Islands or Films? – New Aspects on the NbHx-puzzle.

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Abstract

Analyzing in further detail the experimental data presented in the 1991 review on Q-degradation in niobium cavity resonators [1] and combining the results with the findings in TEM studies on hydride pecipitation in thin Nb foils [2] it is evident in both cases that the hydrogen starts to cluster as small islands in thin layers close to the metal surfaces. Furthermore it comes out that the anomalous rf losses increase linearly with the surface magnetic field strength. In addition the losses grow linearly with the storage time in the critical temperature range. These new results are useful to develop a quantitative explanation of the strange behaviour.

Introduction

The precipitation of the interstitially dissolved hydrogen to normalconducting hydride phases increases the surface resistance of niobium cavity resonators significantly [1,3,4]. However, a detailed understanding of the process is still missing. For instance, it has to be determined which phase transformation causes the Q-degradation. This knowledge will not only fix the value of the dangerous hydrogen concentration as a function of the impurity content (RRR) of the niobium. Furthermore it will reveal the critical temperature ranges that have to be passed as fast as possible during cooldown or warmup of the cavities. To develop a model describing the anomalously increased surface resistance correctly it is necessary to know whether the hydrogen precipitates form small islands all over the bulk metal or build up a thin film near the surface. Finally a detailed study of the Q-degradation as a function of the time duration spent in the critical temperature regime will bring valuable input for the model development. The same is true for a measurement of the dependence of the increased surface resistance on the amplitude of the rf field strength. This paper presents experimental facts providing answers to the open questions stated above.

Experimental Observations

Islands in Films !

Even after a buffered chemical polishing with phosphoric acid the typical hydrogen concentration in the bulk of todays niobium cavities (RRR ≈ 250) amounts to only 100 – 400 at ppm [1,3]. Because this value is three to four orders of magnitude smaller than the local concentration in the low-temperature hydrides (e.g. $c_H^\vartheta \approx 46$ at%, $c_H^\varepsilon = 75$ at%), the precipitating hydrogen has to build small islands, surrounded by niobium with a negligible hydrogen concentration (Figs. 1, 2). The formation of a contiguous stoichiometric hydride

crystal or film is impossible. The size of the hydride islands in the bulk depends

- on the concentration of the untrapped hydrogen (c_H^{free}), defining the critical temperature T_K for the transition between the superconducting and the normalconducting hydride phase (e.g. $\alpha \to \varepsilon$) and thus defining the maximum diffusion speed,

- on the storage time (t_v) at temperatures $T \leq T_K$, defining the maximum diffusion range,

- on the number and the mean distance of the nucleation centers.

