MELTING AND PURIFICATION OF NIOBIUM

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Abstract

The aspects involved in the purification of niobium in Electron Beam Furnaces will be outlined and correlated with practical experience accumulated over 12 years of continuously producing high purity niobium metal and niobium-zirconium ingots at CBMM, meeting the needs for a wide range of uses. Also included are some comments regarding raw material requirements and preparation.

Introduction

Since first obtained as a pure metal, the properties of niobium have been attracting the interest of scientists and engineers for several applications involving advanced technologies. Among others, its high melting point (2,468 ºC), its low density in comparison to other refractory metals, its corrosion resistance, its superconductivity properties and its capability for forming dielectric oxide layers have made niobium a material of choice in many different fields.

Almost all of these attractive properties are strongly dependent on the purity of niobium. To meet the very demanding quality requirements for the majority of its potential applications, especially those related to superconductivity, intensive efforts have been made towards the production of the highest purity material and have resulted in an excellent level of knowledge and process development.

The advent of the electron beam melting (EBM) technology represented a great contribution for producing solid niobium metal with the lowest residual impurities ever achieved by any other consolidation process available up to that time. Late in the 1950´s, Hugh R. Smith and Charles Hunt produced the first tantalum and niobium ingots via E.B.M. at the Temescal facilities. Thereafter, in 1959, Wah Chang Ltd. started the production of niobium and tantalum ingots in EB-melting furnaces.[1]

Niobium based alloys were first established as high temperature materials with Nb-10%Hf-1%Ti being the most important. This alloy is currently used in high temperature components of turbine engines. Later, high purity niobium and some niobium-based alloys were introduced for use in superconducting applications. In this case, the Nb-47%Ti continues to be the niobium based alloy with the largest demand. It is present in the superconducting magnets used in Magnetic Resonance Imaging (MRI) units. Currently, high purity niobium powder is regaining interest in the solid electrolytic capacitor industry as a potential competitor for tantalum powder in some applications.

There is already a vast technical literature covering the production process of niobium from extractive metallurgy to its consolidation as a pure metal [3, 6, 9, 13, 14, 15]. Thus, the intent of this paper is to give an overview of the practical experience accumulated over 12 years producing commercial and reactor grade niobium ingots in a fully integrated – from the mine to the final products – niobium company.

Purification Related Aspects

Pure niobium metal is a tough and ductile material that has good cold working properties. Nevertheless, only a few-hundred parts per million (ppm) of oxygen, nitrogen, hydrogen and/or carbon residuals may turn niobium into a hard and brittle material[3]. Furthermore, for some special applications such as superconductivity, only a few ppm of most impurities are tolerable.

In order to produce high purity niobium ingots, electron beam melting has proven to be the most suitable process. The power density, the protective action of the high or even ultra-high vacuum environment along with the flexibility of managing the residence time of the metal in the molten state, represent very important purification factors that can hardly be implemented by any other vacuum metallurgical process.

Under the EB operational conditions, the purification of niobium takes place by distillation and degassing.

Distillation

Higher vapor pressure elements are eliminated by volatilization. The specific evaporation rate can be described by the Langmuir equation that relates the evaporation rate to the partial pressure and molecular weight of the element and the temperature [4]:

$$a_{v1} = \alpha \,.\, 4.4 \,.\, 10^{-4} \,.p_s\, (M_D \div T_v)^{1/2} \qquad (1)$$

Where:

a_{v1} (in $g.cm^{-2}.s^{-1}$) is the specific evaporation rate;

α is the evaporation coefficient – for idealized evaporation $\alpha = 1$;.
p_s (in Pa) is the saturated vapor pressure at a temperature T_v;
T_v (in K) is the absolute temperature and
M_D is the molecular weight.

As a rule of thumb, effective purification can be achieved only if the vapor pressure of the contaminant is, at least, a hundred times greater than the primary element at the melting temperature of the latter.

The great majority of the impurities possibly present in niobium raw material resulting from the Araxa´s pyrochlore processing – such as aluminum, iron, titanium, manganese, barium, potassium and silicon – and many other metals, have their vapor pressures considerably higher than that of niobium. As can be seen below in Figures 1 and 2, at the niobium melting temperature, these residual elements are quite easily volatilized from the molten niobium and then collected by the water-cooled walls and condensers located inside the melting chamber.

For example, during the production of the Nb-1% Zr alloy, which normally requires two EB-melting steps, approximately 30% of the zirconium added to the niobium is lost via evaporation. Meanwhile the niobium recovery can be as high as 96 to 98%.

On the other hand, lower vapor pressure elements such as tantalum, tungsten and, molybdenum cannot, or will hardly be removed from niobium during the EBM process. Once present in the raw material, these elements have to be removed by another process.

