

# Investigations on Hydrogen Contamination of Superconducting Cavities

G. Enderlein, W. Körber, A. Matheisen, D. Proch  
DESY, Notkestraße. 85, 2000 Hamburg 52, Germany  
F. Schölz, W.C.Heraeus GmbH  
W.C.Heraeusstr. 12-14, 6450 Hanau, Germany

## Abstract

All 16 cavities of the energy upgrading program for the HERA storage ring showed increased losses on the second or any successive cool down in contrast to superior values on the first cool down. We attribute this deterioration to Hydrogen which contaminates the Niobium during chemical polishing. The low oxygen content of the new Niobium material (RRR=300) allows the Hydrogen to diffuse to the surface and to produce NbH precipitation at low temperatures. The well known Hydrogen degassing process at 800C cannot be applied to our cavities because of the complex construction. We investigated chemical polishing methods in respect to Hydrogen contamination and tried to find a Hydrogen cleaning procedure at room temperature.

## 1 Introduction

Recently several laboratories reported about a strange behavior of superconducting Nb cavities[1,2,3,4,5] The Q value degraded after the second cooldown or after a warmup to intermediate temperatures (80K to 200K). The observations were made with the new available Nb material with high thermal conductivity. The Q degradation could also be reproduced by a slow cooldown from room temperature to 4.2K (20 hours) but was eliminated by a successive fast cooldown (about 1 hour).

All our Niobium cavities were fabricated from high thermal conducting material (RRR=300). The high thermal conductivity stabilizes quench areas and allows to reach higher accelerating gradients. All cavities showed a Q degradation after the second cooldown. One hypothesis explained this behavior by Hydrogen precipitations[1]. Hydrogen degassing at 800C was successfully applied at different laboratories[1,2]. Q degradation due to Hydrogen has been observed for electropolished cavities[6]. Hydrogen is produced explicitly during electropolishing whereas no free Hydrogen appears in the reaction equation for chemical polishing[7]. In this paper we report on our investigations to understand the nature of the Hydrogen pollution and to find a chemical method to avoid or to reduce the Hydrogen content without the need of a high temperature treatment annealing.

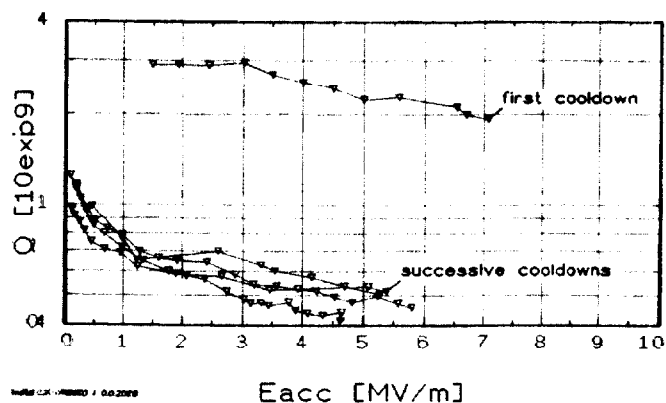


Figure 1: Q degradation after several cooldowns

## 2 Measurements

### 2.1 Cavities

All 16 cavities showed a Q degradation after second cool down. Fig.1 demonstrates a typical measurement. No changes have been made to the cavity other than temperature cycling. The average Q-value at 5MV/m is  $0.7 \cdot 10^9$ . The Q-value depends on the cooldown rate. With the refrigerator at the test area it takes 24 hours to reach 4.2K. In one experiment the cavity was cooled to 200K first. Then the final cooldown to 4.2K was forced in 2 hours. It can be seen from Fig.2, that the Q value recovered as compared to the value of the standard cooldown. A fast cooldown might become difficult for a larger string of accelerator modules.

