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Measurements of Hydrogen Content in Bulk Niobium by Thermal Desorption Spectroscopy

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The hydrogen content of bulk niobium has been studied by Thermal Desorption Spectroscopy. The work has been focussed initially on the influence of the vacuum firing and the surface chemical treatment. It is planned to extend the investigation to niobium samples of different quality and origin to ascertain the interest of using the Thermal Desorption Spectroscopy technique to qualify the raw niobium sheets to be used for cavity manufacturing.

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MEASUREMENTS OF HYDROGEN CONTENT IN BULK NIOBIUM BY THERMAL DESORPTION SPECTROSCOPY

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Abstract

The hydrogen content of bulk niobium has been studied by Thermal Desorption Spectroscopy. The work has been focussed initially on the influence of the vacuum firing and the surface chemical treatment. It is planned to extend the investigation to niobium samples of different quality and origin to ascertain the interest of using the Thermal Desorption Spectroscopy technique to qualify the raw niobium sheets to be used for cavity manufacturing.

1 INTRODUCTION

Although the hydrogen – niobium system is probably one of the most thoroughly investigated hydrogen – metal systems, the influence of hydrogen on the observed tainted behavior in Superconducting Radio Frequency (SRF) accelerator cavities, at high accelerating gradients, is not well understood [1-4]. In the recent past, the observed steep decline in the Quality Factor (Q) of the niobium cavities has been linked to numerous different sources of degradation [5-7]. The progress in techniques such as post purification of niobium, clean-room assembly and high pressure water rinsing have eliminated the two major performance limiting mechanisms, thermal breakdown and field emission [8]. The still remaining symptoms of Q degradation of the niobium RF cavities have several explanations [5, 8-10] including magnetic field enhancement at grain boundaries, segregation of impurities during the polishing treatment of the cavities and hydrogen.

The role of hydrogen to the field dependent degradation, also often referred to as Q or hydrogen disease [2], has mainly been linked to the symptoms that have been observed and the cure that have been developed during the various investigations [2, 11-13]. The main arguments for the hydrogen contamination as a source for the degradation have been the following. The phenomenon seems to be avoided by degassing the cavities at 800°C or higher in an Ultra-High Vacuum (UHV) oven or by using a fast cool down in the temperature range of 70 K < T < 130 K.

It is clear that no other contaminants are expected to escape the niobium during degassing at the observed temperatures. Also, it can be seen from the hydrogen-niobium phase diagram [14] that close to the upper limit of the observed temperature range for fast cooling, the non-superconducting ε phase (Nb_4H_3) starts precipitating from the initial α phase (solid solution). By increasing the cooling rate, the time for the hydrogen precipitation can be reduced and therefore the final stochiometry of these two phases altered.

The Q disease and its effective curing procedures point out strongly to the hydrogen and it's phenomenology in niobium. The source for the contamination is, again, another source for speculations. Since niobium has an extremely high affinity to hydrogen, there are many different manufacturing and chemical processes in cavity production and some or all of them can have their contribution to the hydrogen intake of the niobium [2].

The difficulty in the characterization and therefore understanding of hydrogen-niobium systems is the limitation of the materials characterization tools. In this study the Thermal Desorption Spectroscopy (TDS) has been used as a powerful direct measurement tool for the characterization of hydrogen content in niobium. Although, the full potential for the utilization of this technique has not been explored yet, the measurements have proven it to be an attractive candidate as a standard characterization tool for niobium sheets.

2 EXPERIMENTAL

The basic principle of operation in the TDS system (Fig 1.) is that the sample (in the form of a strip) is heated resistively in a UHV system. Using a Residual Gas Analyzer (RGA) the degassed gases from the sample are then identified and their rate of release is measured by using a known pumping speed applied to the UHV measurement chamber.

During the measurements the sample is heated at a known ramping speed (typically 5 K/min). As a result, the gases from the surface of the sample are desorbed at temperatures depending on their characteristic desorption energies (surface peaks). In addition, the diffusible species (mainly hydrogen) are diffused from the bulk to the surface and finally degassed (usually at higher temperatures). The system can be used to perform measurements up to 1400°C and therefore is capable of investigating the effects of typical heat treatments for niobium cavities. The accuracy of the pressure measurements is about 20%, mainly due to the uncertainty in the calibration of the measuring pressure gauges. The temperature measurements are performed using a Platinum/Platinum-Rhodium thermocouple welded into the middle of the strip. The temperature values are cross-checked by monitoring the resistance of the sample strips, leaving an estimated error of about $\pm 10^{\circ}$C.
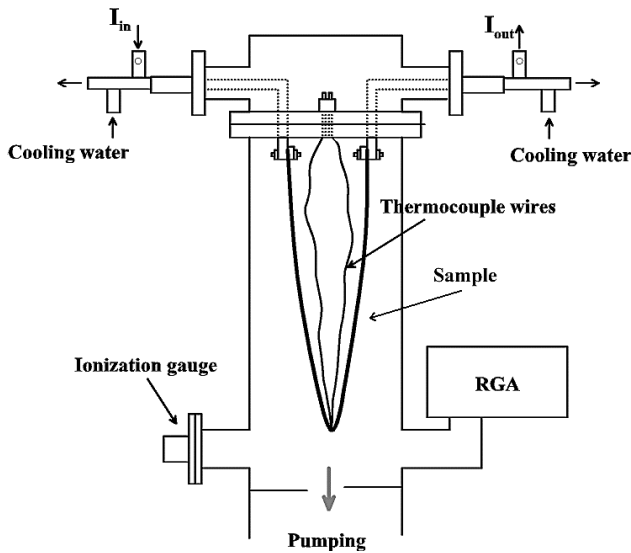
Fig. 1. A schematic picture of the TDS measurement chamber.