$c_H^{free} = c_H - c_{trap}$ means the local concentration of those hydrogen nuclei that are free to precipitate: If a dissolved H-atom becomes trapped by another interstitial impurity (oxygen, nitrogen, carbon) it may still diffuse between the adjacent tetrapores but cannot move away and does not contribute to the condensation of hydrides [5]. This trapping to interstitials is the key to understand why the Q-disease mostly affects high RRR niobium cavities. Reactor grade niobium (RRR ≈ 40) is only affected when it has been heavily loaded with hydrogen (e.g. by electropolishing).
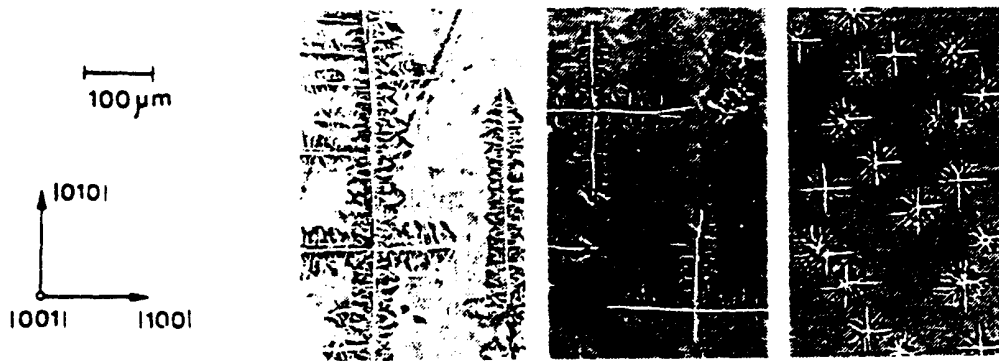
Fig.1: Transmission electron microscope pictures of hydride precipitation in a single-cristalline niobium foil as a function of the cooling speed [2]. (RRR > 1000; c_H < 2 at%)
a) Thermal equilibrium. b) Slow cooling (1–2 K/min). c) Fast cooling (> 25 K/min).
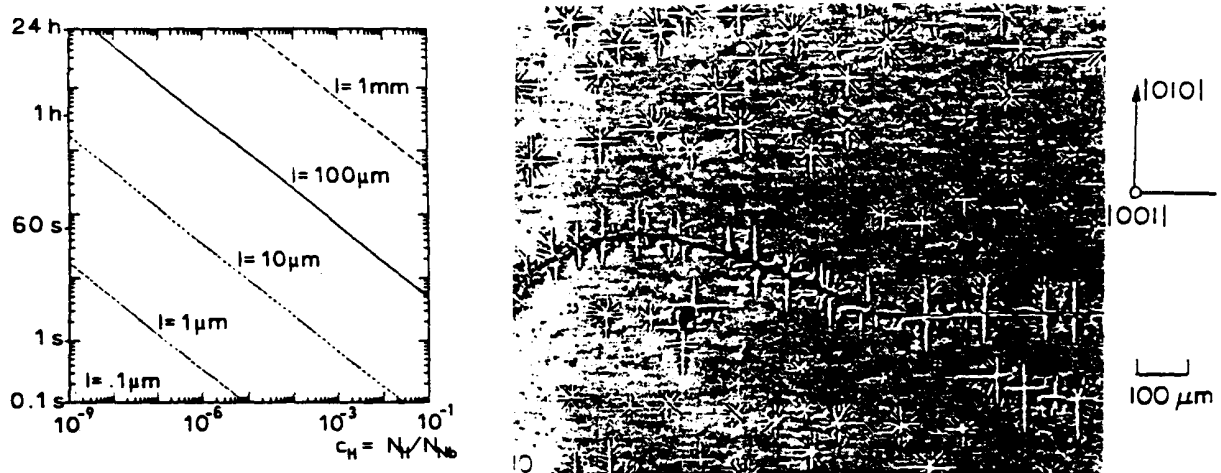
Fig.2: Surface defects like scratches act as strong nucleation centers for hydride islands. The scratch has attracted all the hydrogen from a macroscopic surrounding of about 100 μm radius. (RRR $\approx$ 1000, c_H = 0.6 at%)
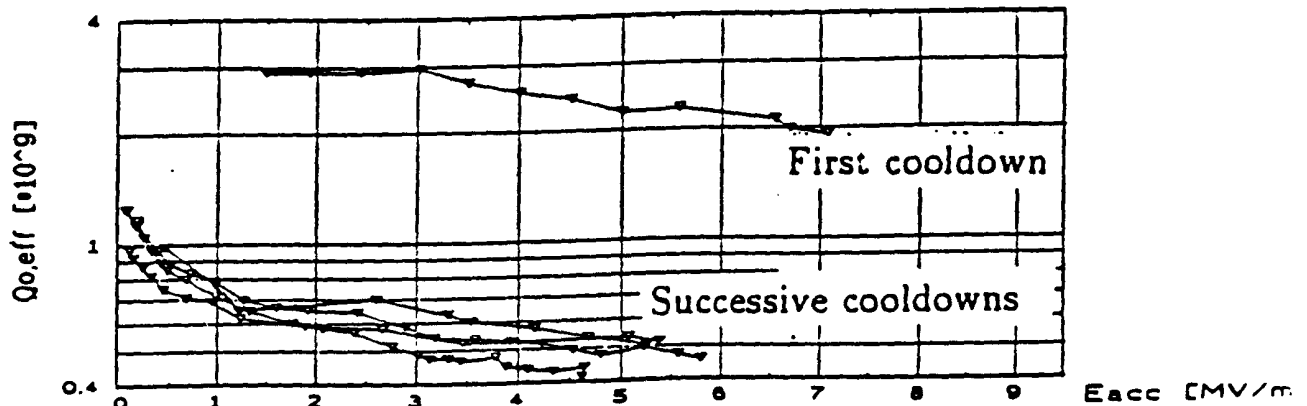
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Fig.3: Field dependence of the quality factor of a 500 MHz cavity at DESY at 4.2 K [1]. Each time the cooling speed was about 0.25 K/h.

