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SOFT CHEMICAL POLISHING AND SURFACE ANALYSIS OF NIOBIUM SAMPLES*

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Abstract

The Superconducting Darmstadt Linear Accelerator S-DALINAC uses twelve Niobium Cavities with a RRR of 280-300 which are operated at 2 K. The operating frequency is 3 GHz; the design value of the accelerating gradient is 5 MV/m. To achieve the target value of $3 \cdot 10^9$ for the unloaded quality factor Q_0, different surface preparation methods were applied and systematically tested using a vertical 2 K cryostat. A well-established technique is the so called Darmstadt Soft Chemical Polishing, which consists of an ultrasonic cleaning of the cavity with ultrapure water (UPW) followed by oxidizing the inner surface with nitric acid (65% HNO_3). After rinsing with UPW again, the niobium oxide layer is removed with hydrofluoric acid (40% HF) in a separate second step. Finally, the structure is rinsed with UPW and then dried by a nitrogen flow. Until now each cavity in operation was chemically treated with a proven record of success. In order to understand and to optimize the process on the niobium surface, systematic tests with samples were performed. The samples were analyzed using material science techniques like Scanning Electron Microscopy (SEM), Secondary Ion Mass Spectrometry (SIMS) and Energy Dispersive X-ray Spectroscopy (EDX). This paper will report on the results of our research and we will give a review on our experiences with varied chemical procedures.

INTRODUCTION

The material of choice for the fabrication of superconducting radio frequency (SRF) cavities is Niobium. The highest critical transition temperature ($T_C = 9.2$ K) of pure metals and the sufficiently high critical magnetic field ($H_C > 1600$ A/cm^2) as well as the metallurgical properties make it convenient for SRF applications [1]. Since the superconductivity of Niobium is a nanoscale, near-surface phenomenon [2], the surface condition is a critical factor in determining the performance of a SRF cavity. A great deal of publications show that post-fabrication treatments and the final surface conditioning treatments are essential for a high electric field gradient with high Q_0 value. After finishing production every cavity needs to undergo at first a removal of ~100 µm of material from the inner surface for disposing the so called damage layer, a surface layer which is contaminated with impurities and whose crystal structures are destroyed by rolling, welding and deep-drawing of the niobium sheets [3]. This removal can be done by different treatments. The most common ones are buffered chemical polishing (BCP) and electrical polishing (EP) [4], both using hazardous acids for material removal. But also acid free procedures like centrifugal barrel polishing (CFB) [5] or laser polishing [6] can be applied. The goal of every procedure is achieving a mirror-like inner surface of the cavity without any impurities. Nevertheless, there is no standard procedure which can be used for each cavity regardless of type, size or operating frequency. So every kind of treatment has to be adapted very carefully to a specific accelerating structure to achieve an improvement. Furthermore, when there are treatment steps applied at maintenance of cavities and not directly after production a much lower removal of material is needed. One of such methods is the Darmstadt soft chemical polishing procedure described here.

At the Superconducting Darmstadt Linear Accelerator S-DALINAC [7,8] twelve 3 GHz Niobium cavities are in use (see Fig. 1). The first production series from commissioning in 1991 was made of niobium with a ratio of residual resistance between 293 K and 4 K (RRR) of 100 and suffered from thermal breakdown due to a low thermal conductivity [9]. A second series was made of RRR = 280 niobium [10]. Recently three more cavities from RRR = 300 niobium were produced [11]. After 25 years of operation in total, the design quality factor has still not been reached, so lowering the residual losses of the cavities is still an ongoing activity. After investigating and optimizing the heat treatment of the structures [12], we decided to look closer into the chemical procedure we use at Darmstadt. This paper describes the Darmstadt Soft Chemical Polishing, its analysis and the results obtained by varying different parameters of the chemical process.

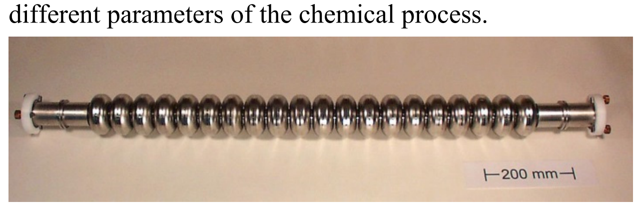

Figure 1: 3 GHz 20-cell Niobium cavity.

