High resolution hydrogen profiling in superconducting materials by ion beam analysis (ERD-EXB)

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† Soumis à : Vacuum
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1. Introduction

Given its importance for the construction of future large particle accelerators, the technology of superconducting r.f. cavities has received recently a sustained Research and Development effort. An important subtopic pertaining to this activity deals with the cavity surface. The quality of r.f. superconducting cavities is closely related to the purity of the cavity surface whatever the manufacturing process involved.

In the case of niobium cavities made from millimeter thick sheets, elaborate methods to purify niobium have been developed, leading to an increased thermal conductivity and enhanced cavity stability. However several laboratories have recently observed a degradation of the superconducting properties related to the conditions of the cooling process. This effect seems to stem partly from hydrogen contamination which occurs during surface treatment. The only solution adopted so far to overcome this loss of r.f. superconducting properties is a high temperature annealing (up to 1000 K) in a UHV furnace.

Another possible cavity manufacturing procedure is to deposit a thin superconducting film into a cavity made of a material with high thermal conductivity such as copper. The magnetron sputtering deposition technique was first applied at CERN to make the 350 MHz Nb/Cu cavities of the Large Electron Positron Collider. This technique is now extended to reactive sputtering deposition of niobium compound films such as NbTiN because of their higher critical temperature. The superconducting properties of the deposited films are shown to be affected by parameters such as grain size, grain boundary, and impurity content most importantly by oxygen and hydrogen which are shown often to occur together.

This paper reports on high resolution hydrogen profiling of superconducting materials by ion beam analysis and the correlation between H and O impurities in the different steps of the preparation. In the first part we will present the experimental procedure. The second part will be devoted to H and O contamination analysis in mm thick niobium sheets used for
manufacturing cavities. In the third part we will present the contaminant control results for each of the successive steps in the deposition procedure.

2. Experiment

The experimental uses alpha beams delivered by the 4 MV Van de Graaff accelerator of the Institute of Nuclear Physics in Lyon. The samples to be analyzed are positioned in a vacuum chamber (10^{-7} Torr cryopumping) equipped with liquid nitrogen cooled traps.

The main part of the present analysis concerns the hydrogen profiling for which a device of high resolution has been designed. However, as the hydrogen and oxygen contaminants frequently go together, we give some details on the oxygen profiling as well.

2.1 Hydrogen profiling. The elastic recoil detection (ERD) technique suggested by L'Ecuyer et al.\textsuperscript{9} is now a technique of choice for determining the depth distribution of hydrogen isotopes in the first several hundred nanometers of a surface. The energy distribution of light impurities recoiled from a target is analyzed by a surface barrier detector placed after a filter foil. The filter foil thickness is chosen in order to stop the elastically scattered beam particles. As energy straggling in the filter foil worsens the depth resolution, various methods\textsuperscript{10,11} have been suggested to avoid this problem. In this paper we present H depth profiling using an EXB filter with 2.5 MeV alpha incident beam. This general method has been first proposed by G. Ross et al.\textsuperscript{12} in order to profile H and He isotopes in light materials (Z < 20) using elastic recoil induced by 350 keV incident alpha particles. We adopted this technique to the analysis performed by 2.5 MeV incident alpha particle beam, the aim being to increase the depth probe and to extend the analysis to heavy targets up to Z = 41. The experimental device is shown on Figure 1. The optimization of the detection geometry\textsuperscript{13,14} corresponds to a detection angle of 30° and an alpha beam incident at an angle of 75° with respect to the normal to the target surface. The length of the EXB filter is 115 mm.
A 0.37 x 4 mm² collimator is placed at the entrance of the EXB filter which is located at a distance of 150 mm from the target. Therefore the detection solid angle is 6.6 \times 10^{-5} \text{ steradian}. Such a narrow collimator is needed in order to select only particles with velocities parallel to the detection direction. The EXB filter is employed in an achromatic mass and charge selector mode. By varying the E/B ratio, this filter selects a given ion while keeping the ion deflection almost energy independent. In our system the B field is created by a permanent magnet. The mean field is 2.9 kG with variations within the cell of less than 5%. The E field can be varied from 0 to 25 kV cm⁻¹ but proton achromatism is reached around 15 kV cm⁻¹.

An example of the energy independent ion deflection is given in Figure 2. This figure shows the results of trajectory simulation, assuming that the velocity of the scattered particles is parallel to the detection direction and that the electric field is equal to 15 kV cm⁻¹. One can observe that the proton recoil energy from 500 keV to 1.2 MeV is focused on a deflexion length less than 3 mm and is clearly separated from the He⁺ and He⁺⁺ ions. In our energy range, the hydrogen recoils as a H⁺ ion with the contribution of neutral atoms negligible.