Close to the metal surface the situation might differ significantly from that in the bulk, since depth profile measurements show a large hydrogen enrichment in the first 50 – 100 nm of the niobium [1,6]. However, this peak is directly correlated to the increased number of interstitial trapping centers in the oxide and suboxide layers. The free hydrogen concentration c_H^{free} still stays far below 5 at% [3]. This keeps the dissolved H-atoms in the disordered, superconducting α-phase at room temperature. (If c_H^{free} were larger than 5 at% there would exist some β-hydride islands already at room temperature. Since β-NbH is always normalconducting ($T_c < 1.3$ K) [7] it would be impossible to prevent the Q-disease by a rapid cooldown. This contradicts the experimental observations [1,3,4].) With $c_H^{free} < 5$ at% the transition to the well ordered and normalconducting low-temperature phase starts below the critical temperature $T_K(c_H^{free})$ given by the solubility limit of the α-phase. This is on principal the same situation like in the bulk.

If niobium is cooled to temperatures below $T_K(c_H^{free})$ in thermal equilibrium, hydride islands build up allover the bulk metal. Due to nucleation problems the precipitaton starts near the metal surface where the number of lattice defects has its maximum. Since the diffusing hydrogen becomes trapped by the lattice defects at temperatures below about 60 K, Q-disease can be totally avoided with a sufficiently high cooling speed. For slower cooling or higher values of c_H^{free} (due to larger c_H or larger RRR) normalconducting hydride islands will grow in a thin surface layer first. This situation applies for example to the experiments on chemically polished cavity resonators with a RRR $\le$ 300 presented in references 1,3, and 4. In the case of the 500 MHz cavities at DESY [1], the cooling speed is fast enough to prevent hydrogen precipitation within the first cooldown of the virgin cavities (Fig.3). During the slow warmup through the critical temperature range the hydrogen atoms near the metal surface do start to form well ordered hydride islands. When these crystals melt at T > $T_K(c_H^{free})$ large dislocation sceletons remain [8]. With the next cooldown these new dislocations act as nucleation centers and the Q_0 degrades significantly. A new chemical etching removes only the nucleation centers but leaves the hydrogen