Among the lower vapor pressure metals, only tantalum is present in CBMM´s ore, however, at levels compatible with most of the current niobium metal commercial applications. The presence of tungsten and molybdenum is almost negligible. Therefore, besides carbon, oxygen and nitrogen, tantalum is the only metallic element that demands special attention when selecting raw material for niobium metal production at CBMM.

It should be mentioned that evaporation of the major constituent also occurs. In the case of niobium processing, a yield loss within the range from 1 to 3% due to evaporation of niobium may be expected. Thus, a small enhancement of the concentration of low vapor pressure elements, such as tantalum, is not abnormal.

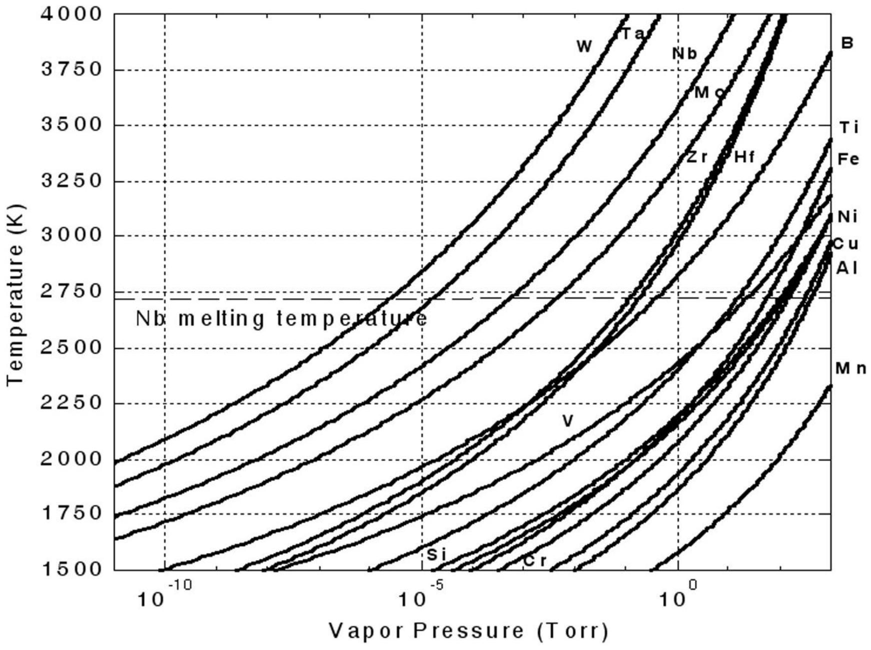

Figure 1: Vapor pressure curves for various elements[4] [5].

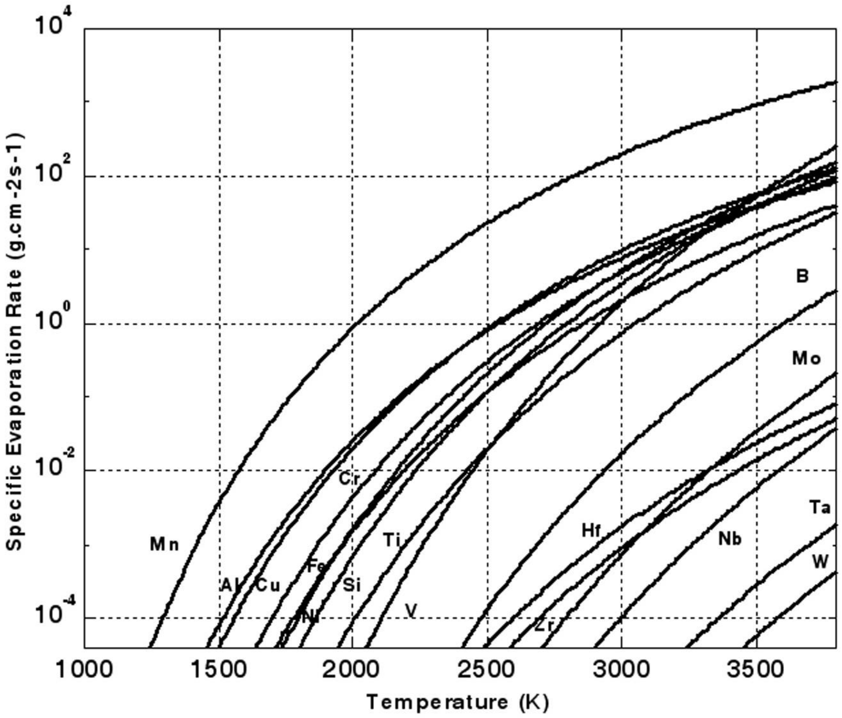

Figure 2: Evaporation rates for some pure elements.

Figure 2 [4,5] Shows the approximate evaporation rate curves for some pure elements. These curves resulted from the application of the Langmuir equation (1) for ideal evaporation conditions. They give a qualitative overview of what can be expected regarding the evaporation rates of different elements compared to niobium.