The work with Nb samples indicated that substituting  $H_3PO_4$  by lactic acid in the buffered chemical polishing (BCP;  $HF : HNO_3 : H_3PO_4 = 1:1:4$ ) results in a decrease of the Hydrogen content. A cavity was treated with this LCP (lactic acid chemical polishing) and the results are shown in Fig.3. The Q degradation effect was clearly reduced but not eliminated completely. It turned out that handling large quantities of the LCP is dangerous. Some hours after the Niobium treatment the acid undergoes a fast thermal reaction. In spite of the promising results we therefore stopped our activities with this chemistry.

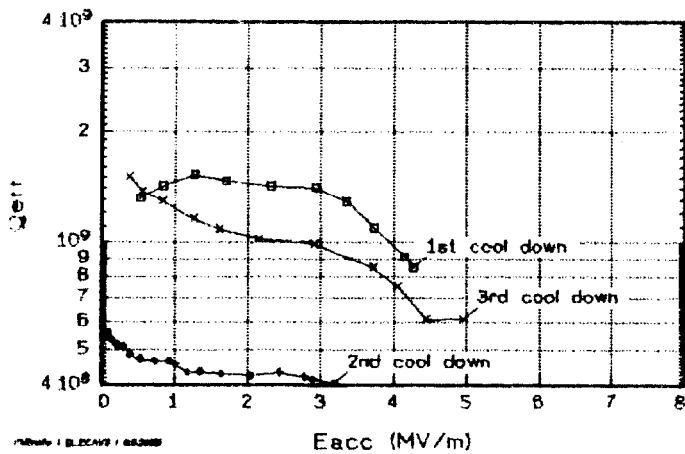


Figure 2: Dependence of Q on cooldown speed (first and second cooldown slow, third fast)

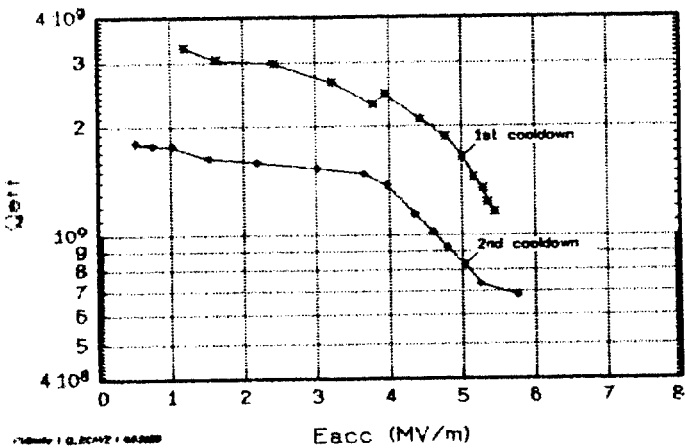


Figure 3: Q degradation for a cavity treated by LCP (slow cooldown).

## 2.2 Niobium samples

We investigated the Hydrogen content of small Niobium samples after different treatments. The Hydrogen was measured by carrier gas hot extraction technique. The sensitivity of the apparatus is better than  $10^{-2}$  wppm, the relative error is smaller than 10%. This method determines the integral Hydrogen content of the sample so that surface effects cannot be distinguished from bulk properties. The size of the samples is  $4 \times 8 \times 2 \text{ mm}^3$ . They are treated in a bath of 1 liter chemicals, the temperature is held constant by a heat exchanger.

Our cavities are treated by BCP. The removal rate and the H-content after treatment of 20min at different temperatures are displayed in Fig.4 and Fig.5. The same measurements are carried out for a mixture of  $\text{HF} : \text{HNO}_3 : \text{H}_2\text{O} = 1 : 1 : 5$  (WCP=water chemical polishing) and the results are given in the same figures. We concluded that BCP at above 30C is the reason for the H contaminations of our cavities. WCP reduces the Hydrogen content at temperatures below 40C. We therefore applied WCP to samples after contamination by BCP to investigate a possible way of cleaning our cavities (see Fig.6).