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content more or less unchanged. Thus, in the DESY case, the BCP treatment cured the Q-disease only for the first of the following cooldowns.
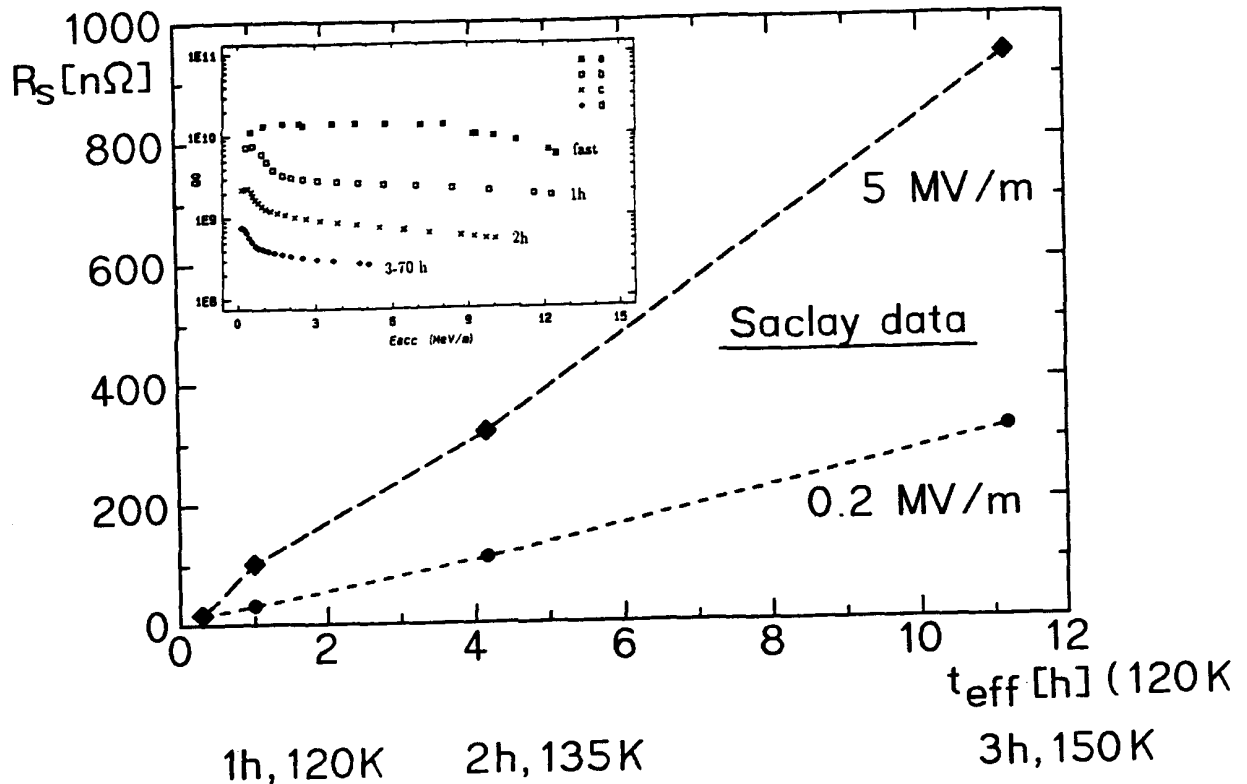
Fig.4: a) Field dependence of the quality factor of a 1.5 GHz cavity at Saclay at 1.4 K [1].
The parameter of the curves is the time duration t_v spent at fixed temperatures in the critical temperature range. b) The corresponding surface resistance R_s increases linearly with t_v. (Storage temperature has been scaled to 120 K (see text).)

Linear increase of R_s with the storage duration in the critical temperature regime

Usually one presents the performance of a superconducting cavity as a half logarithmic plot of Q_0 versus E_{acc} (Figs.3, 4, 5). However, the physical information about anomalous losses is more obvious on a linear scale of the surface resistance $R_s = G/Q_0$: For example the rf losses of a hydrogen contaminated cavity increase linearly with the time t_v spent at a given temperature T_v in the critical range $60 K < T_v < T_K(c_H^{free})$ [3]. While the data presented in figure 5a directly yield this important information (Fig.5b), the experimental results from Saclay (Fig.4) have to be scaled to a fixed temperature first. Taking the diffusion of the hydrogen to be described by

