

THE EVOLUTION OF FeNb MANUFACTURING

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Abstract

This paper describes ferro-niobium manufacturing technology, and comments on alternative methods of production. A brief history of niobium illustrates the evolution of its applications and, as a consequence, the evolution of ferro-niobium manufacturing. The execution of industrial projects by the major niobium supplier, CBMM, is described, including the recent expansion plan, which has increased ferro-niobium production capacity to 45,000 t/y. CBMM's future plans regarding ferro-niobium manufacturing technology are also discussed.

Introduction

In less than two centuries niobium has evolved from being an unknown metal to a rare and high-priced material in the market, and then to the opposite extreme, becoming readily available, with an excess of supply and reduced price.

In 1801, Charles Hatchett, a British chemist, discovered an element that he named columbium, since the mineral sample he was working with came from New England in the United States. However, Hatchett did not isolate the element. This was done by Heinrich Rose, a German, who separated an impure Nb₂O₅ from tantalite in 1844. Thinking that he had found a new element, Rose renamed it niobium, which remained a laboratory curiosity for nearly 100 years. In 1948, niobium was adopted as the name for the element by the International Union of Chemists, although the original name columbium is still widely used by metallurgists in North America.

Applications of niobium began around 1925 when it was added to tool steels as a partial substitute for tungsten, and later in 1933 when it was first used to stabilise interstitial in austenitic stainless steels. In the 40's niobium was added to super alloys for use in gas turbines. Interest in using niobium in plain carbon steels dates back to the late 30's. However, due to its high cost, more than US \$ 25 per kg niobium ctd, and lack of availability, the use of niobium in plain carbon steels did not materialise until the late 50's and early 60's. During this period, the source of niobium was the mineral columbite-tantalite, mainly processed for the production of tantalum through a costly separation process.

In the mid 50's, with the discovery of large pyrochlore reserves in Araxá, Minas Gerais-Brazil and Oka, Quebec-Canada, and the subsequent development of these deposits, niobium became available in abundance. It motivated a number of groups to explore its use in carbon steels.

The reserves in Araxá, Brazil, are the largest in the world, and their exploitation by CBMM has played an important role in consolidating the position of niobium as a metal with a permanently reliable supply. CBMM's continuous dedication to maintaining this stable scenario for niobium is described below.

Other Niobium Products at CBMM

The excellent quality and the huge reserves of the niobium mine operated by CBMM makes the company a natural leader in the production of ferro-niobium and other niobium products. This leadership is maintained through continual strategic planning and investment.

Since the industrial start up in 1961, frequent technological modernisation and expansion of capacity have been introduced in the several stages at the production of ferro-niobium. In 1980, CBMM began production of high purity niobium oxide. This enabled the addition of more value-added niobium products to the product mix of the company. In the same year, the company ceased to market niobium concentrate, the raw material for ferro-niobium and niobium oxide.

In 1982, CBMM began the production of special alloys (ferro-niobium and nickel-niobium high purity), allowing the company to get closer to the end-users of niobium. The policy of developing more and more value-added niobium products continued. In 1989, CBMM began production of high purity niobium metal by electron beam refining. Throughout the 90's,

CBMM adjusted the process to produce special purity niobium oxides, and in 1998 a plant for producing optical grade oxide was started-up.

Table I summarises current range of CBMM's products, their typical niobium content, and production capacity:

Table I CBMM products and production capacity

Products	Content %	Capacity (tons per year)
Ferro-niobium std	65-67 Nb	45,000
Niobium oxide high purity	99 Nb ₂ O ₅	3,000
Ferro-niobium VG and Nickel-niobium	65-67 Nb	1,500
Niobium oxide optical grade	99.9 Nb ₂ O ₅	150
Niobium metal	99.9 Nb	60

Basic Technology of FeNb Manufacturing

Niobium is a plastic metal, grey in colour, with a body-centered cubic structure and the following physicochemical properties:

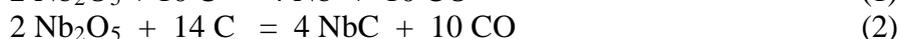
Atomic number	41
Atomic weight	92.91
Density (g/cm ³)	8.57
Valence	2,3,4,5
Melting point (°C)	2,468
Boiling point (°C)	4,927
Heat of fusion (cal)	4,773
Specific heat (kJ/kg °K)	0.26

Niobium forms a compound with iron, Fe₃Nb₂, which dissolves a large amount of iron. The melting point of ferro-niobium alloy is approximately 1,600 °C.

