

Q-Degradation in High Purity Niobium Cavities* - Dependence on Temperature and RRR-Value -

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1. INTRODUCTION

The observation in 1989 that the Q-value of superconducting cavities fabricated from high purity niobium could significantly degrade when these cavities were kept for longer periods of time at temperatures between 50K and 200K became a major concern for accelerator projects employing superconducting cavities. A large number of investigations were carried out at various laboratories and the initial hypothesis expressed in [1] of precipitation of a niobium-hydride phase was supported by additional experimental data by other laboratories. The detrimental effect of hydrogen precipitation in niobium has been known for many years [2], but nevertheless the performance degradations of the cavities came as an unexpected surprise, when a rather uniform additional loss distribution over the whole cavity surface was measured on a temperature map [1].

It was experimentally verified that the Q-degradation could be avoided, if the cavities were cooled down quickly through the dangerous temperature region; hydrogen degassing at temperatures above 700° C eliminated the deterioration, but subsequent extensive chemical surface treatment seemed to reverse the process. A summary of the experimental observations has been given in [3].

For large scale accelerator projects like CEBAF the cryogenic system might prefer certain cooldown cycles; therefore it is of great interest to determine the exact temperature range which does not effect cavity performance, if a string of cavities were held at these temperatures. In the following we report on the investigation of the Q-degradation of a niobium cavity under various conditions.

2. CAVITY PREPARATION AND TESTING

For the investigations single cell and 5-cell 1500 MHz cavities of the Cornell/CEBAF-design were used. The cavities were manufactured of niobium from different suppliers with varying RRR-values ranging from 40 to 370. After the manufacturing all cavities were surface treated in a standard way:

After degreasing in a caustic solution combined with ultrasonic agitation, approximately 60 μm of niobium were removed from the cavity surface by chemical polishing in a buffered solution of equal parts of hydrofluoric (49%), nitric (69%) and phosphoric (85%) acids at room temperature. The cavities were thoroughly rinsed with ultra-pure water combined with ultrasonic agitation at 50° C for a total of one hour with several exchanges of water. A final rinsing with reagent grade methanol was carried out in a class 100 cleanroom, where the assembly of the rf-

probes took place. The cavities were subsequently attached to a cryogenic test station under extreme caution to avoid particulate contamination of the inner cavity surface.

The anodic oxide layer on the 5-cell cavity used for the investigation of the temperature dependence of the Q-degradation [Figure 1] was grown in a solution of 10% ammonium hydroxide at a voltage of 65 V and a current density of $\approx 0.8 \text{ mA/cm}^2$. The resulting Nb_2O_5 -layer had a thickness of 1300 Å. Rinsing in ultrapure water and methanol as described above followed prior to cleanroom assembly and attachment to the test system.

Heat treatments of some of the cavities were carried out in a cryo-pumped horizontal high vacuum furnace at 710° C and 1400° C, respectively, for several hours. During these annealing steps the cavities were surrounded by a titanium box acting as a solid state getter and the pressure in the furnace at temperature was in the low 10^{-6} torr range.

Before fast cooldown, within one hour the cavities were evacuated to a vacuum of $< 6 \times 10^{-7}$ torr; the external magnetic field in the vicinity of the cavity was shielded to better than 10 mG by an active compensation coil and two layers of μ -metal.

During the experiments the temperature dependence of the surface resistance at low rf-fields ($E_p \leq 4 \text{ MV/m}$) was measured between 4.2K and 1.7K and data for the dependence of the Q-value on the cavity fields were taken at the lowest temperatures.

3. EXPERIMENTAL RESULTS

3.1 Effect of "Holding" Temperature on Q-Degradation

The dependence of the Q-degradation on the intermediate "holding" temperature was investigated with a 5-cell cavity for the two cases of an anodized and a "bare" niobium surface. The cavity was held at each temperature for 24 hours prior to fast cooldown within 1 hour to 4.2K. In the cases, where a degradation of the cavity was observed, a complete warmup to 300K was carried out before an additional test at helium temperatures followed. Figure 1 summarizes the results of these test series, where Q_0 at 5 MV/m and 2K is plotted versus the "holding" temperature. A few observations are important to note:

- For both surface conditions a Q-degradation was observed, but to a far lesser extent with the anodized surface; even at the maximum of the degradation, the anodised cavity still exceeds CEBAF's design Q-value of 2.4×10^9 at $E_{acc} = 5 \text{ MV/m}$.
- Dangerous temperature regions in both cases are $70\text{K} \leq T \leq 150\text{K}$.