Degassing

Nitrogen, hydrogen and carbon monoxide evolve from the molten material in the form of gases and have to be removed by the vacuum pumps. Thus, besides the capability of achieving very low end pressures, the furnace's vacuum system has to have enough pumping capacity to handle these gases.

Oxygen, on the other hand, is released from molten niobium in the form of volatile metal-suboxides (mainly NbO and NbO_2) or combined with the carbon (CO). For oxygen concentrations below 1at.% the degassing via NbO is predominant. The metal-suboxides volatilized from the molten pool also solidify at the melting chamber water-cooled walls and condensers.

Niobium decarburization is extremely dependent on oxygen excess in the bulk. Thus, if the carbon content is not reduced to a desirable level during the first steps of purification it will not be effectively reduced in further remelts under high vacuum. In this case, an alternative approach could be remelting it under vacuum with high oxygen partial pressure. An increase of the oxygen content may also be expected from this procedure.

Although the process is performed under high vacuum conditions, niobium has the ability to readily react with residual gases – oxygen, nitrogen, carbon monoxide, carbon dioxide and water vapor. Depending on the partial pressure of these gases in the melting chamber, the reactions may be significant. So, the final pressure in the melting chamber can be a detrimental factor for the purification process.

The thermodynamic, kinetic and interstitial concentrations involved in the niobium-gas reactions are discussed in reference 6.

Niobium Feedstock for EB Furnaces

The flexibility provided by the modern EB furnaces and by the electronic control of the beams allows a wide variety of raw materials to be used: sponge, compacted powder, lump and solid bar.

For niobium, the most important raw material is the solid bar type, resulting from the reduction of the niobium-oxide either by aluminum or carbon. The aluminothermic reduction (ATR) is the most widely used technique to produce feedstock for EB furnaces. This is due to the high reactivity and relatively low cost of the aluminum and also to the feasibility of obtaining a carbon free niobium feedstock.

The carbothermic reduction (CTR) of Nb-oxide has also been an important source for EB feedstock. Usually, the output material from this route has lower oxygen residuals and a better yield after EB remelting, when compared to the product resulting from the aluminothermic reduction. Nevertheless, the carbon may react with niobium and tantalum forming very stable compounds – Nb_2C, NbC, TaC - whose melting points are far above that of pure niobium. Once these compounds are present in the feedstock, their dissociation and the subsequent carbon elimination during the EB processing is highly dependent on the availability of oxygen, as previously mentioned. Thus, a strict control of the carbothermic reduction process parameters, especially concerning stoichiometry, is mandatory. Otherwise, the result may be undesirably high carbon containing Nb ingots. In contrast, the contaminants remaining from the aluminothermic process are more easily removed during the EB melting steps.

The charge for the aluminothermic reaction is a mixture of Nb-oxide with aluminum powder and may also include a booster and a flux. The amount of aluminum in the mixture is usually determined with the purpose of keeping its residual within 3 to 5% w/w in the cast Nb-ATR bar. Practice has shown that higher aluminum containing Nb-ATR bars become brittle and may burst when heated, making the EB-melting process control very difficult. On the other hand, the lower the aluminum content is, the higher the oxygen residuals are, and as a consequence, the yields are lower. The oxygen content of Nb-ATR bars normally ranges from 4,000 to 8,000 wppm.

Pre-selection of Nb-oxide regarding both chemical composition and particle size is of great importance in order to obtain the best results in the EB-melting process. The residuals of low vapor pressure contaminants – W, Ta and Mo – demand special attention. These elements cannot (or will hardly) be removed from niobium by EB processing.

The refractory lining in the casting moulds used for the aluminothermic process may also introduce undesirable impurities. Special care should be taken when using carbon-containing refractory that may transfer high amounts of carbon to the cast niobium bars. On the other hand, calcium oxide or magnesium oxide containing refractories may contaminate the metal with these impurities. Although they are not difficult to be removed during the EBM process, due to their high vapor pressure, they may induce poor yields.

A Practical Example: Niobium EB-Melting and Refining at CBMM

Figure 3 presents all the steps used in the manufacturing of niobium metal ingots at CBMM´s facilities in Brazil.