With carbon, niobium forms carbides of varying composition from NbC to Nb₄C. The melting point of NbC is 3,500 – 3,800 °C. The hardness of niobium carbide is 9-10 Mohs which determines its uses in cemented carbide tool alloys.

With oxygen, niobium forms three oxides: niobium pentoxide (Nb₂O₅), niobium dioxide (NbO₂) and niobium protoxide NbO. Niobium pentoxide is an acid oxide, white in colour and with a melting point of 1,460 °C. The character of niobium oxides vary from acid to basic, with a decrease in the amount of oxygen linked to niobium.

Niobium pentoxide may be reduced by carbon, silicon and aluminium:



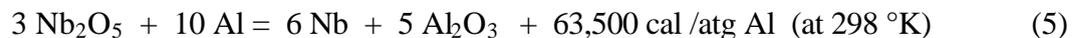
Thermodynamic calculations show that these reactions are feasible.

The theoretical temperature for the beginning of carbothermic reductions is 1,100 °C (Nb formation) and 890 °C (NbC formation). However, ferro-niobium is not produced via carbothermic reduction. Ferro-niobium is used for alloying low carbon steels, but high residual carbon in ferro-niobium and/or the presence of high melting point niobium carbides obviously make the alloy produced via carbothermic reduction, inappropriate for such applications.

The reduction of niobium pentoxide by silicon generates an incomplete reaction. Lower niobium oxides are formed. The reduction of these lower oxides by silicon is extremely difficult. Thus, the reactions lead to the production of silicon-bearing alloys, and to high niobium losses in the slag.

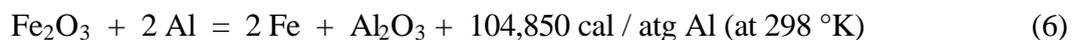
The highest ratio of niobium recovery is obtained by reducing niobium pentoxide with aluminium. Therefore aluminothermic reduction is the process used worldwide to produce ferro-niobium.

The energy associated with the reduction reaction is as follows:



When reducing pyrochlore concentrates, the amount of energy evolved from the above reaction (5) is not sufficient to keep the bath liquid, even in the presence of metallic iron, which decreases the melting point of the alloy. Thus the separation of slag and ferro-niobium is not reached, and consequently niobium losses in the slag are high.

Some extra energy is necessary to allow a complete reduction reaction, to melt the charge, and to promote a molten phase to separate the ferro-niobium from the slag. This extra energy is normally supplied by the following reaction:



Fluorspar and lime are normally added to the aluminothermic mix in order to lower the melting point of the slag and to decrease slag viscosity, improving conditions for ferro-niobium/slag separation and thus maximizing recovery.

The Evolution of Ferro-niobium Manufacturing at CBMM

From 1965 to 1991 ferro-niobium was produced in Araxá using the conventional aluminothermic process as described above. This aluminothermic process was one of the largest in the world, firing simultaneously 6 reactions with 6,000 kg of aluminium per reaction, and producing 66,000 kg/day of ferro-niobium. The size of the batch increased from 3,000 kg of concentrate in 1965 to 18,000 kg of concentrate in 1980.

The typical charge for one batch of ferro-niobium production in 1991 was as follows:

Pyrochlore concentrate	18,000 kg
Aluminum powder	6,000 kg
Hematite	4,000 kg
Fluorspar	900 kg
Lime	300 kg

The raw materials were weighed and mixed. An open reactor was charged with the aluminothermic mix which was ignited with magnesium turnings. After the reaction was complete (approximately 15 min) all the components had melted, and the slag was separated from the ferro-niobium by gravity. The slag was tapped from the reactor and the ferro-niobium was left to solidify and cool down.

Approximately 11,000 kg of ferro-niobium containing about 65 per cent niobium were produced per batch.

