Purification of Selective Laser Melting Additive Manufactured Niobium for Superconducting RF-Applications Transactions on Applied Superconductivity

Fritz Motschmann, Romain Gerard, and Favre Gilles

***Abstract*—Superconducting radio frequency (SRF)–cavities in the field of particle accelerators are mostly manufactured from bulk or sheet niobium (Nb). Complex shapes of SRF-components like high order mode-couplers or cavities working at high fields are high in cost and lead-time. The fabrication of these parts via additive manufacturing promises a more effective production and higher flexibility in geometries. At CERN, additive manufacturing with pure Nb by selective laser melting (SLM) is under development for future particle accelerator components. In comparison with conventionally produced Nb SRF-components, made of highly pure Nb, the SLM-manufactured Nb material contains considerable impurities due to raw material processing and the SLM-process conditions itself. Contaminations with light elements, such as oxygen and nitrogen, introduced into the material's structure by the powder and the SLM process, contribute to an important lowering of the residual resistance ratio (RRR). In order to increase the RRR-values for conventionally manufactured SRF-cavities, titanium (Ti) gettering-heat treatments were investigated since the 1980s. This paper introduces the first representative Nb-material realized at CERN by additive manufacturing by SLM and the current studies on the post-treatment of sample material by vacuum firing and Ti-gettering-heat treatments. The samples are analyzed by mass spectroscopy and RRR-measurements in correlation with different process parameters. First trials with Ti-gettering heat treatments demonstrate an increase in the RRR from 7 to above 100, whereas the oxygen content could be reduced from 600 to 17 ppm. These results show that a purification post-treatment of SLM-manufactured Nb-components is feasible and pave the way for functioning SRF-components made by additive manufacturing.**

***Index Terms*—Heat treatment, impurities, laser fusion, niobium.**

I. Introduction

THE acceleration of particle beams with a high acceleration gradients often relies on superconducting-RF cavities in current machines, providing high quality factors during operation.

In almost all cases the superconducting material, or at least the superconducting functional layer, is made of high purity Nb.

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The authors are with the Mechanical and Materials Engineering Group, CERN, Geneva 1211, Switzerland (e-mail: fritz.motschmann@cern.ch).

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TABLE I
CHEMICAL ANALYSIS OF SLM-MANUFACTURED NIOBIUM

Element	Concentration (wt-ppm)			Test Method
	Powder	As build	Purified[d]	
C	39	39	18	IGA (C-IR[a])
N	99	150	<5	IGA (IG-TC[b])
O	510	590	17	IGA (IG-IR[a])
Ti	66	31	100	GDMS[c]
Al	120	90	90	GDMS[c]
Ta	35	30	30	GDMS[c]

[a]Analysis by infrared spectroscopy in combusting/inert gas atmosphere.
[b]Analysis by measurement of thermal conductivity in inert gas atmosphere.
[c]Glow Discharge Mass Spectrometry.
[d]First Ti-gettering test of Nb-RRR samples proposed in [11] and presented in [2] (RRR from 72-75)

Where currently applied SRF-cavities are mainly manufactured by sheet metal forming and machining, complex components or small cavities for high frequencies create an interest of using additive manufacturing technologies to realize parts of pure Nb. Components produced by electron beam melting show some encouraging results [1]. At CERN, SLM was applied to fabricate first samples and components.

SLM-manufactured Nb from CERN shows a residual closed porosity of down to 0.2% which allows to fabricate Ultra High Vacuum-leak tight components, such as for SRF cavities. An according leak tightness was measured to wall-thicknesses down to 0.5 mm [2].

Due to the raw material and the process conditions, SLM-processed Nb contains a large amount of impurities, mainly oxygen and nitrogen which are generally detrimental for the thermal conductivity of Nb at very low temperatures, which contributes to the SRF-performance of cavities [3].

During first tests of fabricating bulk Nb by selective laser melting at CERN [2] the purity of the processed material was tested by means of chemical analysis and RRR-measurements. In Table I the major impurities of the as built-material are listed. Apart from the light elements a high amount of aluminum was found in the powder. This pollution origins from the powder fabrication process, where the production chamber was polluted by previously processed Al-powder.

