© 1991 IEEE. Personal use of this material is permitted. However, permission to reprint/republish this material
for advertising or promotional purposes or for creating new collective works for resale or redistribution to servers
or lists, or to reuse any copyrighted component of this work in other works must be obtained from the IEEE.

Increase in RF Surface Resistance of Niobium as a Result of Acid Treatment*

D. Moffat, P. Barnes, J. Kirchgessner, H. Padamsee, J. Potts, D. Rubin, J. Sears, Q. Shu‡
Laboratory of Nuclear Studies, Cornell University, Ithaca, NY 14853-5001
and D. Proch
Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

Abstract

We have systematically studied the effect on R_S of several different acid mixtures and the conditions of their use. Reverse electropolishing, which generates large quantities of hydrogen at the niobium surface, can drastically increase R_S. R_S can be decreased by subsequent heat treatment for 2 hours at 200-300°C, indicating that the hydrogen is concentrated in a thin surface layer. This was confirmed by RRR measurements on thin samples. Etching niobium with 1:1:1 BCP (buffered chemical polish) under "open" conditions, i.e. copius amounts of room temperature acid with no flow restrictions, does not seriously load a sample with hydrogen. Using the same acid under "closed" conditions, i.e. restricted flow of acid which leads to a substantial increase in temperature, can increase R_S significantly. A 1:1:4 LCP acid mixture[1], in which phosphoric acid is replaced by lactic acid, does not introduce hydrogen under "closed" conditions. This mixture can even remove the hydrogen enriched layer in a previously contaminated sample, restoring R_S to its theoretical value. Vacuum heat treatment for 2 hours at 900°C removes all dissolved hydrogen and restores R_S.

I. INTRODUCTION

Several SRF groups around the world have reported on the infection of their cavities by the "Q virus" [1-5]. Our infection has been limited to our S-band and "mushroom" cavities. The Q_o's of our L-band cavities have not been affected. The symptoms of our "virus" are that the 4.2K Q_o's are lower than expected, and the residual Q_o's are substantially below theoretical. When low, the Q_o's of our cavities are low on the initial cooldown. Unlike the experiences at other laboratories, they are not high on the first cooldown and then low on subsequent cooldowns.

Data from two of our experiences are shown in Figures 1 a and b. As can be seen, the effects of acid treatment are variable. Both the "mushroom" and S-band type cavities had tests with good Q_o's following 1:1:1 BCP, which were then followed by more acid treatment and dramatically lower residual Q_o's. High vacuum heat treatment at 900°C cured the "mushroom" and S-band cavities.

In this paper we will discuss the conditions and acid solutions which lead to Q degradation. We will present methods by which to avoid the problem and/or recover from it. The last section of this paper deals with the underlying cause of the problem.

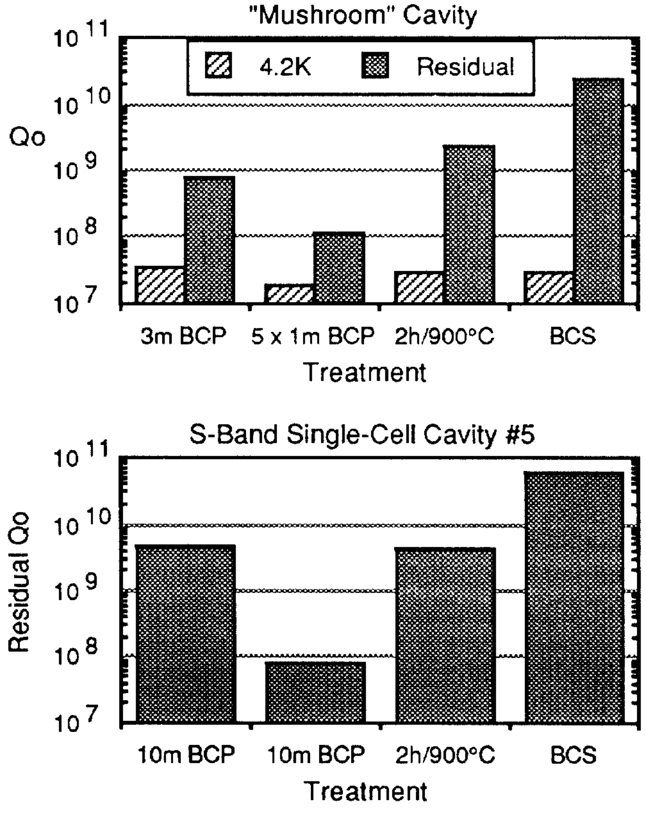

Figure 1. Q_o values for two cavities showing the onset and cure of the "Q virus".