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- c. A warmup to 200K (for ≥ 2 hours) completely eliminated the 100K-degradation.
- d. In a series of tests the cavity was cycled between 100K and He-temperature with varying "holding" time at 100K as shown in Figure 2: the Q-degradation is accumulative and seems to saturate after ≈ 24 hours.

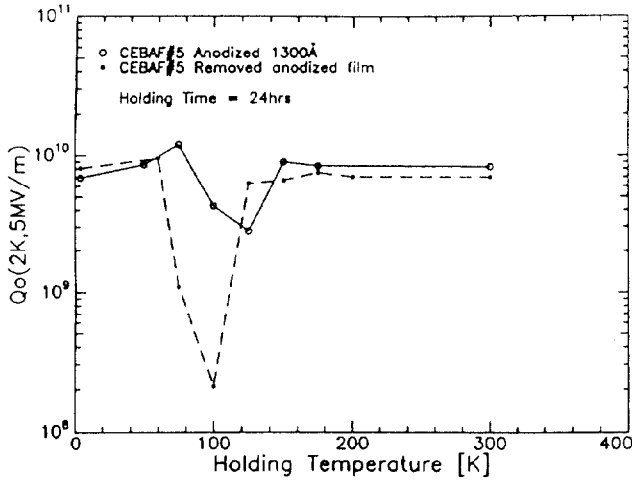


Figure 1. Temperature Dependence of Q-Degradation.

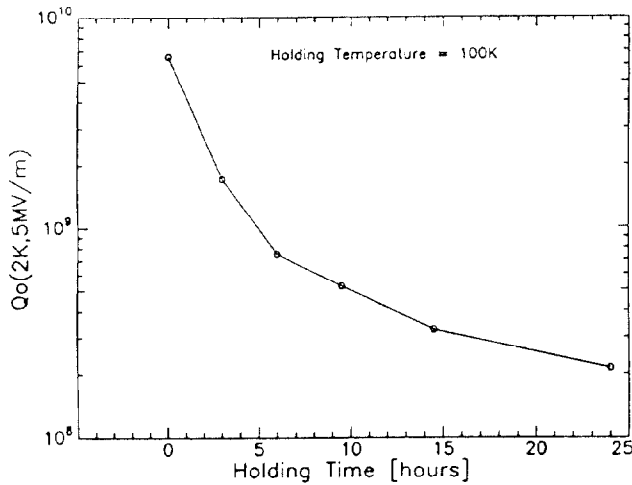


Figure 2. Time Dependence of Degradation at 100 K.

3.2 Effect of RRR-Value

Several single cell cavities made from niobium ranging in RRR-value from 40 to 370 were fabricated and the Q-degradations after standard treatments as described in the previous section were measured. The experimental results are summarized in Table 1:

- a. Reactor grade niobium with $RRR \approx 40$ did not show any signs of degradation; $R(T)$ showed exponential BCS-like behavior and $Q(E)$ did not exhibit low field variations.
- b. Cavities made from high purity niobium exhibited Q-degradations and non-exponential $R(T)$ -dependences as well as Q-decreases at low fields. The extent of the degradation increased with the purity of the material.

Table 1. Dependence of Q-disease on RRR-Value

RRR	Q_0 (fast cooldown)/ Q_0 (after warmed up)	Q_0 -Disease
~ 40	0.47	NO
200	19.4	YES
230	15.4	YES
330	117	YES
370	60.3	YES

3.3 Effect of Heat-Treatment and Subsequent Chemical Treatment

One of the cures for eliminating the Q-degradation in a high purity niobium cavity is degassing of the hydrogen at $T > 700^\circ C$. Sometimes cavities have to be reprocessed by chemical treatments and it is of interest, to which extent a "cured" cavity will survive such treatments.

To investigate the effect of heat-treatment and subsequent chemical polishing, we fired two cavities at two different temperatures: an electropolished cavity was heat treated at $710^\circ C$ for three hours and a chemically polished cavity was heated up to $1400^\circ C$ for four hours. In both cases no Q-degradation was measured after the cavities had been held at 120 K for >16 hours. In subsequent tests we successively removed material from the surface of the cavities by buffered chemical polishing (BCP). During each minute of exposure to the acid bath $\approx 10 \mu m$ are removed. As shown in Figure 3 the Q-value of the moderately heated cavity started to drop after 5 min of exposure to the acid, whereas the fully annealed cavity remained insensitive to degradation up to 22 min of BCP-time. Obviously in the case of the moderately annealed cavity the "cure" was reversed by the exposure to the chemicals.