For the as built samples a RRR-value of 7.2 ± 0.2 was measured with no superconductive transition above the minimum test temperature of 6 K. Apart from the superconductive transition the maximum acceleration gradient that can be applied in a SRF-cavity increases with the thermal conductivity of the Nb-material, which is at low temperatures proportional to the RRR-value [3]. Current cavities, i.e., the SRF-Crab cavities manufactured at CERN, use Nb-raw material with an initial RRR of 300 in order to obtain the specified electric peak fields [4]. Nb with a purity grade providing a RRR above 120 were found to be usable for SRF-cavities with a good performance [12].

The high amount of light element impurities, particularly O, N and C, lead to the very low measured RRR-values [5]. It is important for the use of additive manufactured Nb-SRF-components to obtain a sufficient purification by removing the named light elements.

The only possibility to remove the intrinsic impurities from bulk material is by their diffusion to the outside. A common method is to outgas impurities in metals at high temperatures in vacuum furnaces. The efficiency of this process is determined by diffusion coefficients and the thermodynamic equilibrium of the chemical reaction of the impurity element with the base metal at a given temperature and partial pressure in the surrounding atmosphere. In order to purify Nb to low contents of oxygen, nitrogen and carbon in the range of a few ppm requires very high temperatures above 2000 °C and ultra-high vacuum with partial pressures below 10^{-8} mbar [7]. In order to limit the temperature and with that an excessive recrystallization, the approach of solid state gettering by using getter-elements like yttrium and Ti enable a significant purification of Nb for SRF-components [6]. The SLM-manufactured samples were treated with Ti as getter material as described in [8]. In [11] an "optimized heat treatment" was proposed to obtain best results by deposing quickly sufficiently Ti at 1300 °C for a short time and a subsequent long decrease in temperature down to 1000 °C in order to permit the diffusion of light elements to the Ti-layer and limit the diffusion of Ti into the bulk. This was conducted prior to this study with a set of three RRR-samples. Subsequent RRR-measurements and a chemical analysis of a representative sample were performed. The concentrations of the impurities shown in Table I for the "Purified" samples indicate the first achieved RRR-values between 72 and 75 after purification [2].

As the before mentioned RRR is still not in the range of pure Nb used for SRF-cavities and in order to obtain some more knowledge, a series of experimental solid state gettering heat-treatments were conducted and compared with theoretic models.

II. Experimental Procedure

A. Preparation of RRR-Samples and Ti-Gettering Treatment

The raw material used is Nb-powder fabricated by Electrode Induction Gas Atomization (EIGA) with a particle size ranging from 20 to 63 µm. To prevent the reactive Nb-powder from direct combustion with the environmental atmosphere, the particle surface is intentionally oxidized in order to passivate the material which results in an initial oxygen content of around 500 ppm. During the SLM-process the locally molten powder is protected by argon as shielding gas inside the machine chamber. Due to leakage and out-gassing of the powder, the residual oxygen content in the protective atmosphere is nevertheless around 1000 ppm at the start of a process.

To produce square rods with a dimension of 2 mm × 2 mm × 116 mm, a plate with a cross section of 116 mm × 2 mm was printed vertically which was cut afterwards in 2 mm wide stripes by wire cutting electric discharge machining (EDM). All tested samples have undergone a buffered chemical polishing process which removed around 100 µm of material.

For the heat treatment, a high vacuum-furnace with a hot zone composed of molybdenum, tungsten and alumina-insulators is used. The HV-pump is a conventional oil-diffusion pump with a cryo-baffle to inhibit back-diffusion of oil into the furnace's vacuum chamber. The ultimate vacuum of the used furnace goes below 10^{-7} mbar. Prior to any Ti-gettering process, the furnace and the used components for supporting the Nb-samples are baked out at around 1400 °C for at least 2 h. The samples are then each placed vertically into alumina tubes with a wrap of Ti grade 1-foil inside, covering at least the full length of the RRR-sample bar.

The heating cycle is then started after a pressure around 1×10^{-6} mbar is reached. The furnace is then heated with a ramp of 300 °C/h to the wished temperature following the dwells of 1000 and 2000 min. The heating cycles were repeated several times to increase the total treatment time. It was chosen, similar as performed by H. Safa *et al.* [8], to treat samples at 1000 °C, 1200 °C and 1300 °C for dwell times of 1000 min, 3000 min, 5000 min and 7000 min in total.

During the heat treatment the vapor pressure of Ti lays around 2×10^{-9} mbar at 1000 °C and 8×10^{-6} mbar at 1300 °C [9]. This leads, to a significant deposition of Ti on the sample surface which reacts with the light element impurities of the sample. Before performing the RRR-measurement, this deposition is again removed by BCP of 100 µm.

