ADDITIONAL LOSSES IN HIGH PURITY NIOBIUM CAVITIES RELATED TO SLOW COOLDOWN AND HYDROGEN SEGREGATION

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I. INTRODUCTION

Several years ago the SRF—community was unpleasantly surprised by the discovery that superconducting RF–cavities made from high purity niobium showed significant degradations of the Q–values when kept for longer periods of time at intermediate temperatures around 100K. The first temperature map taken on such a degraded cavity showed a rather uniform distribution of the additional losses.[1] This fact and the roughly 100 K holding temperature resulted in the hypothesis of precipitation of hydride phases in niobium. A large number of investigations in several laboratories followed this discovery and the results supported the initial explanation of hydride precipitation. It was experimentally verified that the Q–degradation could be avoided, if the cavities were quickly cooled down through the dangerous temperature region; hydrogen degassing at elevated temperatures eliminated the cavity deterioration, but subsequent extensive chemical surface treatment seemed to reverse the process. A summary of the recent experimental observations has been given in [2], but the detrimental effect of hydrogen precipitation in niobium cavities has been known for many years.[3]

For large scale accelerator projects like CEBAF the cryogenic system might prefer certain cooldown cycles and it is important to know the cooling conditions under which the cavity performance is not effected. Such investigations were done in the past [4] and have extended to other temperature regimes. The results and the analysis of these experiments are reported in the following based on a model of weak links between hydrogen segregates and the niobium matrix, which has been developed by one of the authors (JH) for high T_c and "classical" superconductors.[5]

II. CAVITY PREPARATION, TESTING AND EXPERIMENTAL RESULTS

Three questions were pursued in this investigation: first, at which holding temperature is the Q–degradation most severe; secondly, how is the Q–degradation developing in time at the most unfavorable temperature and thirdly, what is the RF–field dependence? For answering these questions, a 5-cell cavity of the Cornell/CEBAF design made from high purity niobium of RRR–value of about 250 was used and the dependence of the Q–degradation on intermediate "holding" temperatures was investigated for the two cases of an anodized and a "bare" niobium surface.

Prior to the cryogenic testing, the cavity was surface treated in buffered chemical solution resulting in a removal of approximately 60 μm Nb, followed by thorough rinsing in ultrapure water supported by ultrasonic agitation. A final rinsing with reagent grade methanol was done in a class 100 clean room, where the assembly of peripheral parts such as RF–window, input coupler, field monitoring probe and gate valves took place. After establishing a vacuum of $\leq 10^{-6}$ torr the cavity was assembled to a cryogenic test station under clean conditions to avoid particulate contamination of the inner cavity surface.

The anodic oxide layer on the inner surface of the 5-cell cavity was grown in a solution of 10% ammonium hydroxide at a voltage of 65 V and a current density of ≈ 0.8 mA/cm^2. The resulting Nb_2O_5–layer had a thickness of 130 nm. Rinsing in ultrapure water and methanol as described above followed prior to cleanroom assembly and attachment to the test station.

The "fast cooldown" from room temperature to helium temperatures occurred within 1 hour; the ambient 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 ($E_p \leq 4$ MV/m) was measured between 4.2 K and 1.7 K and at the lowest temperature the Q–value was measured as a function of cavity field. The T–dependence has been analyzed in [2] and can be summarized as follows: above a temperature of 3 K "H–precipitates" cause an additional $2 \cdot \Delta / k \cdot T_c \approx 3.4$–term aside from $2 \cdot \Delta / k \cdot T_c = 3.8$ for clean niobium. Below 3 K losses become field and therefore T–dependent with $2 \cdot \Delta / k \cdot T_c \approx 2$ at very low fields. At the same time additional RF residual losses are observed.

Figure 1 shows the results of a series of experiments during which the cavity was always held for 24 hrs at the "holding "temperature prior to cooldown to 4.2 K. In the cases, were a degradation of the cavity was observed, a complete warmup to 300 K was carried out, before an additional test at helium temperatures followed.

Figure 2 shows the experimental results of a test series, during which the "holding time" at a "holding" temperature of 100 K was prolonged up to 24 hours. As can be seen in both figures, there is a rather sharp decrease of Q–value with RF–field level occurring at accelerating fields ≤ 1 MV/m, which correspond to a peak magnetic field of ≤ 50 Gauss. This degradation is followed by a less severe decrease of Q–value as the RF–fields in the cavity are increased above 80 Gauss.