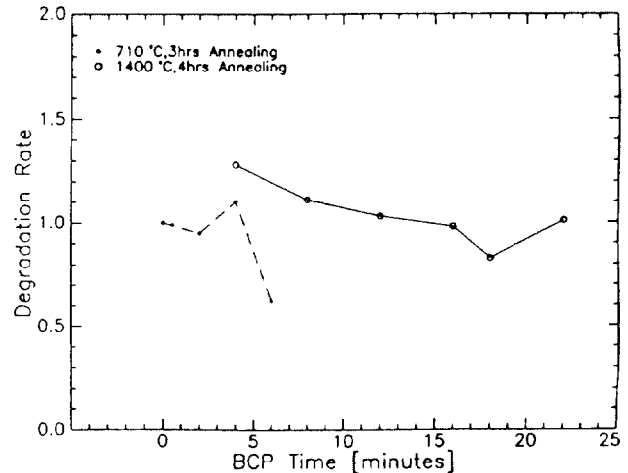


Figure 3. Effect of Exposure of "Cured" Cavities to BCP-Solution.

4. DISCUSSION

It is generally accepted that the observed Q-degradations in cavities manufactured from high purity niobium are caused by hydrogen dissolved in the niobium matrix

at room temperature. It is believed that hydrogen is absorbed by the niobium during the manufacturing and surface preparation steps, predominantly during chemical polishing [3]. Figure 3 supports the observation of the influence of the chemical treatment. Because of the high diffusion rates of hydrogen in niobium (diffusion length \approx several cm/day) it seemed obvious that hydrogen would uniformly diffuse through a niobium sample and establish a constant concentration profile through the sample. This was supported by measurements reported in [4], which in addition showed a suppressed hydrogen concentration in a surface layer of approximately 2500 Å due to surface sub-oxides, which act as a barrier against hydrogen diffusion. More recent measurements using Elastic Recoil Detection Analysis (ERDA) [5,6] revealed that chemically polished niobium samples exhibited an enhanced hydrogen concentration in a surface layer of \sim 500 Å, reaching several atomic% depending on the sample preparation. As has been pointed out in [5] interstitial impurities like O,N,C can act as traps for the hydrogen and lower the diffusion rates significantly; more importantly, crystal defects like dislocations, grain boundaries, impurity atoms or stresses can act as nucleation sites for hydrogen trapping and at lower temperatures, hydrogen precipitation.

Two pictures have emerged to account for the observed degradations [3]:

Since there is an enhanced hydrogen concentration at the surface, this hydrogen may form a uniform hydride film on the surface - either weakly superconducting or normal-conducting - after a cavity was held for some time at 100K. On the basis of such a model, experiments at Saclay have been explained in [3].

The second possible mechanism for the Q-degradation is the formation of "hydride" islands: the interstitially dissolved hydrogen atoms, which form the α -phase at room temperature, start during cooldown to precipitate into Nb-hydride clusters at crystal defects as soon as the solubility limit becomes smaller than the bulk hydrogen concentration. This model can quantitatively explain, why there exists a dangerous temperature region around 100K, even though the details of the phase transitions in the complicated niobium-hydrogen system are not yet understood. This model also can explain the accumulative effect of exposure to 100K [Figure 2]: at 100K hydrogen becomes mobile in the lattice again except for the atoms trapped at crystal defects; in a certain period of time a certain number of hydrogen atoms are statistically trapped and precipitate. When cooled down to 4.2K, this process is frozen-in, but sets in again upon subsequent warm-up to 100K and the effect of Q-degradation worsens until a saturation is reached. As shown in Figure 3, the reappearance of the Q-degradation of annealed cavities after exposure to chemicals depends on the annealing temperature. Even though annealing at 710° C seems high enough to remove

sufficient hydrogen and eliminate the Q-disease initially, it reappears after a short time of exposure to chemicals in contrast to the fully annealing at 1400° C. This observation is also compatible with the "island" model; after the annealing at 710° C sufficient crystal defects remain in the material to act as nucleation sites for additional hydrogen introduced by the chemical process; in the fully annealed material all nucleation sites are removed and the bulk concentration of hydrogen has to exceed the solubility limit. This apparently does not happen during 22 min of exposure to chemicals.

5. CONCLUSION

Operational procedures for large accelerator systems using superconducting niobium cavities of high purity like CEBAF have to avoid holding the cavities in the temperature range $70\text{K} \leq T \leq 150\text{K}$ during cooldown. This temperature region should be passed through as quickly as possible and as the time dependence measurements show, already a few hours in that temperature region might effect the cavity performances. An anodic oxide layer certainly significantly reduces the sensitivity of the cavities to Q-degradation. So far, the only lasting cure for the disease has been a fully annealing of the niobium at $T \geq 1400^\circ\text{C}$, which could even withstand long periods of exposure to chemicals in the case of reprocessing needs.

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7. REFERENCES

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