B. RRR-Measurements

At CERN the RRR-measurement is conducted in a liquid helium cryostat taking up to six samples with the above mentioned dimensions. Using a sample current of 5 A, the resistance is measured at room temperature and during cooling down below 20 K until the samples completely went through the superconductive transition, which is for pure Nb around 9.2 K. In the case of Nb, assuming a flat profile for the resistance below 10.2 K and the same sample dimensions, the RRR is calculated as:

$$RRR = \frac{R_{RT \approx 297\,K}}{R_{10.2\,K}} = \frac{\rho_{RT \approx 297\,K}}{\rho_{10.2\,K}} \tag{1}$$

C. Microscopic Investigation

Two representative sample bars treated at 1200 °C respectively 1300 °C with a dwell of 1000 min each were prepared by Focused Ion Beam (FIB) for a subsequent Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS). An up to 50 µm deep hole was milled by FIB in order to investigate the cross section of the superficial layer and the first few 10 µm of the Nb-bulk.

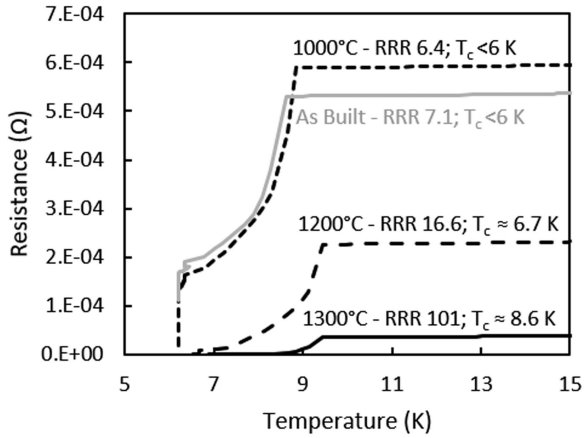

Fig. 1. Resistance of as built and purified Nb-samples at cryogenic temperatures. Purified samples were treated during 1000 min at the indicated temperatures. RRR-values and critical Temperatures (T_c) are indicated for each sample, where for "As Built" and 1000 °C no T_c could be measured.

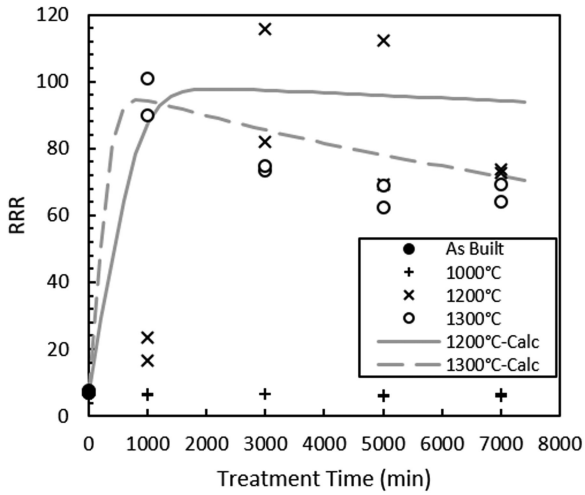

Fig. 2. RRR-values measured for different treatment-temperatures over the dwell time and from (2) calculated RRR-curves for 1200 and 1300 °C.