In 1991, CBMM began a new metallurgical operation – the FeNb semi-continuous autothermic reduction process in a closed vessel. This process had the main objective of introducing and developing improvements in environmental control and working conditions. The following improvements were developed during this step:

- Automatic blending of raw materials
- Control of fumes.
- Slag granulation.
- Ferro-niobium casting

In 1994, CBMM introduced a submerged electric arc furnace, to the ferro-niobium production, incorporating all the advantages developed in the previous step, and allowing a 25 per cent saving in aluminium consumption by the replacement of iron oxide (hematite) with metallic iron powder.

Since 1994 more than 150,000 tons of ferro-niobium have been produced in a 4,25 MVA electric arc furnace at CBMM. The furnace, initially designed to produce 15,000 tpy reached a capacity of 30,000 tpy in 1998. The present production capacity of the electric arc furnace is 39,000 tpy of ferro-niobium.

The figure 1 below shows the evolution of CBMM’s ferro-niobium sales compared to total world demand. It also shows CBMM’s ferro-niobium production capacity.

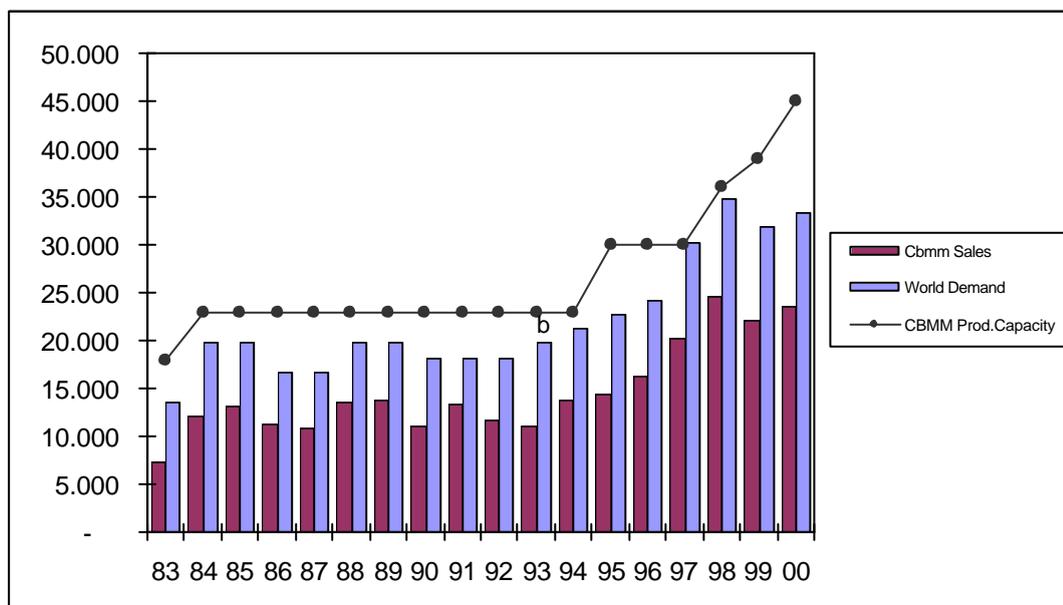


Figure 1: World demand for ferro-niobium, CBMM’s ferro-niobium sales and CBMM’s production capacity.

Recent Developments in Ferro-niobium Manufacturing at CBMM

Because of its relatively high phosphorous, sulphur and lead contents (1.0, 1.0 and 0.2 per cent respectively), the floated concentrates must be refined before conversion into ferro-niobium. From 1976 to now, the floated concentrate is treated in a calcination and leaching plant, where the levels of those impurities are reduced to much lower levels prior to conversion into ferro-niobium,

The leaching process consists of the following steps:

- Calcination of a mixture of floated concentrate with calcium chloride and lime, in a rotary kiln at a temperature of 800 to 900 °C.
- Cooling and leaching of the calcined mixture at 50 % solids, with 5 % hydrochloric acid followed by filtration. This step is carried out twice.
- Washing the concentrate with water at 50 % solids, filtration, drying and packaging of the concentrate. The final concentrate is ready for ferro-niobium production.

During calcination, hydrochloric acid and lead chloride are formed; these are volatilised and captured in the cooling tower, venturi and packing tower.

Also during calcination, calcium replaces barium in the crystal structure of the pyrochlore. Barium chloride is formed and eliminated as barium sulfate after precipitation with sulphuric acid.