II. SMALL SAMPLE TESTS

We sought to introduce hydrogen into our samples in ways which were similar to actual practice. The acids we use have the following strengths: HF-49%, HNO_3-70%, H_3PO_4-85%, H_2SO_4-96%, Lactic-85%. The solutions used in this study are given in Table 1. ***Because of the great explosion hazard associated with storing the LCP solution, its use is strongly discouraged.***

Table 1
Acid solutions used

Solution	HF	HNO_3	H_3PO_4	H_2SO_4	Lactic
1:1:1 BCP	1	1	1		
1:1:4 BCP	1	1	4		
EP	10			105	
1:1:4 LCP	1	1			4

---

*Work supported by the NSF and the US-Japan collaboration
‡Present address: SSCL, Dallas, TX 75237
[1] The use of this solution was suggested by Heraeus

0-7803-0135-8/91$01.00 ©IEEE

Samples were prepared under three different conditions. To produce gross hydrogen contamination, the samples were made the cathode in an electropolishing cell. This is the reverse of the polarity used for electropolishing and is referred to as REP. Samples were etched in a sacrificial container of niobium to produce contamination typical of S-band cavities. Under such "closed" conditions the acid flow is restricted, causing an increase of the solution temperature and etch rate. The evolved gas is confined because of the flow restriction. "Open" conditions are characterized by a low ratio of niobium area to solution volume, and unrestricted acid and gas flows.

Measurements of RF surface resistivity were made in our "High T_c" cavity. This cavity operates in the TE_{011} mode at a frequency of ~6 GHz. (More information on this cavity can be found in [6].) The R_s samples were machined from 1.6 mm thick high RRR niobium sheet in the shape of an annulus with an ID of 19.1 mm and an OD of 33 mm. This sample shape was chosen in order to maximize the amount of niobium in the high H fields, while at the same time restricting the total sample surface so as not to lower the cavity Q_o below ~10^7. These samples were supported in the cavity on a 38 mm diameter sapphire disk. The minimum R_s we could measure was $1.8 \times 10^{-5}\ \Omega$ when the bath temperature was 4.2K. Samples with a lower resistivity could not be distinguished from the cavity at 4.2K. All samples were given the same initial cleaning treatment of 5 minutes of "open" 1:1:1 BCP.

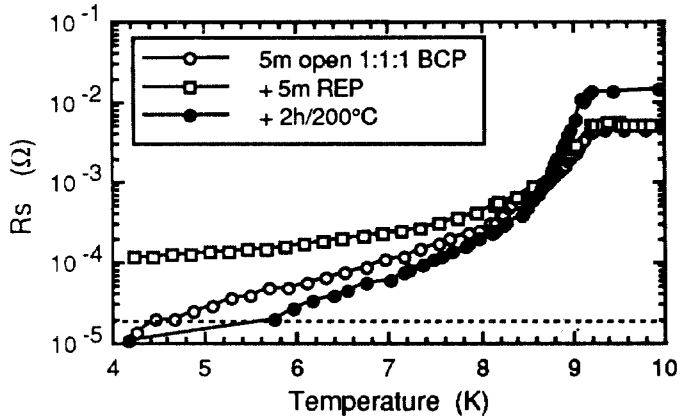

Figure 2. Temperature dependence of R_s. The dashed line indicates the measurement limit for a 4.2K bath.

Figure 2 shows the temperature dependence of R_s for a sample in the "clean" state, after 5 minutes of REP, and after vacuum heat treatment for two hours at 200°C. The effect of REP was to load the surface with hydrogen and/or cause the precipitation of a hydride phase. Heat treating drove the hydrogen into the bulk, increasing the normal state R_s, but lowering the superconducting R_s. A sample that received 30 minutes of REP did not show a superconducting transition before a 200°C heat treatment but did after.

Figure 3 shows that the acid solution used under "closed" etching conditions has an effect on R_s at 4.2K. 1:1:1 BCP contaminates samples, whereas 1:1:4 BCP and 1:1:4 LCP do not. Ten minutes of 1:1:1 BCP removed ~110 μm/side, 30 minutes of 1:1:4 LCP removed ~80 μm/side, but 90 minutes of 1:1:4 BCP removed only ~30 μm/side. It should be remembered that 1:1:1 BCP used under "open" conditions does not contaminate the surface.