As an example in Figure 3 the additional losses as extracted from the Q–values of Figure 2 of the non-degraded cavity and the degraded cases are plotted. Two distinct dependencies of the additional resistance on field level–in both cases the dependence is linear in field–are observed.

In the following sections these dependencies will be analyzed and discussed.

III. HYDROGEN PRECIPITATION IN NIOBIUM

It is well known that niobium crystals can dissolve large quantities of hydrogen on interstitial sites [6, 7]. For example, at room temperature in the atmosphere (partial pressure of hydrogen is 4×10^{-4} torr) the equilibrium concentration of hydrogen in niobium is as high as 5×10^5 at ppm and up to $NbH_{0.7}$ can be picked up at 300 K as solid solution with some percentage of lattice expansion.[6] Ordered and disordered arrangements of hydrogen in the host metal are possible with homogeneous phases existing over a wide range of compositions ranging from dilute solutions to concentrated hydrides.

Phase transitions of the hydrogen interstitials cause lattice distortions in the host matrix, introducing lattice parameter increases.[6]

The NbH–system phase diagram is rather complicated, but shows the following general features: at room temperature in the concentration range up to $NbH_{0.07}$ hydrogen is interstially dissolved into niobium as α–phase; above this concentration, in the range $NbH_{0.09}$ to $NbH_{0.7}$ the α–phase coexists with the ß–phase. Above $NbH_{0.7}$ only the ß–phase is present. At temperatures below 200 K a new phase–the ε–phase–will precipitate in α–NbH. [6] Hydrogen has a very high mobility in niobium at and below room temperature. But the natural oxide layer prevents usually the absorption of large amounts of hydrogen [7,8]. In addition, subsurface precipitates of NbO_x ($x \approx 1$) forming in reactor grade niobium with RRR ≈ 30–40 or cold–worked niobium shift hydrogen away from the sub–surface regime (≈ 1 μm) by compressional strain.[7,9] Aside from these pressure effects, H is pinned by O in niobium at special sites.[10] But niobium, where the oxide is dissolved into the bulk at elevated temperatures or where Nb_2O_5 has been chemically removed, can reabsorb large amounts of hydrogen .

As electronic properties, H precipitates cause at first a reduction of the mean free path of conduction electrons in the niobium matrix and NbH precipitates have been found to be metallic and non-superconducting above 1K. [11]

IV. MECHANISMS CAUSING RF RESIDUAL LOSSES

RF residual losses by normal conducting precipitates in proximity to pure niobium have specific temperature–and magnetic field dependences such as $\delta R \approx H_{rf}^2$ and saturate after $NbH_{0.7}$ has been driven normal conducting. More effective than island segregates [2] in contributing as parallel resistances to residual losses are planar segregates interrupting the paths of the RF–currents , i.e. as series resistances. Such interruptions as series resistances, usually called weak links (WL), occur as a result of crack corrosion in niobium caused by oxidation [7] or e.g. during epitaxial film growth.[5,6,12] Electrically, such weak links are described by a critical Josephson current j_{cJ}, shunted in parallel by normal conducting leakage currents j_{bl}.

The weak Josephson coupling yields a long penetration depth

$$\lambda_J = \sqrt{\phi_0 / 4 \cdot \pi \cdot \mu_0 \cdot j_{cJ} \cdot \lambda_I} \qquad (1)$$

causing the destruction of RF–shielding deep into the superconductor. λ_I is the intrinsic penetration depth of the superconductor, and $\phi_0 = 2 \cdot 10^{-7}$ Oe cm^2 is the flux quantum . In a two fluid model this destruction causes RF–residual losses given by [5,12]

$$R_{res}(H) \propto \mu \, (\omega \cdot \mu_0)^2 \cdot \lambda_J^{\,3} \; a/2 \cdot R_{bl} \qquad (2)$$

with $\mu \approx 2\,\lambda_I / a < 1$ as a geometrical factor describing the density of WL in a mean distance a and $R_{bl} \propto 1/j_{bl}$ as the resistance across weak links describing the normal leakage current j_{bl} below T_c.