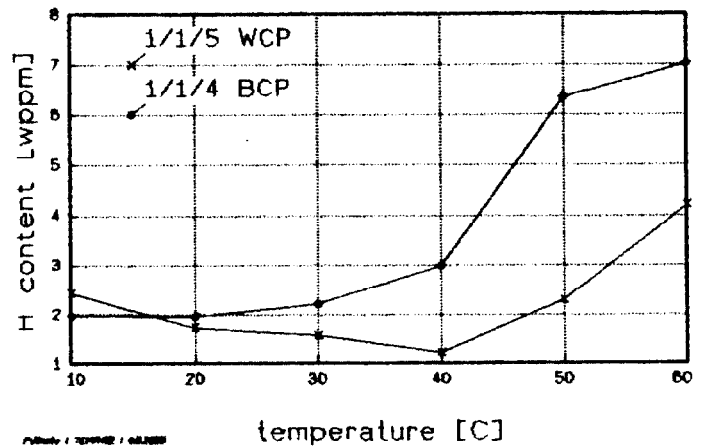


Figure 4: Hydrogen contamination of Niobium samples (20 min BCP and WCP at different temperatures)

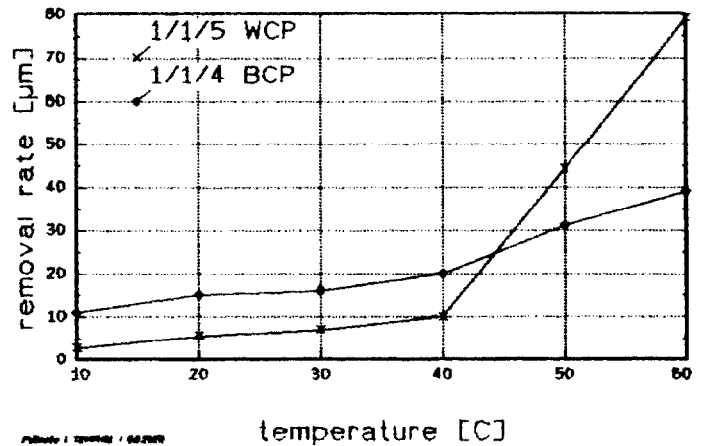


Figure 5: Removal rate of BCP and WCP at different temperatures

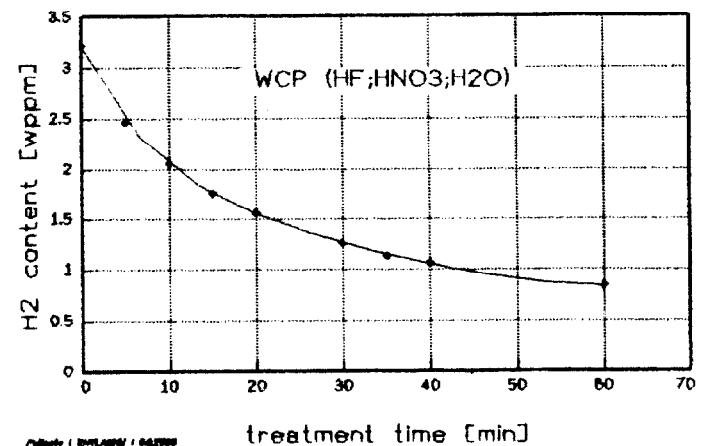


Figure 6: Reduction of Hydrogen content in Niobium by WCP (The sample was polluted with Hydrogen by BCP before)

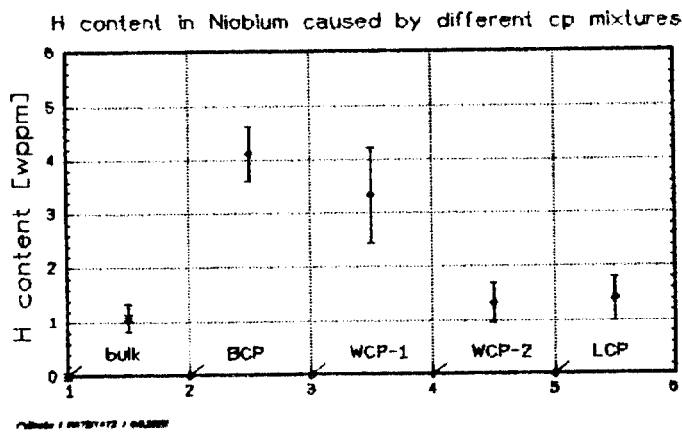


Figure 7: Average value of Hydrogen for Niobium samples treated differently

- 1: bulk value; 2: BCP of cavity condition; 3: 2+WCP, 5ml/cm<sup>2</sup>; 4: 2-WCP, 500 ml/cm<sup>2</sup>; 5: 2-LCP