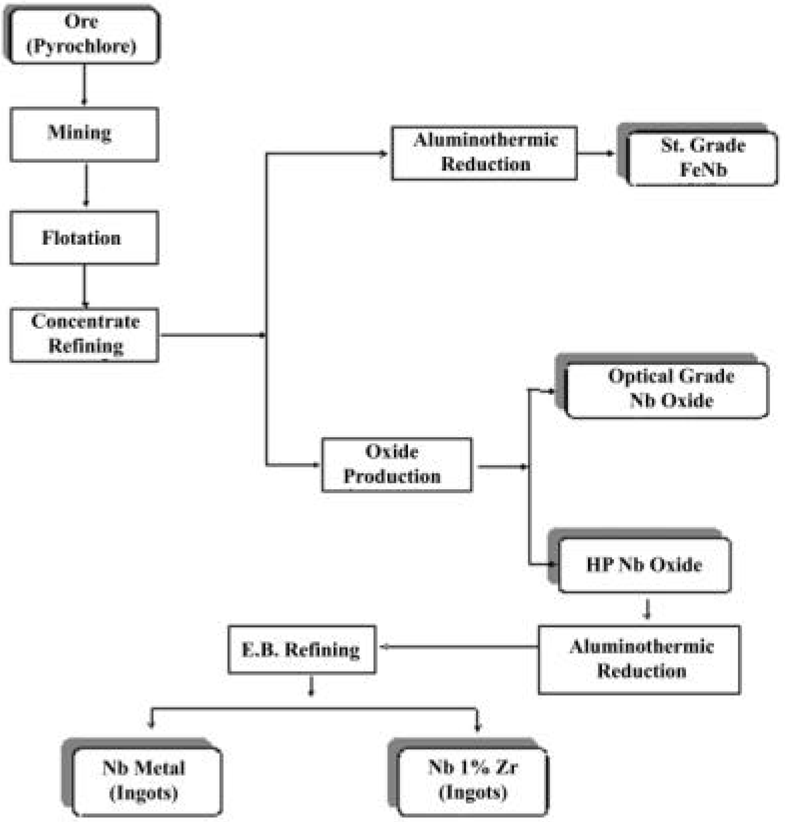

Fig. 3: Production flow chart at CBMM.

The first EB-melting step is carried out by drip melting horizontally fed Nb-ATR bars. The melting rates have to be adjusted in accordance with the raw material gas load, the desired vacuum in the melting chamber, the crucible diameter and the power available. As a reference, in the 500 kW powered furnace equipped with 50,000 liter per second pumping capacity, used at CBMM, the melting rates vary from 40 to 50 kg/hr while the melting chamber pressure varies from 5×10^{-4} to 3×10^{-3} mbar.

The purification process has some limitations during the horizontal feeding step. There is a region of the melting pool, underneath the feeding bar tip, where the impinging electron beam cannot reach without jeopardizing the copper crucible. As a consequence of the lower heat flow, the corresponding region of the resulting ingot generally shows poorer quality, especially regarding oxygen and aluminum residuals and surface smoothness. Figure 4 presents a sketch of the first melt arrangement.

In an attempt to reduce this shadow effect, an alternative approach to casting large and cylindrical shaped Nb-ATR bars (200 mm in diameter x 1,250 mm long and approx. 300 kg each) suitable for vertical feeding, has been used. The ingot material produced by vertical drip melting these Nb-ATRs, shows excellent results regarding quality and high homogeneity of oxygen content (always lower than 300 w ppm) over the ingot length and its cross section [2]. However, since the Nb-ATR bars have a tendency to exhibit thermal cracks, heavy pieces could fall into the molten pool resulting in lower productivity and damages to the crucible. Thus, this procedure has not been implemented for regular production.

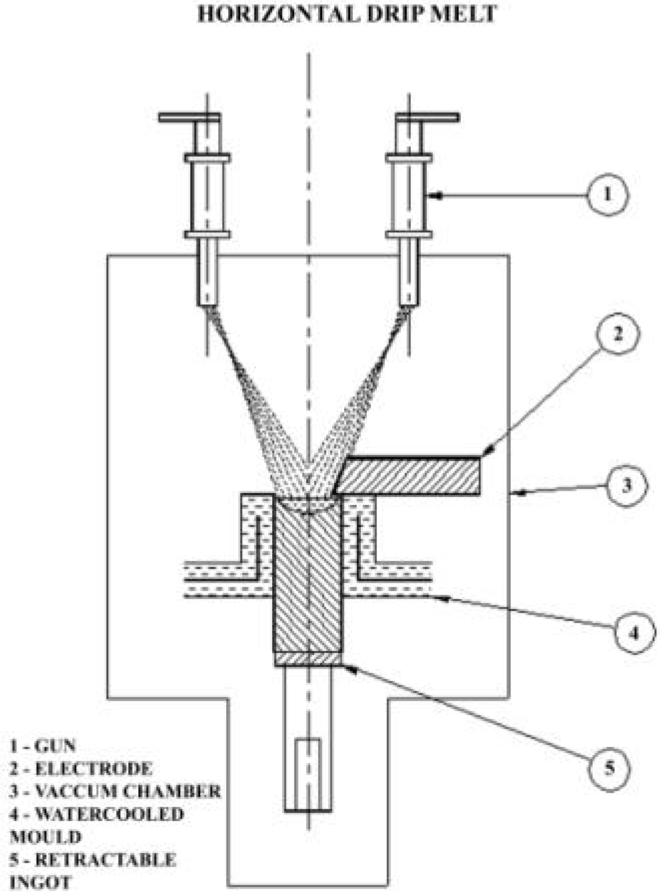

Figure 4: Diagram of CBMM first melting arrangement.