Before the measurements, the TDS system goes through a typical UHV bake-out cycle at 250°C. However, the measurement chamber, current feed-through and thus the strip, are kept at about 100°C to minimize the hydrogen release from the sample.

Samples with Residual Resistivity Ratio (RRR) of 150 and dimensions of 600 mm in length, 5 mm in width and 1 mm in thickness were used for the measurements. Both, BCP and EP treated (see Table 1) samples were measured in order to see the possible difference in the hydrogen release.

Further more, samples with RRR of 300 (provided by the Jefferson Lab., USA) were measured to ascertain the importance of the production process on the hydrogen content of the niobium. The RRR=300 strips were 490 mm in length, 3 mm in width and 3 mm in thickness. The samples from this series were polished with the BCP method.

Table 1.

The chemical bath compositions for the used BCP and EP treatments

BCP (2:1:1)	H_3PO_4	HF	HNO_3
	84 % conc.	40 % conc.	60 % conc.
EP (9:1)	H_2SO_4	HF	
	96 % conc.	40 % conc.	

The observed positive effect [6, 15-16] for the niobium cavities that have gone through a long (typically tens of hours) bake-out at low temperatures (about 150°C) was also investigated in terms of hydrogen degassing.

3   RESULTS AND DISCUSSION

The surface peaks of the measurements for the BCP and EP treated niobium RRR=150 strips showed very similar quantities for CO, CO_2 and H_2O, the main components for the desorbed gases from the TDS sample surface in the temperature range of 250°C-350°C. The surface peaks from the BCP treated sample (RRR=150) can be seen from Fig. 2.

The tail of the diffusion peak starts appearing at about 300°C and its peak is located at about 500°C (Fig. 3). The position and the shape of the diffusion peak is related to the speed of the ramping. This can be used as a tool to distinguish the diffusion peak from surface peaks, which are characteristic to their binding energy and therefore will remain stationary.

During the measurements the high temperature tail of the hydrogen diffusion peak was observed to have a slope that differs from the expected Gaussian diffusion peak form. This slope may be caused by the presence of the high energy trapping sites in the niobium. To study the observed slope further, a test was implemented by emptying a sample at 1200°C for 1 hour, followed by an injection of hydrogen at a pressure of $1.3 \cdot 10^{-2}$ Pa and temperature of 400°C. After the injection, the sample was ramped (5K/min.) to 1200°C and the shape of the pure hydrogen diffusion peak was observed. The results showed a change towards a more Gaussian shape. The recrystallization temperature of niobium is around 900°C-1300°C [17], therefore the annealing due to the initial heat treatment had at least partially removed the high temperature tail and thus the trapping sites related to dislocations. Also, the water-cooled current leads have an influence on the spectra. Although, holes are machined in the sample strips close to the cooled current leads, the result is a non-uniform temperature distribution. Part of the strip is therefore following behind the measured temperature. Since the injection test showed a slight improvement in the high temperature tail, it seems that the observed effect is a convolution of both.
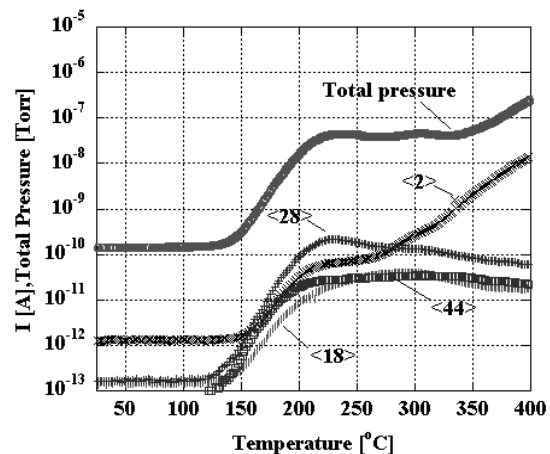

Fig. 2. A TDS spectra of a BCP polished RRR=150 strip showing surface peaks in the temperature range of 25°C-400°C. The rate of temperature ramping was 5 K/min.
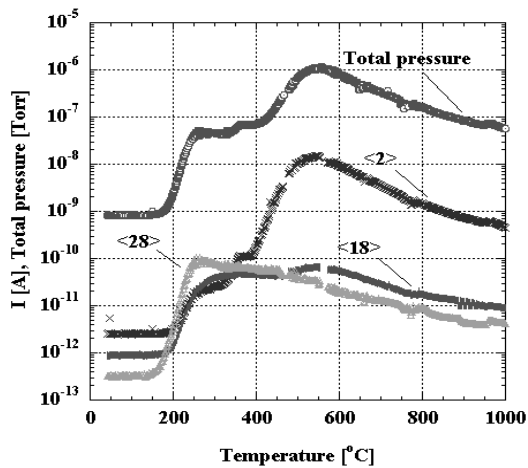
Fig. 3. A TDS spectra of a BCP polished RRR=150 strip showing a hydrogen diffusion peak centered at a temperature of about 500°C. The rate of temperature ramping was 5 K/min.