$$ x(T, t) = \sqrt{2 D(T) t} \quad ; \quad D(T) = D_0 \exp(-E_a/k_B T) $$

with $D_0 = (9 \pm 2) \cdot 10^{-5} cm^2/s$ and $E_a = 68 \pm 4 meV$ ($E_a/k_B = 790 \pm 50 K$) [5] a storage time
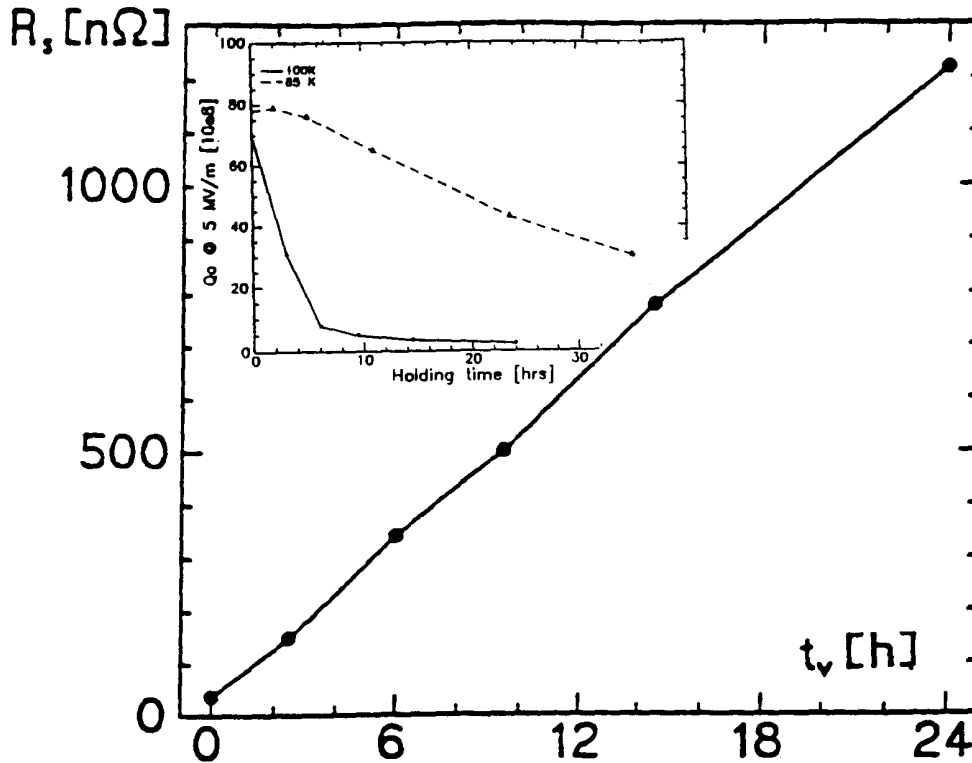
Fig.5: Q-degradation (a) and surface resistance $R_s(t_v)$ (b) of a 1.5 GHz cavity at CEBAF after storage at 100 K for different periods [9].

of 3 hours at 150 K has the same effect as a storage of 11.2 hours at 120 K. This scaling leads to figure 4b. It shows a linear increase of R_s with t_v not only at high field strengths but with the minimum R_s values at low gradients, too.

The data for D_0 and E_a used in the simple scaling calculation have been measured with very clean niobium samples ($RRR > 2000$) [5]. Comparing Figs.4 and 5 shows that they are still good assumptions for our so called high purity niobium ($RRR \lesssim 300$). However, this high diffusion speed allows the hydrogen to travel long distances in very short times. Thus, it should be completely impossible to prevent hydride precipitation with a cooling speed of less than 1 K/min. This contradiction to the experimental observations is solved by the problem of nulceation. The well ordered hydrides need an increase of the lattice parameter of the niobium host. Especially at low temperatures this slows down the growth of the hydride islands significantly. In addition it explains why lattice defects are needed as nucleation centers.