The intrinsic dependence of these losses on temperature and RF–magnetic fields are contained in the expression for the Josephson current. As discussed in detail in [5,12], the flux enters WL at the fluxon entry fields H_{c1J}

$$H_{c1J} = \phi_0 / \pi^2 \cdot \lambda_I \cdot \lambda_J \qquad (3)$$

which is the beginning of a linear growth of λ_J with H yielding

$$R_{res}(H) \propto R_{res}^* \cdot (1 + 3/2 \cdot H_{rf}/H^*_{c1J}) \qquad (4)$$

Here H^*_{c1J} is of the order of H_{c1J}. The change of additional resistance with magnetic RF–field above H_{c1J} is given by

$$dR/dH_{rf,\,max} \propto R_{res}^* \cdot 3/2 \cdot 1/4 \cdot 1/H^*_{c1J} \qquad (4')$$

The factor 1/4 is a result of time–and space averaging of the maximum magnetic field H_{max} of the cavity.

V. DATA ANALYSIS AND DISCUSSION

The experimental data as extracted from Fig. 3 are summarized in table 1–3 for a holding temperatures of 85 K, 100 K and for anodized niobium at 2 different holding temperatures. The tables contain the data for R_{res}^* and for the linearly extrapolated R_{res} ($H \approx 0$), the slope of the linear H - field dependence dR/dE_{acc} and in accordance with equation (4) $H_{rf}^* \approx H_{c1J}^*$ [$H_{rf}^*/E_{acc}^* \approx$ 45 G/ MV/m].

Table 1: **Linear field dependences of additional surface resistance caused by a holding temperature of 85 K.**
$R_{res}(0)$ is the linearly extrapolated surface resistance at 1.7 K, where R_{res} without Q–degradation has been subtracted. H_{rf}^* has been obtained using one type of WL according to equation (4). dR_{res}/dE_{acc}^* is the linear slope in Fig. 3.

Time	$R_{res}(0)$ [nΩ]	dR_{res}/dE_{acc}^* [nΩ/MV/m]	H_{rf}^* [G]
11 hrs	2	1	≈34
23 hrs	3.5	4.6	≈13
35 hrs	6.5	9.4	≈12

Table 2: **Linear field dependences of additional surface resistance caused by a holding temperature of 100 K.**
In this table for each holding time two sets of data are given in accordance with the two slopes observed (see e.g. Figure 3).

Time	$R_{res}(0)$ [nΩ]	dR_{res}/dE_{acc}^* [nΩ/MV/m]	H_{rf}^* [G]
3 hrs	25	28.5	≈ 15
	45	**15.5**	**≈ 49**

6 hrs	70 **150**	85.5 **35**	≈ 14 **≈ 72**
9.5 hrs	100 **220**	196 **60**	≈ 8.5 **≈ 62**
14.5 hrs	150 **425**	425 **77**	≈ 6 **≈ 93**
24 hrs	320 **800**	761 **92.7**	≈ 7.1 **≈146**
35 hrs @ 85 K 17 hrs @ 100K	75 **350**	400 **59**	≈ 3.2 **≈100**

Table 3: Additional surface resistance for anodized niobium by holding at different temperatures.

Time / Temp.	$R_{res}(0)$ [nΩ]	dR_{res}/dE_{acc}^* [nΩ/MV/m]	H_{rf}^* [G]
24 hrs/ 100 K	**7**	**3.5**	**≈ 34**
48 hrs/100K-145K	0.5 **13.9**	8 **1.97**	≤ 1 **≈ 119**

How can all these data be described in a common picture/model?

It is commonly assumed, that the Q–degradation in high purity niobium cavities is related to H–precipitates [1–4]. But the amount and geometrical shape of these precipitates has not been detected quantitatively. In Ref. [2] two possibilities are discussed: a thin hydride film at the niobium surface or the formation of random hydride islands in the bulk material. The latter hypothesis has a problem in explaining the large observed Q–degradations since only islands located within the penetration depth would contribute additional losses. Also $T_c^* \leq 1.0$ K [11] of Nb-hydride has not been observed until now in cavity–measurements and is not in line with the above two explanations.