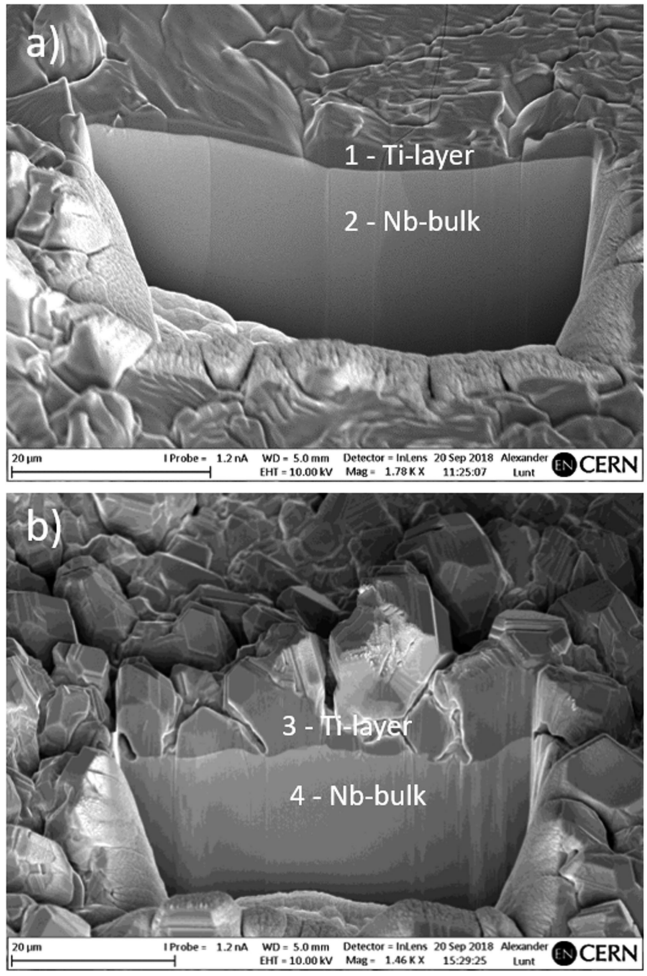

Fig. 3. SEM-images of FIB-milled cross sections of Ti-gettering treated Nb-samples: (a) 1200 °C for 1000 min; the superficial layer (Point 1) is up to 4 µm thick and is composed mainly of Ti, the bulk below contains maninly Nb (Point 2). (b) 1300 °C for 1000 min; the superficial layer (Point 3) is up to 12 µm thick, contains mainly Ti with a significant amount of Nb diffused from the bulk (Point 4).

III. Experimental Results

A. RRR-Measurements

As shown in Fig. 1 it can be seen that the resistance before the superconductive transition decreases for samples with a higher treatment temperature keeping the same dwell of 1000 min. The samples treated at 1000 °C show no improvement in electrical resistance at low temperature compared to the non-treated samples. With decreasing resistivity, the temperature at which the complete superconductive transition takes place increases. The samples with a low RRR show no transition above 6 K.

Increasing the dwell time at constant treatment temperature increases the diffusion of light element impurities towards the Ti deposited on the surface but at the same time the diffusion of Ti into the bulk Nb. At 1000 °C the dwell time has no influence on the RRR-value that remains at the initial value of 6-7 as shown in Fig. 2. This can be explained by a too low Ti-deposition on the the Nb-surface at this temperature. Treating the samples at temperatures above 1200 °C shows a significant purification and leads in this case to maximum RRR values slightly above 100, with decreasing values at 1300 °C after reaching the maximum RRR.

B. SEM and EDS-Analysis

The temperature difference between 1200 °C and 1300 °C causes a significant difference in the surface topology of the deposited Ti-layer as it can be seen in Fig. 3. EDS-measurements reveal that at 1200 °C the layer contains around 71 at.-% Ti, 4 at.-% Nb and the rest C, N, and mainly O with 19 at.-% that were gettered. In the bulk, a few µm below the surface, which is mainly Nb with 81 at.-%, the amount of diffused Ti is relatively low with just 1 at.-% measured. A still relatively high amount of C could be found there (13 at.-%). In the 1300 °C treated sample a fairly higher inter-diffusion between Nb and Ti could be observed in the layer and the bulk (see Fig. 4). This allows to investigate the diffusion properties of Ti in SLM-Nb. The big drop of Ti-concentration in the Nb-bulk at the interface could

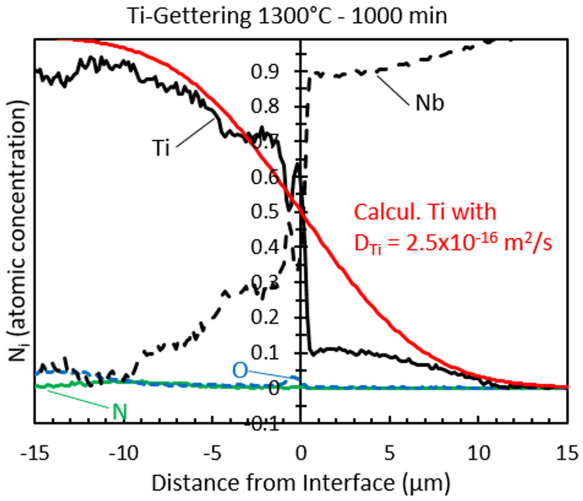

Fig. 4. EDS-line profile of the sample treated at 1300 °C for 1000 min as shown in Fig. 3(b). The origin of the x-axis is positioned at the interface between the Ti-layer and Nb-bulk, with positive x-values in the bulk. A theoretical diffusion profile of Ti into Nb was adjusted to a diffusion depth of roughly 10 µm using (3).

not be explained yet. The concentrations of C, N and O inside the Nb-bulk falls below 1 at.% which is in the range of the detection limit of the EDS. This sample (see Fig. 1) shows with 90 one of the higher RRR-values.