Usually two or three EB-melting steps are necessary in order to produce niobium ingots complying with ASTM-B391-96 [11] reactor-grade specifications.

Therefore, in the subsequent remelts, ingots produced in the previous steps are used as electrodes for vertical drip melt. Since the gas loads of these electrodes are considerably lower than those of the Nb-ATR bars, much higher melting rates are possible during the second and third melting operations. Figure 5 presents a sketch of the vertical melt arrangement.

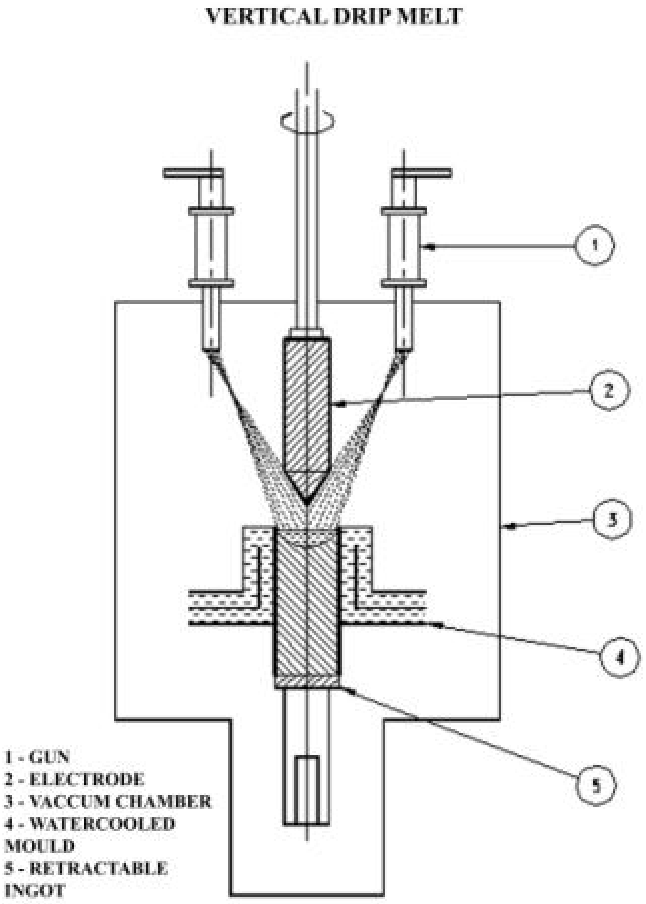

Figure 5: Vertical Drip Melt Configuration.

The operating data for 250mm (10 inch) diameter Nb-ingot production in a 500 kW EB melting furnace[2] are presented in Table I.

Table I 500 kW electron beam melting furnace – operating data

Melt	Feedstock	Dimensions (mm)	Melting rate (kg/hr)	Electron guns power (kW)	Chamber pressure (mbar)	Yield Average w/w (%)
1st	Nb-ATR bar	110 x 110 x 800	40-50	320-350	< 3 x10^{-3}	84
2nd	Nb-1st melt ingot	ϕ250 dia. X 1,600	60-65	390-420	< 3 x10^{-4}	97
3rd	Nb-2nd melt ingot	ϕ250 dia. X 1,600	65-70	420-440	< 5 x10^{-5}	98

Results

Since 1989, CBMM has been continuously producing pure niobium metal and niobium 1% zirconium ingots, complying with ASTM B 391 standards as per Table II.

Table II ASTM B-391-96 Standard Specification for niobium and niobium alloy ingots[11]

Chemical Requirements

Element	Type I (Reactor Grade Unalloyed Niobium) R04200	Type II (Commercial Grade Unalloyed Niobium) R04210	Type 3 (Reactor Grade Niobium – 1% Zirconium) R04251	Type 4 (Commercial Grade Niobium – 1% Zirconium) R04251
	Max Weight % (Except where otherwise specified)			
Each Ingot:				
Carbon	0.01	0.01	0.01	0.01
Nitrogen	0.01	0.01	0.01	0.01
Oxygen	0.015	0.025	0.015	0.025
Hydrogen	0.0015	0.0015	0.0015	0.0015
Zirconium	0.02	0.02	0.8 to1.2 (range)	0.8 to1.2 (range)
Tantalum	0.1	0.2	0.1	0.5
Iron	0.005	0.005	0.005	0.005
Silicon	0.005	0.005	0.005	0.005
Tungsten	0.03	0.05	0.03	0.05
Nickel	0.005	0.005	0.005	0.005
Molybdenum	0.010	0.02	0.02	0.02
Hafnium	0.02	0.02	0.02	0.02
When Specified:				
Boron	2 ppm	-----	2 ppm	-----
Aluminum	0.002	0.005	0.002	0.005
Beryllium	0.005	-----	0.005	-----
Chromium	0.002	-----	0.002	-----
Cobalt	0.002	-----	0.002	-----

Figures 6 to 11 present statistical data regarding chemical analyses and hardness results collected from 1994 to 2000 at the CBMM laboratory. During this time, more the 400 metric tons of niobium ingots have been produced and supplied for a wide variety of applications.