The conditions of treating our cavities differ from those applied to the samples: the temperature of the outer cavity surface is limited to below 30C, the volume to surface ratio is much smaller and the filling and rinsing procedure is longer. In a second set of experiments we tried to simulate more realistic conditions (see Fig.7):

1. Reference samples are cleaned by a short but effective chemical polish ( $HF : HNO_3 : H_2O = 2 : 2 : 1$ , 5min, 50 $\mu$ ) to get a baseline for the bulk properties.
2. Samples are treated by BCP according to the conditions of a cavity.
3. After treatment 2 the samples were polished by WCP (5 ml/cm<sup>2</sup>).
4. After treatment 2 the samples were polished by WCP (500 ml/cm<sup>2</sup>).
5. After treatment 2 the samples are cleaned by LCP.

A depth profile (50 $\mu$ ) of the H-and O-content of two samples was measured by SNMS. One sample was treated by BCP, the other sample was treated in addition by LCP to reduce the amount of Hydrogen in the Niobium. The graphs show no significant differences, especially there is no hint of a Hydrogen-enriched Niobium layer.

### 3 Discussion and Conclusion

- The NbH phase diagram postulates the formation of Niobium-Hydride around 80K for the amount of Hydrogen content measured. Only a fraction of the measured Hydrogen content is needed to explain the observed rf-losses by normal-conducting NbH precipitations on the surface of the Niobium. The reduction of the additional rf-losses for a fast cooldown can be explained by the strong temperature dependent diffusion constant of Hydrogen in Niobium. The good

results at the first cooldown can be explained by the observation, that NbH precipitations produce surface stress in the Nb which enables the creation of much more NbH precipitations at the second cooldown.

- BCP results in Hydrogen pollution of Niobium, especially at temperatures at or above 40C. The typical increase of the integral content is 3 wppm for a standard BCP. The measured amount of 15 wppm for a sample, which was successively used in 6 cavity treatments for monitoring the removal rate, indicates that there is no saturation effect. Care should be taken to avoid a temperature increase above 20C, especially at the end of BCP and before rinsing the cavity. The thin surface film of acid might heat up fast. Special care has to be taken in the time between BCP and final rinsing.
- WCP is a method to reduce the Hydrogen content after pollution. It should be mentioned that the Niobium surface after WCP is not as smooth as after BCP and LCP. The positive result on samples could not completely be transferred to a cavity application. Obviously the diffusion of Hydrogen from the Niobium to the acid is limited by a small solubility constant of Hydrogen in the acid. This results in the need of large volume of acid. Further work will be done to increase the Hydrogen solubility and to reduce the surface roughness.
- The use of LCP eliminates the Hydrogen pollution and produces smooth surfaces. But special care has to be taken to handle the afterwards exothermic reaction. From the safety point of view this procedure is not recommended for cavities.

### 4 Acknowledgments

Stimulating discussions with G. Müller, H. Padamsee and R. W. Röth are gratefully acknowledged.

### References

- [1] R.W.Röth et al., Proc. of the Europ. PAC, Nice, June 1990 p.1097
- [2] H.D.Graef, TH Darmstadt, priv. comm.
- [3] B.Aune et al., Proc. of 1990 Linear Acc.Conf. Albuquerque, USA
- [4] K.Saito et al., CEBAF-SRF-90-12-01-EXA, USA
- [5] D.Moffat et al., CLNS 90/1035, Cornell University
- [6] K.Saito et al., Proc. of the 4th Workshop on Superconductivity, August 1989, KEK
- [7] Gmelin Handbuch der Chemie, Band 49, "Niob"