SOFT CHEMICAL POLISHING

Procedures like BCP or EP behave strongly exothermic and have a high wastage rate. The proportions of our cavities do not allow too much abrasion due to the change of the resonant frequency. So usually after initial BCP for removing the damage layer at the cavity vendor this treatment is not pursued anymore at Darmstadt [11]. Moreover, there is no infrastructure at Darmstadt for these procedures. Nevertheless, to achieve a clean superconducting surface, a special chemical process was established as a final treatment [13], which also can be applied, when necessary, after

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cavity maintenance e.g. after retreatment due to cold leaks [14] or testing optimized heating procedures [12] in the past. The soft chemical treatment is very similar to the HF rinse procedure used at several labs as final step for 1.3 GHz TESLA shape cavities [15,16] and has been used successfully for decades on the 3 GHz resonators at Darmstadt by now. The idea was to separate the acids to make the chemical reaction controllable instead of using an acid mixture. In a first step, after an ultrasonic cleaning with ultrapure water (UPW), the inner surface is oxidized by a treatment with nitric acid (HNO_3) and rinsed again with UPW. This ensures at least a monolayer of niobium oxide on the surface. The second step removes the oxide layer by a treatment with hydrofluoric acid (HF) followed by a final rinse with UPW. The remaining niobium surface is dried afterwards by a flow of hot filtered nitrogen in the clean room. This treatment is done only once which ensures an abrasion of at most a few nanometers which is similar to one single step of a HF rinse. The chemistry steps involved in the Darmstadt procedure is the following [17,18]:

$$6Nb + 10HNO_3 \rightarrow 3Nb_2O_5 + 10NO + 5H_2O$$

$$Nb_2O_5 + 6HF \rightarrow H_2NbOF_5 + NbO_2F \cdot 0.5H_2O + 1.5H_2O$$

$$NbO_2F \cdot 0.5H_2O + 4HF \rightarrow H_2NbOF_5 + 1.5H_2O$$

Sample Treatment

For the surface investigations bulk niobium samples were ordered from our cavity vendor. These samples were cut from the same type of niobium sheet our newest cavities are made of. The size is 5mm x 5mm x 2.8mm; the grade is RRR 300. The samples have been treated with a BCP by the vendor for removing the damage layer from rolling the sheets. Afterwards they have been rinsed with UPW and packed within clean room conditions. So the surface treatment of the sample was equal like the treatment of the S-DALINAC cavities before 800C bake [11]. For all kind of subsequent chemical treatments at Darmstadt, the samples were handled manually. We had to be extremely cautious due to the perilousness of the acids used, first of all hydrofluoric acid which is potentially lethal.

Experiments

For the investigation of the Darmstadt Soft Chemical Polishing, three different analysis methods were chosen: surface topography and elemental analysis and depth profiling. The available instruments are: A Philips XL 30 FEG High Resolution Scanning Electron Microscope for the surface topography analysis with Energy Dispersive X-ray Spectroscopy for elemental analysis and a Cameca ims 5F Secondary Ion Mass Spectrometer with mass separation via sector fields for elemental depth profiling. To get some reference data and for comparisons, an untreated sample was analyzed with these three technologies, too (Fig. 2).

Darmstadt Standard Procedure

Two samples were prepared according to the standard Darmstadt Soft Chemical Polishing procedure, which consists of the following steps:

- Ultrasonic cleaning with UPW, 1 hour, 60° C
- Oxidation with HNO_3 (65%), 30 minutes
- Rinsing with UPW, 15 minutes
- Removal of the layer with HF (40%), 6 minutes
- Rinsing with UPW, 15 minutes
- Drying in wet bench