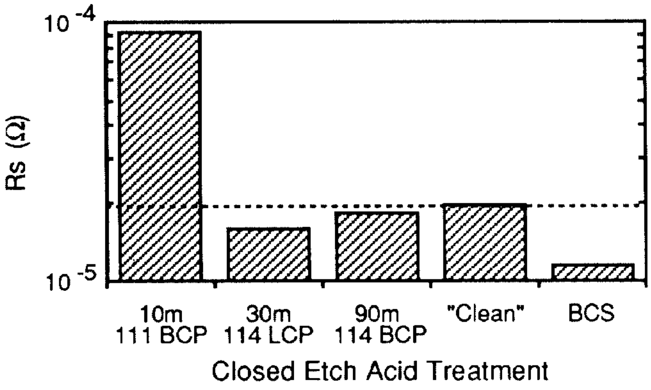

Figure 3. Effect of etching solution on R_s at 4.2K for samples etched under "closed" conditions. The dashed line indicates the measurement limit for a 4.2K bath.

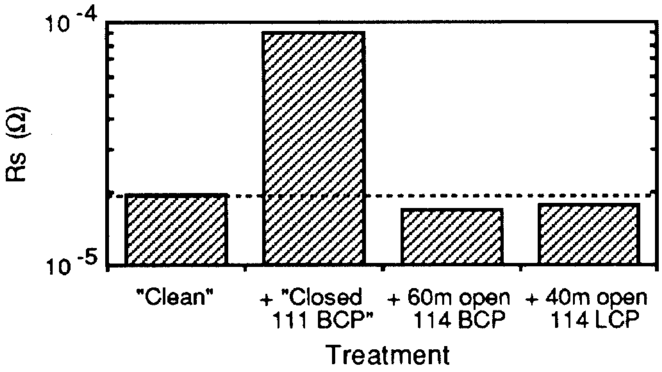

Figure 4. Effect of post-contamination etching with 1:1:4 BCP or 1:1:4 LCP. The measurements were made at 4.2K. The dashed line is the measurement limit for a 4.2K bath.

Figure 4 shows that both 1:1:4 BCP and 1:1:4 LCP can remove the heavily hydrogen-contaminated surface layer from a sample. The first two data pairs are averages obtained from other samples. The data for the last two pairs were obtained from two samples that had been cleaned, contaminated by "closed" etching for ~10 minutes with 1:1:1 BCP, and then etched under "open" conditions. An S-band single-cell cavity acid treated with 1:1:4 LCP had a high residual Q_o and field emission activity similar to that of other acid treated cavities.

As part of our structures development work, an S-band 9-cell cavity was cleaned by giving it a 10 minute acid treatment in 1:1:1 BCP. The results are shown in Figure 5. The residual Q_o of the first test was extremely low. The cavity was vacuum heat treated for 2 hours at 700°C to remove hydrogen. This resulted in an improvement in the 4.2K Q_o, but the residual Q_o was still low. A vacuum heat treatment at 900°C was required to enable the cavity to achieve its full potential.

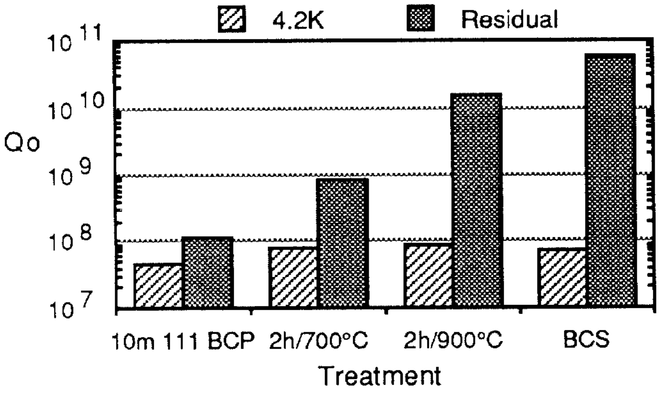

Figure 5. Q_o values for an S-band 9-cell cavity.

III. NB-H PHASE DIAGRAM CONSIDERATIONS

The Nb-H phase diagram has been reviewed by [7]. The hydride phase at 300K accessible by our techniques is β-NbH. This phase exists over the stoichiometry range Nb_4H_3 to NbH. If the composition is Nb_4H_3, the hydrogen atoms become ordered below 225K to form the ε phase. The maximum solubility of hydrogen in niobium is given by [8]:

$$C_{max} = 6213 \exp(-1079/T) \text{ wppm} \qquad (120\text{-}180\text{K}) \qquad (1)$$

Using this equation and other phase diagram data, the area fraction of ε at equilibrium at a holding temperature T_H, $A_\varepsilon(T_H)$, can be calculated. With this, the Q_o of a cavity can be estimated using the equation:

$$Q_o = \frac{G}{R_s} \approx \frac{G}{A_\varepsilon(T_H)R_\varepsilon + (1-A_\varepsilon(T_H))R_{Nb}} \qquad (2)$$

where R_ε is the RF surface resistivity of ε, and R_{Nb}, the surface resistivity of niobium. R_{Nb} at 500 MHz at 4.2K is $1.47 \times 10^{-7}\ \Omega$ for high RRR niobium. Based on our measurements of the 30 minute REP sample we estimate R_ε at 500 MHz, 4.2K to be $4.3 \times 10^{-3}\ \Omega$. G is the geometry factor of the cavity, which for a typical accelerating cavity is $\sim 280\ \Omega$. The results of Q_o calculations based on (2) are shown in Figure 6.

