How to produce $Nb_{RRR\sim600}$ on an industrial scale

Friedhold Schoelz, W.C.HERAEUS GMBH&CO KG, MATERIALS TECHNOLOGY DIVISION, HERAEUSSTRASSE 12-14, 63450 HANAU, GERMANY

1. Introduction

To produce high purity Niobium (RRR ≥ 600) on an industrial scale, some points have to be considered. One of the factors that limits the RRR-values, in addition to the gas content, is the residual Ta content of the starting-material: the Ta content enriches during electron beam-melting and forms very stable carbides and nitrides, which makes the degassing process very difficult. Thus it is absolutely necessary to use a starting material with a low Ta content. Additionally it is possible to have a better degassing of the niobium by using appropriate changes during the melting process. On the other hand it is very importand to exclude all steps during processing, which return the gases or carbon to the material, e.g. welding etc. Also new getter-materials were tested during the last treatment like Ca. To control the very purity, it was necessary to create a special high precise referencematerial. This material was developed in cooperation with BAM Berlin and the working group for analytical chemistry of GdCh in Germany. Finally, it is also necessary to control the semifinished products like sheets or tubes before starting the expensive processing, to prevent failure of the finished cavities. That is the reason, why we have used Squids that are very sensitive and have a high resolution.

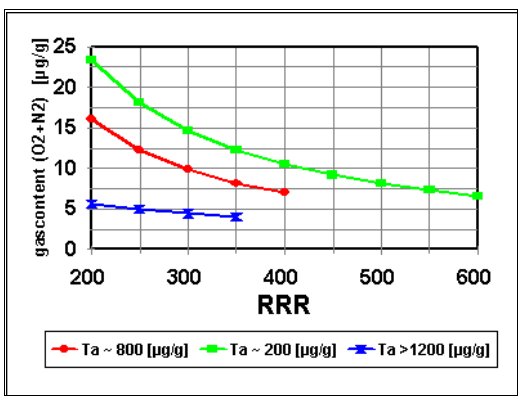
2. Correlation between RRR, the gas content and the Ta content

During the last year we made an extensive calculation based on 400 measured RRR samples and integrated them with a multiple regression over the Ta content and the gas content. We discovered that RRR values >400 could only be reached by a Ta-content lower than 200 [µg/g]. The best method to produce such a raw material on an industrial scale is the liquid-liquid-extraction with MIBK or MIPK as showen in the following description:

$NbCl_5$ + $TaCl_5$ + MIBK / MIPK + H_2O
Ta in the aqueous phase
Nb in the organic phase

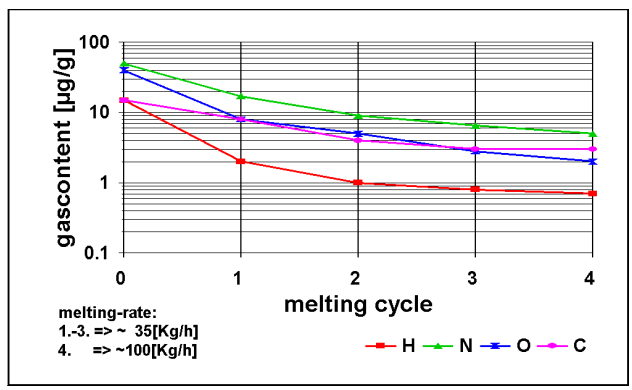
K_2NbOF_5 + K_2TaF_7 + MIBK / MIPK + H_2O
Ta in the organic phase
Nb in the aqueous phase

After a cascade of 20 extractions the Ta content is down to about 200 [µg/g]. The theoretical value after 36 extractions is < 20 [µg/g].
So we produced more than 2 [to] of Nb with a Ta content of 200 [µg/g] in the standard sheet process and reached a RRR value better than 450 at once.