In the following charts the elements that are subject to variances are represented. Most of the others are systematically below the detection limits for the analysis equipment.

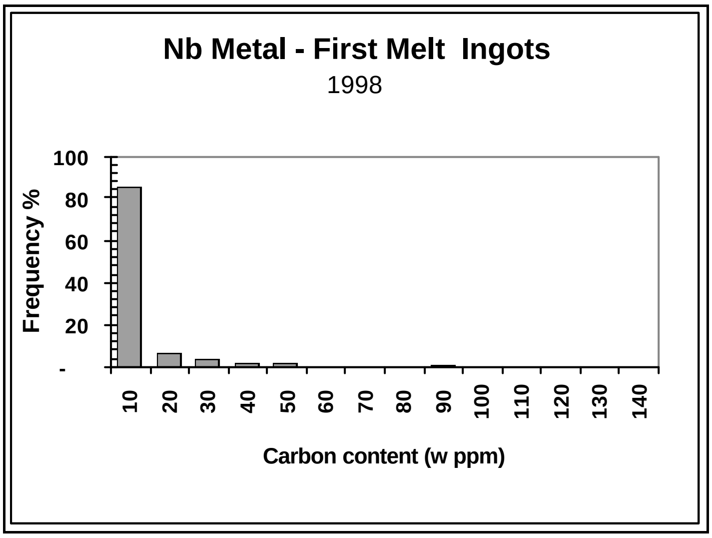

Figure 6: Carbon analysis. 1st melt Nb ingots, 1998.

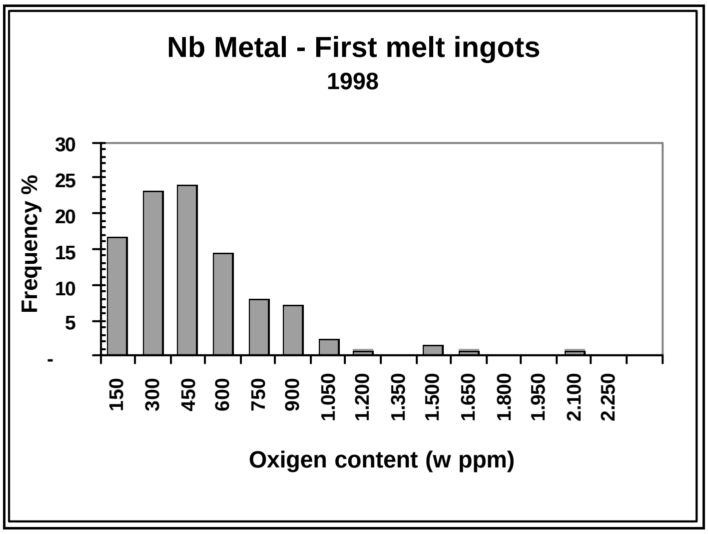

Figure 7: Oxygen analysis. 1st melt Nb ingots, 1998.

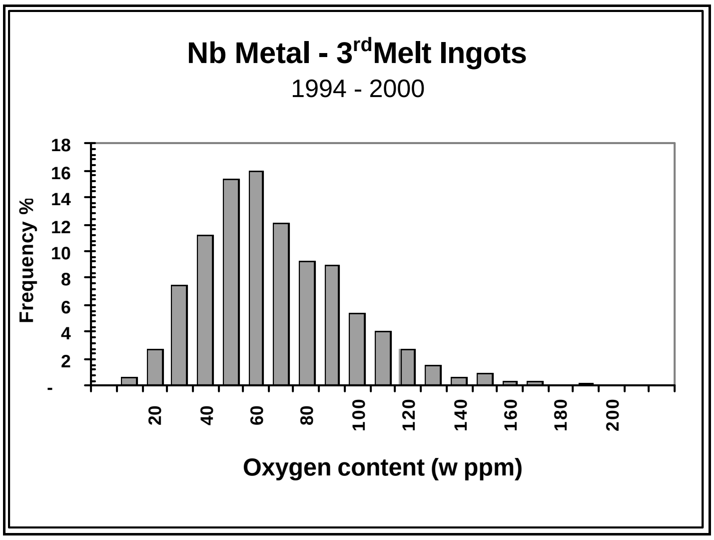

Figure 8: Oxygen analysis. 3rd melt Nb ingots, 1994-2000.

