7$ is contaminated by $K_2NbOF_5$, powders with a high oxygen content are obtained.

The reduction of niobium chlorides to niobium metal is made:

- metallothermically (with Na, Mg, Zn. . .)
- with hydrogen
- by fused salt electrolysis.

## The metallothermic reduction of NbCl

Several processes are known which employ the reduction of niobium chloride with sodium (33, 34).

CIBA AG developed processes for the reduction of niobium pentachlorides with zinc (35) and magnesium (36, 37). Reduction with magnesium is unusual for the following reason. A mixture of $NbCl_5$ and fine magnesium is burnt in reactors. Retarding additives in the form of alkali chlorides are added. The reaction mass is washed with diluted hydrochloric acid and water and then dried. The resulting niobium metal is characterized by a large surface area and therefore a high gas content. The material is often pyrophorous. Corrosion of the reactor material is primarily responsible for the impurities.

This "Thermite" process proved to be too expensive when compared with the aluminothermic reduction of niobium oxide. However, several tons of niobium were produced by this method. The following Table VI presents a typical analysis of niobium metal powder and niobium ingots manufactured by electron beam melting of this powder.

## Reduction of niobium chloride by means of hydrogen

There are numerous publications on and patents for this process. Du Pont (38) produced very pure niobium metal by this method. CIBA developed **a** process for the reduction of $NbCl_5$ with hydrogen in alkali chloride melts (39) as well as for the production of fine niobium metal powder by means of a reduction of niobium pentachloride in hydrogen plasma (40, 41). Niobium carbides and niobium nitrides were also produced by the same method (42, 43). Also Union Carbide had a process for producing submicron niobium powder by means of hydrogen (44).

The production of niobium layers by reduction of $NbCl_5$ with hydrogen was discussed as early as **1948** by Powell (45). Today the Chemical Vapor Deposition (CVD) of niobium made of $NbCl_5$ and hydrogen is probably the only process based on the reduction of halides with $H_2$ which is still used for production. Hermann C. Starck Berlin produces extremely pure niobium chlorides for this purpose.

Niobium metal powder of the highest purity results from reducing niobium halides with hydrogen. Unfortunately, the production costs are very high.

Table VI. Typical Analysis of Niobium Powder and after electron beam remelting

| | Niobium Powder and Themite-Reduction (ppm) | Niobium ingot from Thermite Nb (ppm) |
|---|---|---|
| H | 2600 | 10-20 |
| O | 5900 | 200-400 |
| N | 60 | 70 |
| C | 200 | 40 |
| Ta | 140 | 150 |
| Ni | 50 | < 1 |
| Fe | 320 | 15 |
| Cr | 75 | < 10 |
| Mg | 1670 | < 10 |
| Mn | < 10 | < 10 |
| Al | < 10 | < 10 |
| Si | 80 | 20 |
| Ca | 200 | < 10 |
| Cu | < 10 | < 10 |
| Ti | < 10 | < 10 |
| V | < 10 | < 10 |
| Sn | < 10 | < 10 |
| Mo | < 10 | < 10 |
| W | < 30 | < 30 |
| Hf | < 30 | < 30 |
| Zr | < 30 | < 30 |

## Production of niobium metal by means of fused salt electrolysis:

The following distinction must be made:

- melts containing oxygen

  $Nb_2O_5/CaCl_2-CaO$
  $K_2NbOF_5/KCl$
  $K_2NbF_7-Nb_2O_5/KCl + KF$
  $Nb_2O_5/NaF$

- oxygen free chlorides-fluoride melts

  $Nb_3Cl_8/KCl-NaCl$
  $K_2NbF_7/KCl-NaCl$
  $NbCl_5/KCl-NaCl-KF$

- pure fluoride melts

  $K_2NbF_7/NaF + KF$ (+ LiF)

Senderoff (46) and Rockenbauer (47) presented a general review of laboratory and industrial processes. Ganda Schenk has worked on processes for the fused salt electrolysis of niobium (48) and reported on processes for electro raffination (49).

First CIBA and then Hermann C. Starck Berlin, after the latter acquired CIBA's Rare Metals department, have been involved in the production of niobium by means of fused salt electrolysis and in the production of electrolytic tantalum on an industrial scale. Special processes were developed whereby niobium chloride was continuously evaporated in melts of KCl, NaCl and KF and afterwards electrolyzed. The cathodes were periodically stripped in an argon atmosphere inside the electrolysis system and then dipped into the melt. After cooling, the raw metal was discharged, washed and dried.

The melt temperature was 850 - 950 C, material yield was 85 - 90 percent, however, the electric power yield was only approximately 30 percent. The process proved uneconomic due in part to corrosion problems. Figure 10 presents the flow-sheet of production by electrolysis.

A typical analysis of niobium metal produced by fused salt electrolysis is shown in Table VII.

During electrolysis tantalum is separated from niobium. $NbCl_5$ containing 0.1 - 0.3 percent $TaCl_5$ results in niobium metal containing <30 ppm Ta.