However, as we are analysing heavy targets (Z = 41) we are confronted with a background observed in the H spectra. Because, alpha scattering cross section on niobium is very large, the number of alpha particles with a velocity component perpendicular to the detection direction is not negligible. These ions scatter on the high voltage plates, giving rise to a continuous background increasing at low energy. We used beryllium plates in order to minimize this effect, but we did not succeed in completely avoiding this problem. This effect starts to be important for samples of atomic number larger than 25. An example of H distribution measured on a niobium sample is given on Figure 3. The H profile is obtained after background subtraction. The background was fit to a polynomial expression which includes both the low energy background contribution and the sparse counts observed at high energy. This effect limits the depth probed and the sensitivity obtained.
In case of hydrogen analysis in Nb samples the depth probe was restricted to 200 nm with a surface depth resolution of 17 nm and a sensitivity limit of 0.5% atomic concentration. (Hereafter denoted as at %.) Hydrogen profiles were obtained by reconstruction of the experimental spectra based on a calibration with a muscovite foil. Such simulations take into account the non-Rutherford cross section, data of which are given in ref. 16.

2.2 Oxygen profiling. Oxygen profiling has been performed by 7.5 MeV alpha backscattering ($\theta = 172°$) spectroscopy. An advantage of high energy alpha backscattering analysis of materials is that the nuclear elastic scattering cross section for alpha particles on low Z elements is sometimes orders of magnitude larger than the Rutherford cross section. A previous study$^{17}$ of the $^{16}\text{O}(\alpha,\alpha)$ excitation, demonstrated that oxygen sensitivity could be optimized by using 7.5 MeV alpha incident particles. The reason for this is a high cross section plateau of 750 mb/sr (140 times the Rutherford cross section) in the 7.3 - 7.5 MeV energy range. In case of oxygen profiling in niobium this plateau corresponds to a maximum analyzed depth of 0.9 µm, a sensitivity limit equal to 0.4 at %, and a surface depth resolution about 18 nm. An example of alpha backscattered spectrum obtained at 7.5 MeV in case of niobium film analysis is given in Figure 4. Oxygen at the film's surface, in bulk of the film, and at the interface between the Nb and the copper substrate is observed. Oxygen profiles are deduced from simulations of the experimental spectra in which the only free parameters are the elementary atomic concentrations corresponding to sample depths bins.

3. Characterization of Nb used in r.f. superconducting cavities

An important surface segregation of hydrogen contamination has been observed in the last years.$^6,^{18}$ This contamination has been related to the degradation of performance of Nb superconducting r.f. cavities. Therefore special attention has been paid to select the primary Nb sheets and to optimize the etching procedures. In fact the Nb sheets have a high purity
of 99.99% with hydrogen impurities less than 1 wppm. However, this estimation of hydrogen content is based on a thermal method and assumes uniform distribution over the depth of a few millimeters. Because of surface contaminant segregation a study of hydrogen profiling has been undertaken. At first, we have investigated samples obtained from various manufacturers that have only been surface degreased with HCl (N) solution. Two extreme cases are shown on Figure 5. In the case of sample 1, one sees a high surface hydrogen contamination (> 16 at %) which decreases over the depth probe. In contrast, the hydrogen contamination of sample 2 is less than 10 at % at the surface and the inner contamination is around 2 at %.

We used for the rest in the present work only sheets of the same origin as sample 2 to study the influence of the chemical treatments. The results are given in Table 1 for both hydrogen and oxygen contaminants. Two components are observed in the case of hydrogen contamination. Notice the surface component covering the first 17 nm corresponding to surface depth resolution and the intensity of which depends on etching time. Over this depth range, oxygen follows the same behaviour. A detailed study of Nb-Nb₂O₅ interface performed by Halbritter¹⁹ indicated a heavily strained transition zone between Nb and Nb₂O₅ oxide coating. In this disturbed zone hydrogen can be trapped either by the solution of oxygen in Nb or by the defects, as suggested by several experimental and theoretical approaches²⁰,²¹,²²,²³. The second component displays a small and constant hydrogen contamination which is observed up to 200 nm, i.e. the depth we could reach in the present experiment.

The analysis of experimental data shows that a careful choice of Nb sheets followed by an etching procedure leads to consistent results. Our earlier investigation¹⁸ of UHV annealed Nb gave a hydrogen surface contamination of about 1 at %. The small difference in hydrogen contamination between chemically and thermally treated Nb, cannot entirely account for the better performance observed in case of annealed Nb r.f. cavities. It was shown that the grain size of the superconducting material²⁴,²² plays an important role in determining the
r.f. superconducting material properties. The annealing procedure not only decreases the hydrogen content but at the same time increases the grain size, both effects improving the r.f. cavity performance.