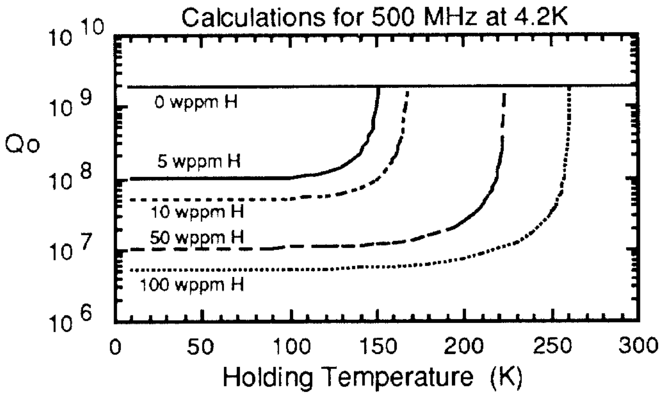

Figure 6. Qo as a function of holding temperature. Equilibrium at the holding temperature is assumed.

IV. DISCUSSION

This work shows that the conditions of acid use are as important as the acid solution used. 1:1:1 BCP used for short times under "open" conditions does not contaminate a sample with hydrogen, whereas the same solution used under "closed" conditions does. Our results concerning the use of 1:1:4 BCP under "closed" conditions, however, appear to conflict with those of DESY. We believe this discrepancy can be explained by the lower sensitivity of our techniques. Our measurements on small samples are sensitive only to severe contamination. The surface area of a cavity is much greater than that of our samples and, therefore, will show the effects of hydrogen contamination at much lower levels. In addition, the amount of material removed from our sample etched for 90 minutes in 1:1:4 BCP was only ~30% of that removed from the other samples. This test needs to be repeated with longer etching times.

The hydrogen-contaminated surface layer of a sample can be removed in several ways. It can be absorbed by the bulk by heat treating at 200°C or it can removed by vacuum heat treatment at 900°C. This layer also can be etched away using 1:1:4 BCP or 1:1:4 LCP under "open" conditions.

The ultimate concern is how hydrogen contamination affects the Q_o of a cavity. Figure 6 indicates that a cavity with a surface concentration of 5 wppm H can be held indefinitely at ~160K and then rapidly cooled to 4.2K with no degradation of Q_o. A cavity with 50 wppm can be precooled only to ~230K. Warming the cavity to an intermediate temperature will result in hydride precipitation and a subsequent loss of Q_o (this has been the experience of others).

An expanded version of this report was distributed by the authors as Internal Report CLNS 90/1035.

V. REFERENCES

[1] D. Moffat, et al., "Superconducting Niobium RF Cavities Designed to Attain High Surface Electric Fields", in *Proceedings of the 4th Workshop on RF Superconductivity*, KEK, Tsukuba, Japan, August 1989, pg.445-465. Also distributed as Internal Report CLNS 89/934.

[2] K. Saito, et al., "R&D of Superconducting Cavities at KEK", in *Proceedings of the 4th Workshop on RF Superconductivity*, KEK, Tsukuba, Japan, August 1989, pg.635-694.

[3] R. Röth, et al., "Suppresion of Field Emission in Superconducting S-Band Acceleration Structures", presented at the 2nd EPAC, Nice, France, 1990.

[4] B. Aune, et al., "Degradation of Niobium Superconducting RF Cavities During Cooling Time", presented at the 1990 LINAC Conference, Albuquerque, NM.

[5] V. Nguyen-Tuong, "Q-disease and CEBAF Superconducting Cavities", distributed as Internal Report CEBAF TN 90-285.

[6] D. Rubin, et al., "Observation of a narrow superconducting transition at 6 GHz in crystals of $YBa_2Cu_3O_7$", Physical Review B, vol. 38(10), pg.6538-40, 1988

[7] J. Smith, "The H-Nb (Hydrogen-Niobium) and D-Nb (Deuterium-Niobium) Systems", Bulletin of Alloy Phase Diagrams, vol. 4(1), pg. 39, 1983

[8] G. Schaumann, J. Völkl and G. Alefeld, "The Diffusion Coefficients of Hydrogen and Deuterium in Vanadium, Niobium, and Tantalum by Gorsky-Effect Measurements", Physica Status Solidi, vol. 42, pg 401-13, 1970