Pyrometallurgical Refining of Concentrate

The pyrometallurgical process developed by CBMM has been in operation since the beginning of 2000. The process described below substitutes the acid leaching process, incorporating such benefits as costs savings and improvements in quality.

The new process removes the P, Pb, and S in two consecutive steps: sintering and smelting in an electric arc furnace.

Sintering

Before the sintering, the floated concentrate is pelletized with petroleum coke and bentonite. The green pellets are fed into the steel belt-sintering furnace, design by Outokumpu Oy, where the H₂O and Sulphur are removed. The gases are washed in two stages of wet scrubbers, which remove the sulphur and particulate matter. The water is treated and recycled within the system.

Following this, the sinter produced is crushed and classified. Part of it returns to the sinter belt as a bedding protection, and the balance goes to the stock feed pile for electric arc furnace smelting.

Electric Arc Furnace Smelting

The sinter, mixed with petroleum coke and steel scrap are fed into the 10,5 MVA electric arc furnace, design by SMS Demag, where the concentrate is refined in terms of phosphorous and lead.

The carbon from the coke reduces phosphorous and lead oxides. The lead is fumed off, reoxidises, and is collected in the bag-house as lead oxide. The iron from the scrap collects the

phosphorous, forming ferro-phosphorous alloy (about 11 % P) which concentrates at the bottom of the furnace.

The process is carried out in a molten phase at 1450 – 1500 °C. The refined concentrate is tapped from the furnace and granulated by water. Following this, the refined concentrate is filtered, dried, packaged and transferred to the metallurgical plant for Ferro-niobium production.

The ferro-phosphorous alloy is tapped periodically and is currently being disposed of as waste material.

Ferro-Niobium Production

In order to guarantee an excess of production over world demand, CBMM decided to build an aluminothermic shop to increase production capacity, incorporating an extra 6,000 tpy, giving a total of 45,000 tpy. This production began in October 2000.

Crushing and Packaging

The new crushing and packaging plant, which has been operating since June 1999, incorporates the best state-of-the-art technology available. The plants are fully automated. The crushing is completely dust and noise proof. Cameras do the supervision, which allows the operators to monitor the process without being exposed to the noisy environment. Wherever dust is generated, devices have been installed to collect and carry the dust to a bag house.

The ferro-niobium lots are automatically sampled during the production.

After crushing and sampling the lots of the product are stored in individual silos to await the quality approval.

Packaging is carried out in specific sites for big-bags, drums or boxes. Palletising is also automated and carried out by a robot designed by Asea Brown Boveri.

The plant has the capacity to crush and pack 50,000 tpy.

Future Developments in Ferro-niobium Manufacturing at CBMM

As described above, the production of ferro-niobium through aluminothermic reduction of pyrochlore concentrate needs additional energy to that which comes from the chemical reduction of niobium pentoxide.

In conventional manufacturing, this energy comes from the reduction of iron oxides (normally hematite), by aluminium.

At present, CBMM uses electricity via an electrical arc to supply this extra energy to the process.

Trials were run, on a pilot scale, reducing the molten concentrate available after refining at pyrometallurgical process. In this case, the extra energy comes from the enthalpy of the molten concentrate. Another advantage of the reduction of the liquid concentrate is the possibility of replacing aluminium powder by wire cuts, shots and other chipped forms of aluminium. The

pilot tests showed very promising results, with even better recovery compared to conventional and electric arc furnace processing.

References

- (1) Bordignon, P., Vargas, J. I. De, Sousa C. A de F., “Niobium – Reserves for Centuries, Permanent Reliable Supply” (Paper presented at the Metal Bulletin Conference – Monte Carlo – 1999).
- (2) Sousa, C. A de F., Telhado A, “Recent Developments on Niobium Manufacturing at CBMM” (Paper presented at TIC Conference – San Francisco – 2000).
- (3) Sousa, C. A de F., Fuccio Jr, R., “The Production of Ferro-niobium in an Electric Arc Furnace at CBMM” (Paper presented at TIC Conference – Goslar – 1995).
- (4) Habashi, F.,ed, Handbook of Extractive Metallurgy - Volume 3 – Wiley-VCH – Edition 1997.
- (5) Riss, M.; Khodorovsky, Y.; translated from the Russian by I. V. Savin, Production of Ferroalloys – MIR Publishers Moscow – second edition.