4. Analysis of Nb superconducting film

The film growth procedure based on a magnetron sputtering system has been presented in detail in ref. 7,8. The quality of r.f. superconducting cavity performance is related to the structure and impurity content of the cavity's surface film, and also to good adhesion of the Nb coating to the copper substrate. At this stage of the work, the copper substrate has been electropolished yielding a good adhesion of the coating. After electropolishing, hydrogen profiling in the copper substrate indicated a quite large contamination in the surface region (8 at % in the first 17 nm) and a hydrogen contamination of around 1 at % is observed in the first 200 nm of the copper substrate. Such contamination can be partly removed during the baking of the copper cavity (24 h at 150°C) which takes place prior to deposition. As Nb is a strongly reactive element, it behaves as a getter, and light elements of the residual vacuum can be incorporated within the film, specially at the beginning of the deposition process. Figure 6 shows the evolution of the hydrogen contaminant profiles for three values of the Nb layer thickness. As for the bulk Nb sheet analyzed previously, H appears to be concentrated near the surface, possibly incorporated where the samples were brought to atmosphere. There is also an inner H contamination in each analyzed sample. However, a decrease of the whole H contamination is observed with increasing film thickness. Similar behaviour is observed in case of oxygen contamination. These results show that in case of the Nb a major part of contaminants are trapped in the first deposited micrometer. This potentially disturbing zone is "buried" in the deposit and r.f. propagation which is restricted to the first hundred nm of the surface is not influenced. Thus our results suggest an explanation of the better
performances observed with Nb cavity coating larger than a few μm.

5. Conclusions

Over the years an important effort has been dedicated to the improvement of r.f. superconducting cavities. Accordingly the methods of analysis have been improved aiming to a better depth resolution and sensitivity, which allows selection of the most suitable fabrication procedures. In a first stage of method development an electromagnetic field EXB has been used for hydrogen profiling using ERD induced by 2.5 MeV α-particles. A better discrimination has been obtained between the surface and the first few hundred nm which are involved in r.f. wave propagation. In a future development we intend to adapt a similar device to ERD induced by 0.5 MeV/amu heavy ions.
References

1 Superconducting Applications of Niobium, J of the Less-Common Metal, 139, No 1 (1987), edit O N Carlson.


Figures Captions

Figure 1: Schematic diagram of the ERD-EXB method showing the interaction geometry, the EXB filter, collimator positioning and the detector.

Figure 2: Proton and helium trajectories over the length (115 mm) of the E x B filter in the conditions (E = 15 kV cm⁻¹, B = 2.9 kG). Alpha particles energies from 100 keV up to 2500 keV are represented, while in case of hydrogen recoils the energy range is from 30 keV to 1200 keV.

Figure 3: H distribution (dots) measured on a niobium sample which has not yet been chemically etched but only surface degreased with HCl (N). The full line represents the calculated polynomial fit needed in order to substract the background.

Figure 4: Experimental (points) and calculated (solid line) spectra obtained from backscattering of 7.5 MeV alpha particles on a 500 nm Nb layer deposited on a copper substrate.

Figure 5: Comparison of atomic H composition of sample 1 (continuous line) and sample 2 (dots) as defined in the text.

Figure 6: Comparison of atomic H contamination in Nb deposited films of different thicknesses. The origin is the film external surface.
Table Caption

Table 1: Hydrogen and oxygen atomic concentrations in niobium samples for different chemical etching conditions.
<table>
<thead>
<tr>
<th>Chemical polishing: etched depth and bath composition</th>
<th>Oxygen</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface layer at %</td>
<td>Surface layer at %</td>
</tr>
<tr>
<td>10 – 20 μm 1HF 1HNO₃ 2H₃PO₄</td>
<td>17.3 ± 0.1</td>
<td>3.1 ± 0.1</td>
</tr>
<tr>
<td>10 – 20 μm 1HF 9HNO₃</td>
<td>16.0 ± 0.1</td>
<td>3.1 ± 0.1</td>
</tr>
<tr>
<td>150 – 160 μm 1HF 1HNO₃ 2H₃PO₄</td>
<td>14.6 ± 0.1</td>
<td>2.3 ± 0.1</td>
</tr>
<tr>
<td>150 – 160 μm 1HF 9HNO₃</td>
<td>14.9 ± 0.1</td>
<td>2.4 ± 0.1</td>
</tr>
</tbody>
</table>

Table 1
Figure 1

Niobium

H. atom

$^4\text{He}^+$ 2.5 MeV

Collimator (0.37 x 4 mm$^2$)

Movable detector

Collimator (3 x 5 mm$^2$)
Figure 2

[Diagram showing the deflection of ions (He⁺, He²⁺, H⁺) as a function of length in millimeters at energies of 100 keV and 30 keV.]
Figure 3

ERD Yield vs. Channel number
Figure 5

![Graph showing H concentration at % vs depth (nm)]
HYDROGEN PROFILING

Figure 6

H concentration at % vs. depth (nm)

--- Nb/Cu 270 nm
-- Nb/Cu 500 nm
- - Nb/Cu 1000 nm