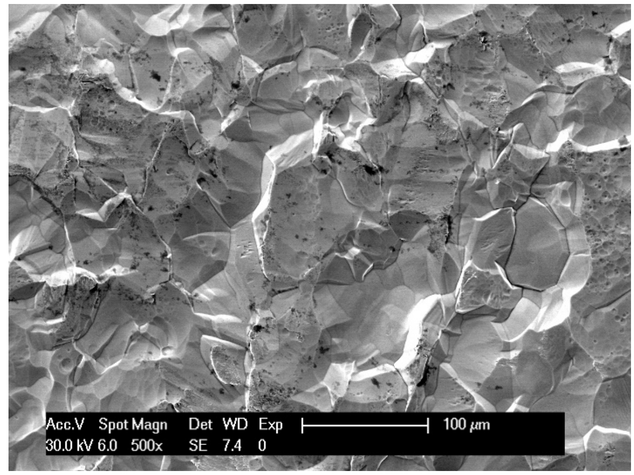

Figure 2: SEM image of an untreated Niobium sample.

After analyzing the two samples, the results were compared with the reference data of the untreated one. The surface topography, visible on the SEM images, showed no

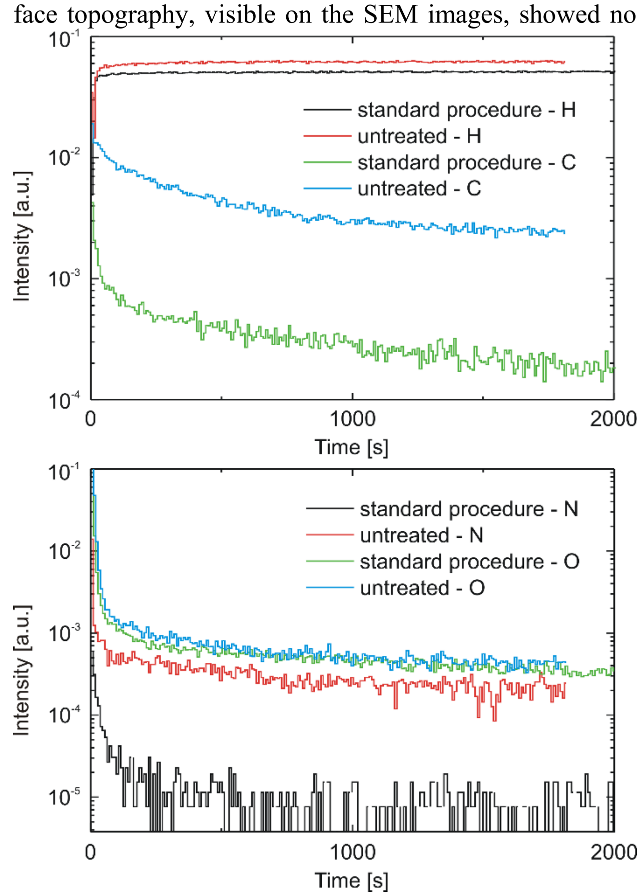

Figure 3: SIMS depth profiles for the elements H, C, N, and O for standard-processed and for untreated samples.

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observable modification. The SIMS measurement was performed concerning the most relevant elements H, C, N, O, and Nb. The data were normalized to the intensity of Nb to make different measurements comparable. The SIMS scans show modifications for carbon and nitrogen but no significant changes in the depth profiles of hydrogen and oxygen (see Fig. 3).

Varying the Parameters

For quantifying the impact of the exposure time to nitric acid, we changed the residence times, so the series provided the following variations to the standard procedure described above:

- No HNO_3 / 6 min HF
- 3 min HNO_3 / 6min HF
- 60 min HNO_3 / 6 min HF
- 24 h HNO_3 / 6 min HF

The analysis was done directly after the HNO_3 treatment and finally after the removal step with the hydrofluoric acid. We expected a little smoothing of the surface tips but the SEM images showed no visible revision. The SIMS data present differences concerning some particular elements (see Fig. 4). The EDX spectra are superimposable, both after building the oxide layer and after removing it (see Fig.5). The expectation was at least a different concentration of oxygen in the virgin sample, the oxidized sample and the one with the removed oxide layer