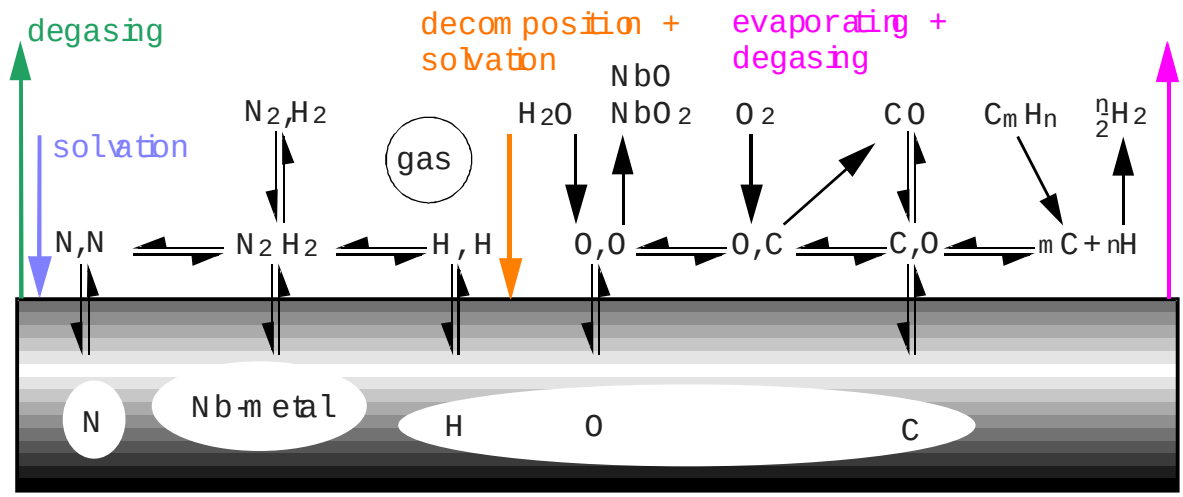


Correlation between RRR, gas, and Ta content

3. Degasing process during EB melting



The purification and degasing process during electron beam melting is very complex. All metals with a lower melting point than Nb will be evaporated. Metals with a higher melting point like Ta and W will be enriched in the melt, because Nb also evaporates as Nb-oxides during the melting process. All gases are continuously in exchange with the hot metal surface. Gases from the furnace atmosphere will at first be adsorped on the metal surface and then dissolved in the metal or they produce evaporable products. Dissolved gases in the metal will diffuse to the surface and produce molecular

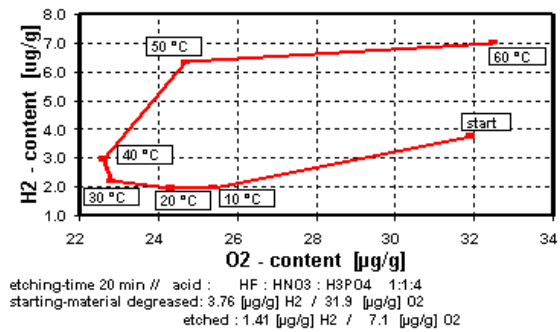


Equilibrium, steady-state, deoxidation, carburization and decarburization reactions between Nb metal and H_2, N_2, O_2, H_2O, CO, C_mH_n under vacuum at T > 2000 K

Both reactions are always in equilibrium. On the surface oxygen reacts with carbon to carbon monoxid and with niobium to Nb oxides, thus the degasing will be quicker than the degasing of nitrogen because nitrogen only produces molecular gas. Beside this the process from atomic nitrogen to a molecular gas is inhibited. Observing the gas contents after every melting process, one sees that the degasing of nitrogen will be the slowest, oxygen and carbon quicker and the quickest will be the degasing of hydrogen. This characteristic makes nitrogen a limiting factor in obtaining high purity Nb. The next source of trouble is represented by the return-flow of oil vapour from the vacuum pumps, because the carbon will be dissolved in the metal and produces stable carbides in it making the degasing of oxygen much more difficult. To optimize the degasing process, the surface of the melting bath must be as large as possible, because the most efficient degasing takes place in the falling drop of liquid metal with the highest surface to volume ratio. The improvement of the vacuum also leads to better degasing. This would be managed by better pumps, refrigerated baffles and getter materials like Zr or Ti. These precautions also should be taken during all annealing processes.

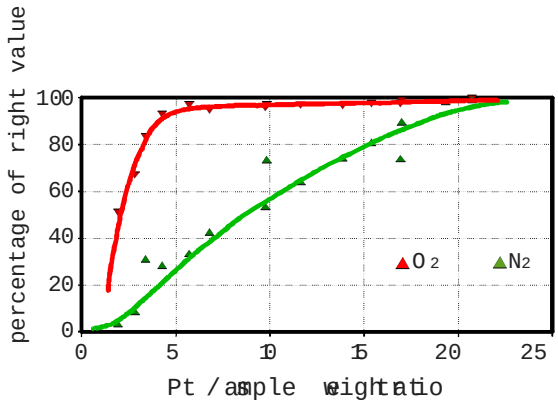
4. Qualification of analytical methods and equipment

To analyse very exactly a total gasc ontent of < 10 [µg/g] , you need a reference sample with certified contents of all elements and a procedure which leads to reproducible values. Also the analyzer must be able to detect such low contents. Therefore it was neccesary to exchange the standard flow- and pressure controller for a special high precision controller and to use highly sensitive IR-detectors. The reference sample was developed together with the BAM Berlin and the working goup for analytical chemistry in the GdCh by many round robin analyses. Also the analytical methods and the sample preparation were inspected. To get reproducible values, it is necessary to prepare every time the same sample size, because a different surface/volume ratio leads to inexact values.