IV. Analytical Evaluation

In order to estimate the necessary treatment durations for parts of different wall thicknesses and impurities, as it will be the case for real components, the evolution of the electrical resistivity at cryogenic temperature (10.2 K in this case) is estimated with the following equation [8]:

$$\rho_{10.2\,K} = \sum_{i=Zr,Ta,Al,Si} \left(\frac{\partial\rho}{\partial c}\right)_i c_i + \rho_{Phonon}\,(10.2\,K) + \sum_{i=N,O,C} \left(\frac{\partial\rho}{\partial c}\right)_i c_0 e^{(-t/\tau_i)} + \left(\frac{\partial\rho}{\partial c}\right)_{Ti} c_{x=0,Ti}\left[1 - e^{(-t/\tau_{Ti})}\right] \quad (2)$$

where $(\partial\rho/\partial c)_i$ are the different specific resistivity contributions of the elemental impurities, c_i the initial concentrations for each impurity, ρ_{Phonon} the phonon contribution at temperatures $T \leq 25$ K and τ_i the different diffusion times as it is further described in [8], depending on the temperature, diffusion coefficients D_i and the sample size. For Ti, $c_{x=0,Ti}$ is taken as 1, assuming having pure Ti at the Ti-layer interface. Furthermore, the material shows a high amount of Al-contamination, whose resistivity contribution $\partial\rho/\partial c$ couldn't be obtained from literature. In this study a value for aluminum somewhere in between the ones for refractory metals like tantalum (0.25×10^{12} Ωm/ppm) and light elements like nitrogen (5.2×10^{12} Ωm/ppm) [7] was assumed with a value of around 3×10^{12} Ωm/ppm.

A diffusion rate for Ti in Nb, as observed for the diffusion of Ti into a Nb-single crystal [10], would not explain the concentration profile of Ti as shown in Fig. 4 for 1300 °C after 1000 min. Therefore, a theoretical diffusion profile was matched with the observed diffusion depth between 10–15 µm (see Fig. 4), by using the following solution of Fick's law taking a constant Ti-concentration at the interface and the bulk-material as a semi-infinite medium as boundary condition:

$$c_{Ti}\,(x,t) = c_{Ti}\,(x=0)\left[1 - erf\left(\frac{x}{2\sqrt{D_{Ti,\ 1573\ K}\cdot t}}\right)\right] \quad (3)$$

This gives with a value for the diffusion coefficient of Ti in Nb of roughly $D_{\mathrm{Ti,1573K}} = 20.5 \times 10^{-16}$ m^2/s an around 30-times higher value than calculated for the same temperature for intracrystalline diffusion in [10]. Calculating a theoretical evolution of RRR by using (1) and (2) for 1200 °C and 1300 °C, taking the higher diffusion coefficient for Ti into account, results in the curves shown in Fig. 2. For 1300 °C it matches with the observation that the RRR quickly reaches a maximum value after 1000 min, and starts decreasing with the dwell time as Ti diffuses into the bulk contributing to an increasing resistivity. At 1200 °C the measured RRR-values after 1000 min are much lower than the calculated ones, as (2) assumes always enough Ti at the interface to getter impurities. In reality, at lower temperatures, the Ti-deposition takes a considerable time and has a significant influence on the purification process.

V. Conclusion

Using the solid state Ti-gettering process for purifying Nb processed by SLM for Additive Manufacturing is proven to be effective for increasing the RRR significantly, and opens the door for using SLM for SRF-components. The RRR can be increased to a value at which the light element impurities nearly don't contribute to the resistivity, in this case up to more than 100. Heavier impurities, in the studied case mainly aluminum due to a contamination problem, might still remain in the Nb-bulk, limiting the maximum value. These impurities can be decreased by improving the powder manufacturing process.

All measurements were done with samples with the same size whereas real parts will have bigger dimensions, which affects the efficiency of the purification process. Taking an analytical model, as presented in [8], matches sufficiently the measured values in the present study considering a remarkably higher diffusion rate for Ti in Nb. This helps to optimize treatment temperatures and times for varying part dimensions in the future. First Ti-gettering treatments, i.e., on manufactured Quadrupole Resonator-samples (QPR), will give more precise properties of the material for superconducting radiofrequency.

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