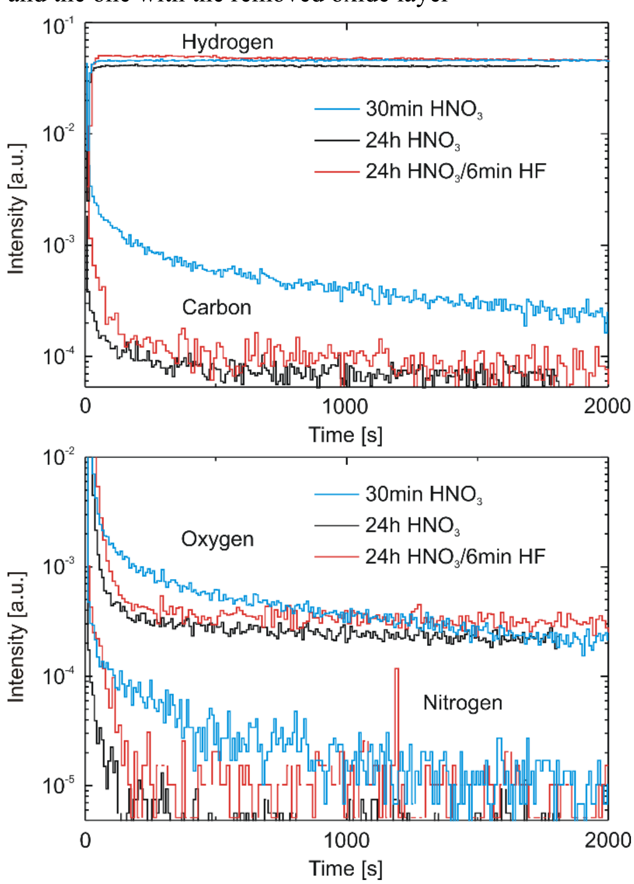

Figure 4: SIMS depth profiles for varied residence times of the nitric acid.

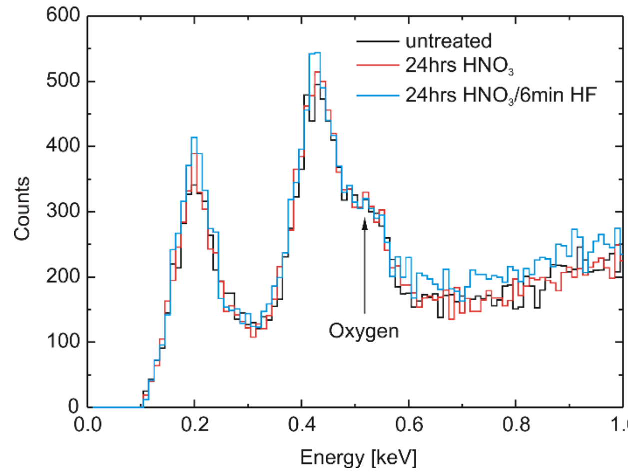

Figure 5: Comparison of the low-energy EDX spectra of three different niobium samples.

CONCLUSION

We analyzed the Darmstadt Soft Chemical Polishing in its standard version and also with varied residence times of the nitric acid. A polishing effect is not visible, the surface-topography is kept and there is no smoothing of the tips. The hydrofluoric acid removes the oxide layer and also adhesive impurities on the layer. So the treatment ensures at least a clean surface after the treatment, which is the goal of this application. The oxide layer itself is native. We assume that the nitric acid treatment is not necessary because the oxide layer is already formed during the contact with water or ambient air. The oxide passivates the surface against a further nitric acid attack, so an epitaxial growth of the layer is not possible, as one can see in the SIMS data. The next step of our investigation will be an increase of the number of the acid treatment steps with UPW rinsing steps in between similar to a HF rinse procedure [15,16]. In addition, the surface roughness, which is in the range of about 15 µm (peak to peak), does not affect the cavity performance negatively at the low accelerating gradients used [19,20]. Nevertheless, it is not beneficial for the SIMS measurements, and for systematic research on chemistry effects with very low material removal of a few nm, so for the next experimental runs on samples we will use mechanically polished samples as well as samples treated with an EP. For the accelerating cavities of the S-DALINAC no further EP step is foreseen by now.

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