Gas content of niobium with different etching temperatures

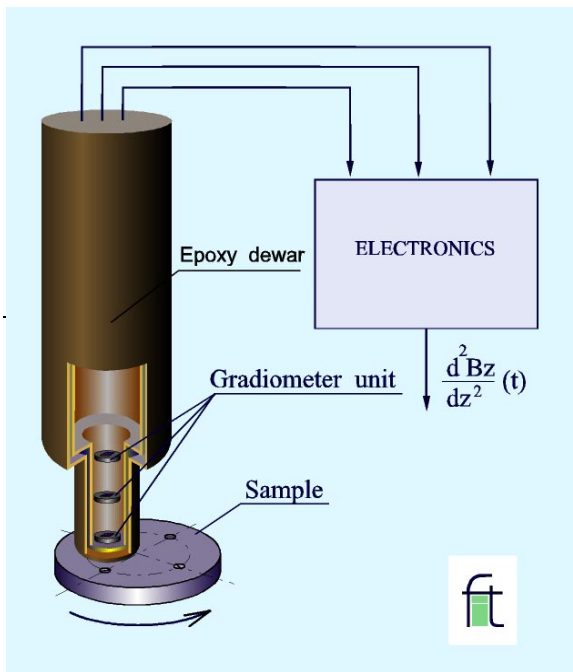
As it was recognized earlier, it is absolutely necessary to etch the samples without any temperature rise. Also a wet grinding or sawing with water cooling is forbidden. Otherwise an uncontrolled absorption of gas will occur. After etching, the samples should be stored for only a short time in a glass container, because the freshly etched surface is very reactive and will getter gases from the atmosphere very quickly.
To extract the gases quickly and completely during the analysis, the Nb samples must be melted together with an adequate amount of platinum in a graphite crusible at a temperature higher than 2400 °C. The ratio of sample weight to platinum weight must be possibly greater then 1:20 or the degasing will not be complete.



Carrier gas hot extraction of Nb with Pt flux

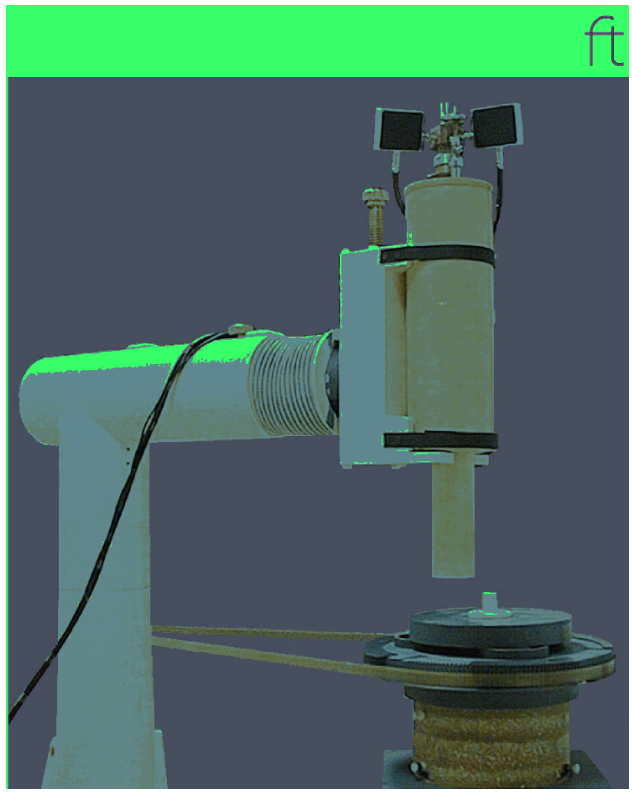
5. Test method for finished sheets and tubes

To control the semi finished products like sheets or tubes before starting the expensive processing various measuring methods are used. The most successful method seems to be a combination of eddy-current and a Squid-magnetometer. An other new method was also developed which uses the Squid-magnetometer to sense the weak thermoelectric current around the affected region of an inclusion or any other type of inhomogenity when the object was heated with hot air at the upper surface and cooled down at the backside.

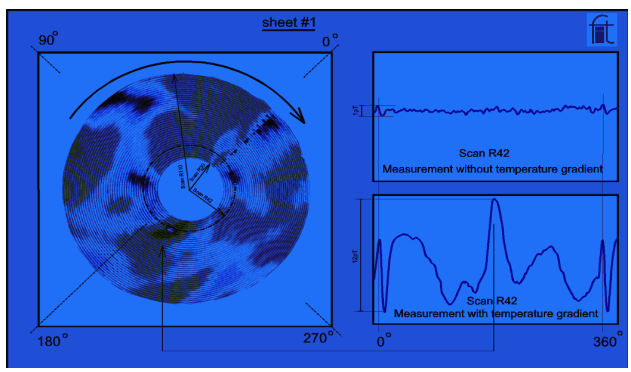


schematic view of a second-order SQUID gradiometer

To control sheets, it is very useful to place them on a nonmagnetic turntable and to scan the sheet with the Squid-magnetometer like a disc recorder.



Test equipment with turntable and SQUID-gradiometer



Example of a measured Nb-sheet with some inclusions. The measurement was made without and with a temperature gradient .