The total hydrogen content, and contribution of the EP and BCP treatments was measured by ramping the temperature of the samples into plateaus of 400°C, 500°C and 600°C and keeping the temperature constant for 4 hours on each plateau. Further ramping was used to empty the samples and to get the total quantity of the degassed hydrogen. The results from these measurements can be seen from Fig. 4.

The results show very similar hydrogen degassing of the EP and BCP treated niobium. Further measurements will be made in order to gain more statistics and verify whether a real difference exists between the two treatments.
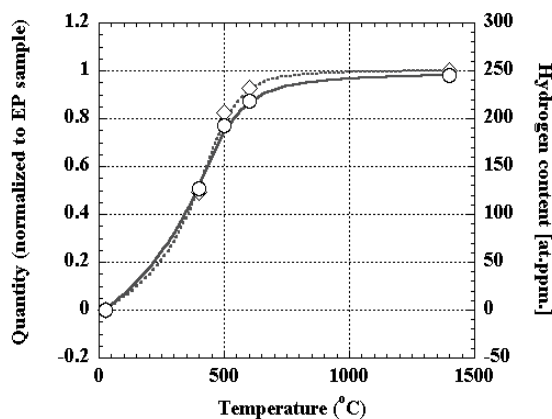

Fig. 4. The comparison of the hydrogen degassing of EP (◊) and BCP (O) treated RRR=150 samples. Heating time on each plateau was 4 h and the ramping rate 5K/min (the solid line is only to guide the eye).

The measurements for comparing the RRR=300 and RRR=150 samples also showed a similar hydrogen degassing (Fig. 5). The samples were again measured by ramping the temperature of the samples into temperature plateaus and keeping the temperature constant for 4 hours on each plateau.

A distinct difference between the two samples is in the hydrogen degassing up to the end of 400°C plateau (RRR=300 sample, 17% and RRR=150 sample, 52% of the total quantity released). Also, the rate of hydrogen release in the region 400°C-600°C was different (RRR=300 sample, 67% and RRR=150 sample, 37% of the total quantity released). The TDS spectra showed a higher level of H_2O, CO and CO_2 (up to 400°C) for RRR=300 compared to RRR=150. In case of RRR=300 sample, the blocked hydrogen became a dominant gas only at 400°C (for RRR=150 at about 300°C). The reason for the higher level of surface peaks may be due to the rougher surface (machining marks) of the RRR=300 samples compared to the more smooth RRR=150 samples.
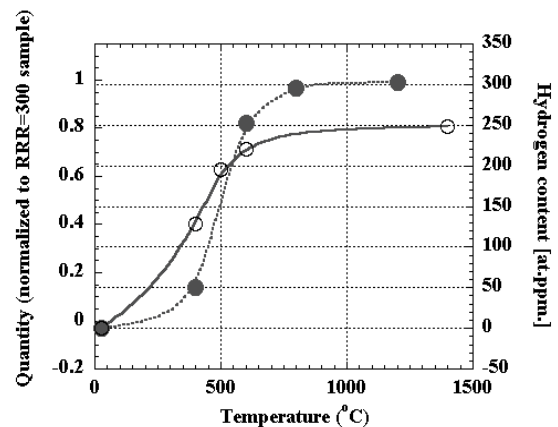

Fig. 5. The comparison of the hydrogen degassing of BCP treated RRR=150 (O) and RRR=300 ( ) samples. Heating time on each plateau was 4 h and the ramping rate 5K/min (the solid line is only to guide the eye).

The results from long, low temperature bake-outs of the niobium cavities have shown beneficial effect to the RF performance. The effect of this treatment in terms of the hydrogen release was investigated by ramping an EP treated sample up to 145°C temperature and keeping the temperature constant for 60 hours. The results showed that only a very small amount of hydrogen (< 1 monolayers) was released, therefore the beneficial effect seems not to be due to a degassing of hydrogen. K. Saito and P. Kneisel have earlier reported a possible explanation for this treatment related to the diffusion of surface oxides and sub-oxides into the niobium [16].

4 CONCLUDING REMARKS

In this paper the TDS measurements for niobium characterization have been reported. The technique has proven to be a powerful tool that can be used for direct measurement of the hydrogen content in niobium. The technique has also proven to be useful for investigating the high energy trapping sites that are seen from the high temperature slope of the hydrogen diffusion peak. Further investigations are in progress in order to fully explore the

feasibility and reliability of this technique as a standard characterization tool for the niobium sheets used for cavity manufacturing. In addition, the use of this technique for the characterization of niobium thin films is in progress.

5 ACKNOWLEDGEMENTS

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