## Production of Niobium Carbide

The most important use for niobium is in tantalum niobium mixed carbides which are used for cemented carbides. Mixed oxides with the necessary addition of reducing - and carburating agents are converted to tantalum mixed carbides using basically 3 furnace types:

- tube furnaces
- open medium frequency furnaces
- vacuum furnaces

Very pure niobium carbide can be produced by converting pure niobium oxide (from niobium chloride) by means of carbon in a vacuum furnace.

Niobium oxide and the necessary quantity of carbon are mixed, compacted or pelletized and converted in a vacuum furnace, Figure 11. The product of the first reaction is crushed, milled and screened to < 250 µ. The carbon and oxygen content is analyzed and corrected by adding carbon or oxide. For the second reaction the powder mixture is directly stamped into a reaction crucible and converted once again in vacuum. The product of this reaction is milled to < 40 µ, sieved and analyzed. The capacity of large furnaces is approximately 400 kgs for the first reaction and 1 t for the second reaction. The only impurities are gases, depending on the grain size and the metal from the milling process. Necessary precautions have to be taken.

In addition to this standard process, attempts have been made to produce very fine carbides by reducing halides with hydrogen and simultaneously carburizing them with hydrocarbons, e.g. (42, 50, 51, 52). However, these processes have never advanced beyond the pilot stage. The hope which many had set in the application of fine carbides for cemented carbides has not been fulfilled.

## Alkali Niobates

Lithium niobate in particular is used today in crystals for surface acoustic wave-filters. Very pure "crystal grade $Nb_2O_5$" is required for this application.

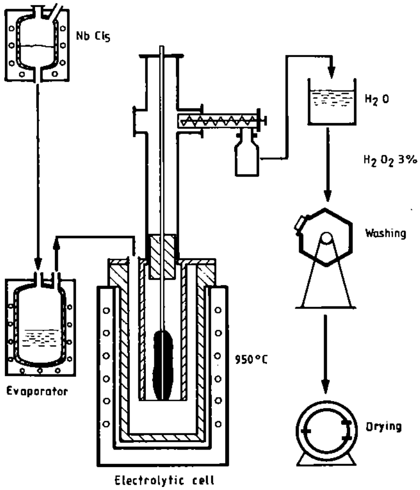


Figure 10. Niobium Electrolysis.

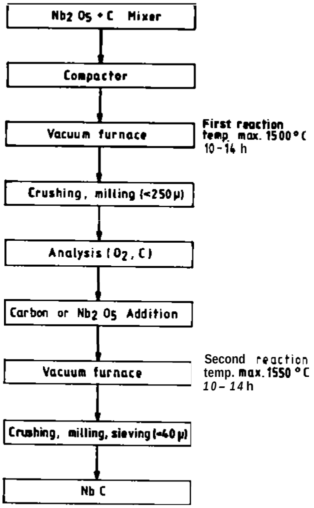


Figure 11. Production of NbC.

Table VII. Analysis of Electrolytic Niobium

| | | (ppm) |
|---|---|---|
| $H_2$ | | 10 - 100 |
| $O_2$ | | 300 - 500 |
| $N_2$ | < | 50 |
| C | | 100 - 300 |
| Ta | < | 30 |
| W | < | 10 |
| Fe | | 100 - 200 |
| Ni | | 100 - 300 |
| Cr | < | 10 |
| Mn | < | 1 |
| Cu | < | 1 |
| V | < | 3 |
| Sn | < | 3 |
| Ti | < | 10 |
| Zr | < | 10 |
| Ca | < | 1 |
| Mg | < | 1 |
| Al | < | 1 |
| Si | < | 3 |
| Mo | < | 3 |

A typical analysis of this type of niobium carbide is presented in Table VIII.

Table VIII. Analysis of Niobium Carbide

| | |
|---|---|
| Ta | < 100 ppm |
| Carbon | 11.4 - 11.5 % |
| Free Carbon | < 0.1 % |
| Al, Bi, Ca, Cr, Cu,<br>K, Mg, Mn, Na, Ni,<br>Pb, Sn, V | each max. 3 ppm |
| Fe, Mo, Si, Ti, Zr, Co | each max. 10 ppm |
| W | max. 100 ppm |
| Nb | Balance |

Niobium oxide produced from the purest $NbCl_5$ meets these requirements. Morawietz (53) developed processes for producing these alkali niobates.

## Miscellaneous Niobium Products

In addition to several special compounds such as sulfides, selenides, alcoholates, etc., niobium nitrides should also be mentioned.

Niobium nitride obtained from $Nb_2O_5 + NH_3$, can be disproportioned to niobium metal relatively easily (54). Nitrides and carbonitrides have been tested for coating cemented carbides but without success (55).

Double salts of niobium chloride and KCl have been recommended as stable chloride complexes for metal production (56).

## Conclusion

A great deal of research and development was devoted to niobium in the 'fifties and 'sixties. Many articles and patents were published, of which this brief study can only present an incomplete survey. The enthusiasm of the early years has been followed by disenchantment and considerable pessimism in the last decade.

Various processes have been successfully developed to produce niobium metal and a great variety of niobium compounds. New applications have to be found beyond existing ones. The manufacturers of niobium metal and compounds must give their support through increased research and development activities to further improve their products.

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