Linear increase of R_s with the field amplitude

Another important feature of the surface resistance of hydrogen contaminated niobium cavities is given by its linear increase with the amplitude of the surface field strengths above a certain threshold (Fig.6). The slope of the curves correlates with the size of the
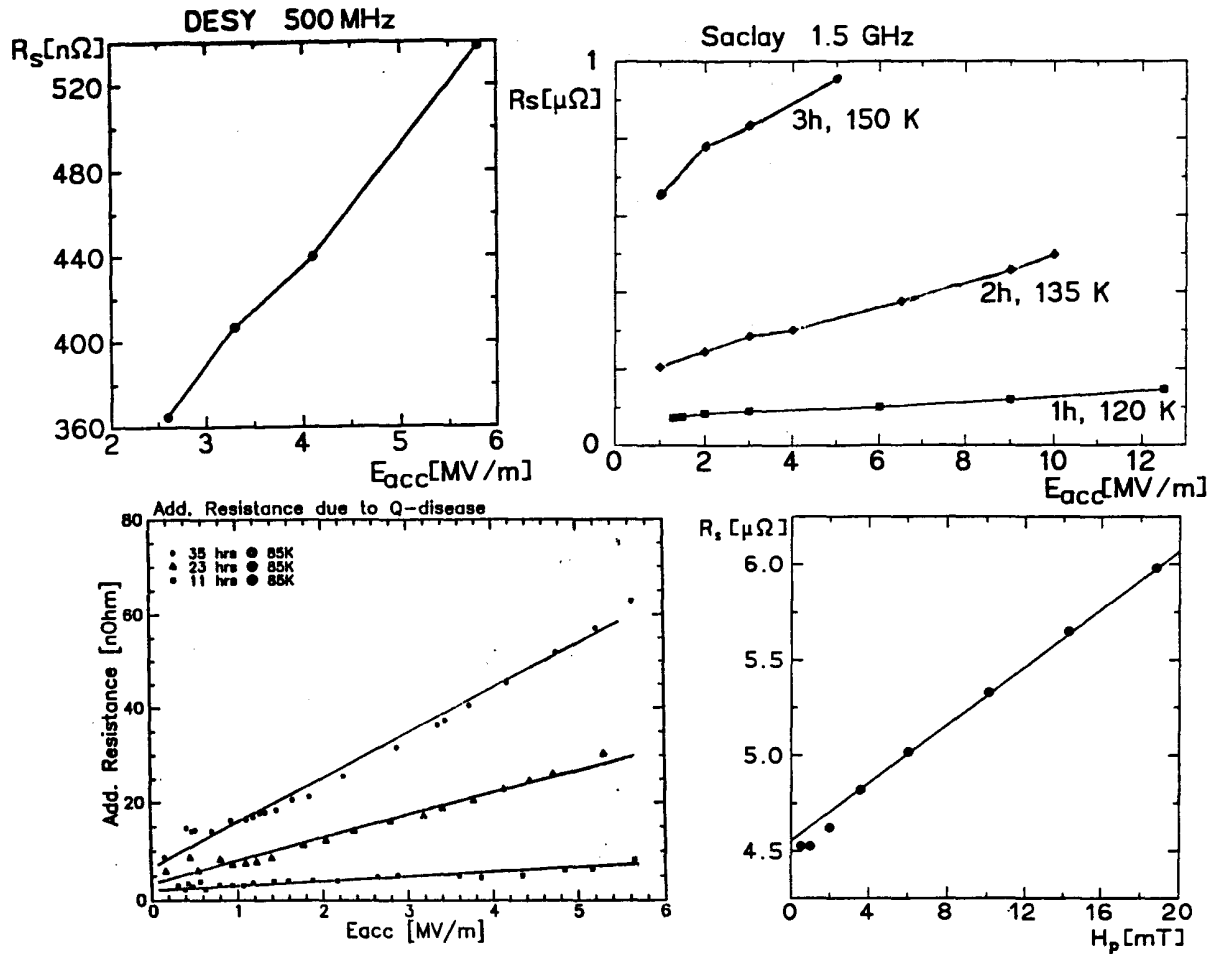
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minimum surface resistance.

Fig.6: Linear increase of the surface resistance $R_s(E_{acc})$ of hydrogen contaminated niobium cavities a) at DESY (data taken from Fig.3), b) at Saclay (data taken from Fig.4), c) at CEBAF ([3,9]), d) at Wuppertal ([3]).

Conclusion

In our present day niobium cavities with RRR $\approx$ 300 and $c_H < 500$ atppm the dissolved hydrogen can precipitate from the disordered α-solution at room temperature to the well ordered low temperature hydride phase below a transition temperature $T_K(c_H^{free})$ given by the solubility limit of the untrapped hydrogen nuclei. The conservation of the number of hydrogen atoms prevents the formation of a contiguous stoichiometric hydride film or crystal but forces the growth of islands around the strongest nucleation centers. Since these exist near the metal surface and since the typical cooling speed dT/dt > 0.25 K/h is much too fast to establish thermal equilibrium the cavities end up with hydride islands in thin surface films of several μm thickness.

The diffusion speed of hydrogen in niobium with RRR $\leq$ 300 is not significantly smaller than in the pure metal. The hydride precipitaion is slowed down by nucleation problems. The result is a linear increase of the surface resistance and the slope of its field dependence with the storage time in the critical temperature range between T_K and $\approx$ 60 K.

The contribution of the precipitated hydrogen islands to the surface resistance of niobium cavities creates a characteristic linear field dependence $R_s \sim H$. This fact has to be accounted for by any theoretical attempt to explain the Q-disease quantitatively. Most probably, the ideas of granular superconductors apply to this problem [9].

Acknowledgement

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