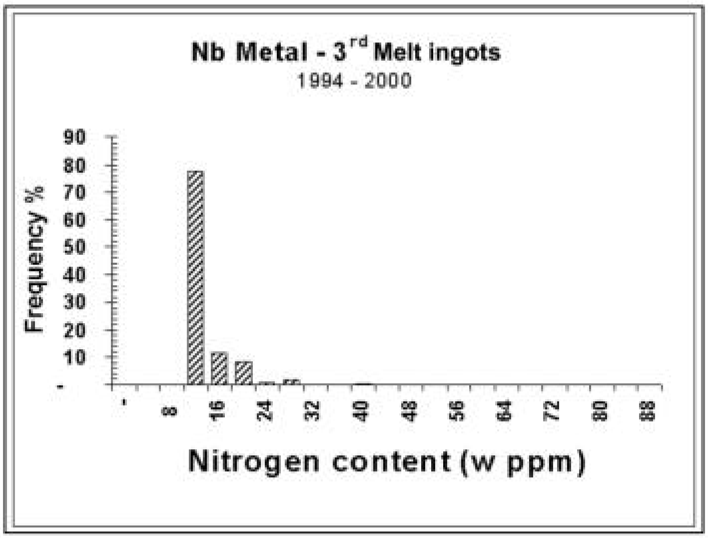

Figure 9: Nitrogen analysis. 3rd melt Nb ingots, 1994-2000.

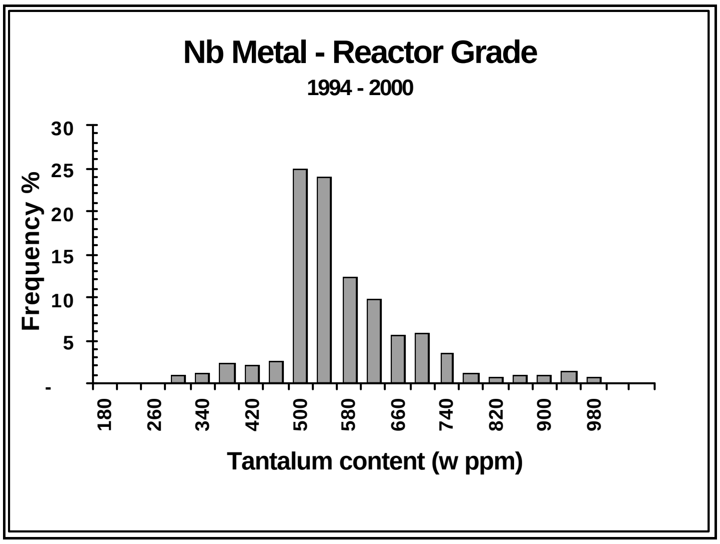

Figure 10: Tantalum analysis. Nb metal reactor grade ingots, 1994-2000.

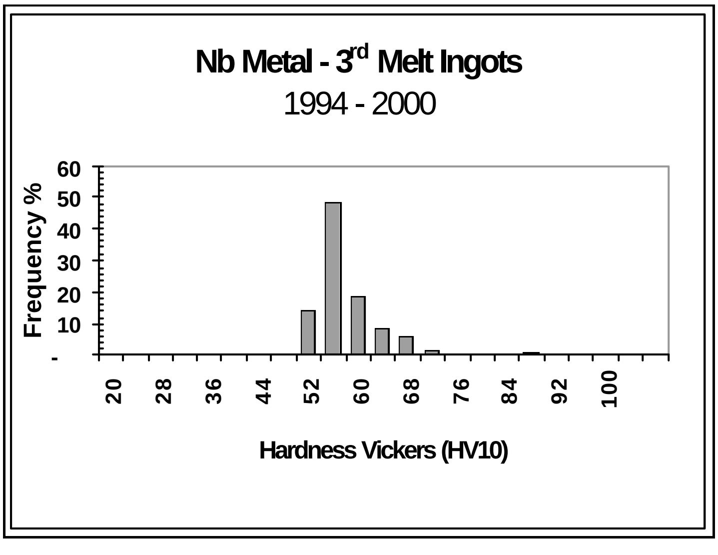

Figure 11: Hardness (HV10). 3rd melt Nb ingots, 1994-2000.

Inter-laboratory studies involving consumers and institutes worldwide have confirmed that the great majority of the interstitial elements present at CBMM´s niobium ingots are far below the ASTM B 391 standard.

Table III and Table IV show chemical analyses performed by Glow Discharge Mass Spectrometry (GDMS). Table III refers to samples taken from the same ingot after the first, second and third EB-melts. Represented in Table IV are the results of` two different third-melt ingots. As can be seen, except for gases – that were not analyzed at this time – and aluminum in the first melt ingot, all the other residuals were already complying with, or even well below, ASTM B 391-96 specification after just the first EB-melt.

Niobium metal produced by CBMM is present in almost all niobium end-uses, including super conducting cavities[9], MRI and NMR magnets.

Table III GDMS Analyses from the same ingot after first, second and third EB-Melting steps

CBMM Ingot nr.	**Melt**	(ppm wt)								
		B	**C**	**Na**	**Mg**	**Al**	**Si**	**P**	**K**	**Ca**
Nb-1018	**1st**	0.5	8	0.3	0.1	60	20	5	<0.1	0.2
	2nd	0.5	2	0.6	<0.1	1	6	5	<0.1	<0.1
	3rd	0.4	2	0.5	<0.1	3	5	2	<0.1	<0.1

CBMM Ingot nr.	**Melt**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ba**	**Sn**	**Pb**
Nb-1018	**1st**	<0.1	2	<0.1	0.2	0.5	<0.1	<0.1	<0.1	<0.1
	2nd	<0.1	0.1	<0.1	0.1	0.3	<0.1	<0.1	<0.1	<0.1
	3rd	<0.1	2	<0.1	0.1	0.6	<0.1	<0.1	<0.1	<0.1

CBMM Ingot nr.	**Melt**	**Ta** (%)	**W**	**Zr**	**Mo**	**Cr**	**Ti**	**Hf**		
Nb-1018	**1st**	0.084	0.9	10	0.5	0.1	3	0.1		
	2nd	0.070	0.6	0.3	0.5	<0.1	0,2	<0.1		
	3rd	0.071	2	0.3	0.6	0.2	<0.1	<0.1		

Table IV – GDMS Analyses for third-melt Nb ingots #10563/01 and #105730/01 (ppm wt)

Element	Ingot nr 1056301	Ingot nr. 1057301		Element	Ingot nr 1056301	Ingot nr. 1057301
Li	<0.001	<0.001		**Ag**	<0.05	<0.05
Be	<0.001	<0.001		**Cd**	<0.05	<0.05
B	0.02	0.02		**In**	<0.01	<0.01
F	<0.05	<0.05		**Sn**	<0.01	<0.01
Na	<0.01	<0.01		**Sb**	<0.01	<0.01
Mg	<0.01	<0.01		**Te**	<0.005	<0.005
Al	0.08	0.39		**I**	<0.005	<0.005
Si	0.21	0.47		**Cs**	<0.05	<0.05
P	0.31	0.45		**Ba**	<0.005	<0.005
S	<0.01	<0.01		**La**	<0.005	<0.005
Cl	0.02	0.03		**Ce**	<0.005	<0.005
K	<0.01	<0.01		**Pr**	<0.005	<0.005
Ca	<0.05	<0.05		**Nd**	<0.005	<0.005
Sc	<0.001	<0.001		**Sm**	<0.005	<0.005
Ti	<0.005	0.02		**Eu**	<0.005	<0.005
V	0.005	0.009		**Gd**	<0.005	<0.005
Cr	<0.001	<0.001		**Tb**	<0.005	<0.005
Mn	<0.005	<0.005		**Dy**	<0.005	<0.005
Fe	0.003	0.009		**Ho**	<0.005	<0.005
Co	<0.001	<0.001		**Er**	<0.005	<0.005
Ni	<0.001	<0.001		**Tm**	<0.005	<0.005
Cu	0.21	0.31		**Yb**	<0.005	<0.005
Zn	<0.01	<0.01		**Lu**	<0.005	<0.005
Ga	<0.01	<0.01		**Hf**	<0.01	<0.01
Ge	<0.01	<0.01		**Ta**	630	700
As	<0.01	<0.01		**W**	0.57	0.51
Se	<0.01	<0.01		**Re**	<0.01	<0.01
Br	<0.01	<0.01		**Os**	<0.01	<0.01
Rb	<0.001	<0.001		**Ir**	<0.01	<0.01
Sr	<0.001	<0.001		**Pt**	<0.01	<0.01
Y	<0.001	<0.001		**Au**	<0.05	<0.05
Zr	0.09	0.14		**Hg**	<0.05	<0.05
Nb	Matrix	Matrix		**Tl**	<0.01	<0.01
Mo	0.48	0.33		**Pb**	<0.01	<0.01
Ru	<0.001	<0.001		**Bi**	<0.005	<0.005
Rh	<0.001	<0.001		**Th**	<0.001	<0.001
Pd	<0.01	<0.01		**U**	<0.001	<0.001

Final Remarks

Niobium metal refined via EB-melting achieves the highest level of purity, exceeding most current commercial specifications. The great majority of metallic elements present in niobium raw materials are easily volatilized under the niobium EB-melting conditions. Few exceptions are those impurities presenting saturation vapor pressures lower than that of niobium, such as tantalum, tungsten and some carbon compounds. These cannot be removed by volatilization. Thus, if the raw material is properly selected, the EB processing is capable of producing niobium metal ingots with most residual impurities as low as few parts per million (ppm) or even within the parts per billion (ppb) range.

Regarding the purification of niobium metal, no other known process has been capable of surpassing the EB-melting process.

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