The hydride film hypothesis could explain the observed losses, if one assumes a $T_c^* \approx$ 2.8K for a thin hydride in proximity with niobium. But the field dependencies [12,14] of the additional resistance should be proportional to H^2 due to pair breaking up to saturation at a field corresponding to T_c^*, e.g. $H_c^* \approx 300$ G. This has not been found. Instead, as can be seen in Figure 3, after a short upturn $\delta R \propto H^2$ at very low fields a linear increase in field above about H^*_{c1J} is obvious. Such a dependence is typical for flux penetration into weak

links as identified for cuprate superconductors and NbN, Nb_3Sn or Nb by one of the authors.[5,12] Thus we conclude that hydrides occurring in parallel to the bulk superconductor are unable to explain the T–and RF–field dependencies.

Prior to discussing the origin and growth mechanism for the weak links, we want to analyze the data summarized in Tables 1–3. Using equation (4), which describes one type of WL with one H_{c1J}^*, one obtains in Table 1 $H_{c1J}^* \approx H_{rf}^* \approx 10$ G for the steep slope, which than turns to $H_{rf}^* \approx 100$ G at higher rf–fields. The steep slope shows a H^*_{c1J} field decreasing with holding time; then according to (3) $H_{c1J} \approx 1/\lambda_J$ decreases due to an increase in $\lambda_J \propto 1/\sqrt{j_{cJ}}$. In other words, the already present WL become even "weaker" by widening due to additional H–segregation and precipitation. This causes (equa. (2)) $R_{res} \propto \lambda_J^2 \propto 1/H_{c1J}^{*2}$ [5,12]. Additionally , the density of the WL $\mu = 2 \cdot \lambda_J/a$ is increasing as indicated by the increase of $R_{res}(0)$ in Tables 1–3 in excess to $R_{res} \propto 1/H^*_{c1J}{}^2$. The slow slope with $H_{c1J}^* \approx 100$ G is typical for NbO_x WL identified in [5] for oxidized Nb. These stronger WL are opened by the weak WL with $H_{c1J}^* \approx 10$ G, i.e. fluxons enter those stronger WL via the weak WL. This may be attributed to geometry, i.e. they are further away from the surface and deeper in the bulk material. A more likely explanation is, that $H_{c1J}^* \approx 100$ G WL in Nb [12] are not penetrated directly above 1 GHz because the nucleation time for fluxons is on the order of nanosecs. However, if these fluxons are preformed in "weak" WL, they exist already and can enter without time lag into the stronger WL.

How can the observed R(T)-dependencies be explained [1,2,4] ?

Because $H_{c1J}(T)$ is temperature dependent roughly like $H_{c1J} \approx 1/\lambda_J(T) \propto (1 - T/T_c^*)$ H_{c1J} becomes negligible at T_c^*. Thus in our model field and temperature dependencies are combined.

Hydrides in Nb are normal conductors at $T \geq 1.0$ K and thus can become superconducting by proximity only. By proximity however, $\Delta/k\, T_c$ is reduced in the adjacent Nb for $T < T_c^*$.[13] That explains the reduction of the measured $2\Delta/k\, T_c$ in the regime below 3 K. Thus for RF–fields $H_{rf} \cong 1$ G, T_c^* (proximity) ≈ 3 K seems to hold, which may increase with increasing H–precipitation. Thus above 3 K such "weak" WL behave actually normal conducting above 1 G. For the strong weak links with $H_{c1J}(1.7K) \approx 100$ G, $T_c^* \approx 5$ K has been found [5], in line with NbO_x WL. Therefore, above 3 K and for RF–fields larger than 1 G only the slow field dependence remains, which is confirmed experimentally. The gap reduction by approximately 10% [4] in this regime may be related to oxygen precipitates [7], but further studies are needed.

In addition it should be mentioned that the loss mechanism described by WL yields $R_{res} \propto \omega^2$ (see equation (3)), which is also nicely confirmed experimentally.[2]

How do such H–precipitate weak links develop?

As discussed in Ref. [7], crack corrosion by oxidation propagates via expansion by Nb_2O_5 nucleation. For hydrogen in Nb the situation is similar: at the surface a hydride nucleus expands the lattice underneath, where further hydride ($NbH_{0.7}$) may precipitate as in crack corrosion. This mechanism forms NbH_x WL starting at the surface, where nuclei are most likely. Their growth depends on the diffusion rate in niobium at the given temperature, but the linear growth of $R_{res}(0)$ with holding time hints towards the nucleation and precipitation of and at WL as the rate limiting process. In line with this model is the

observation that no Q–disease occurs in reactor grade niobium with RRR ≈ 30–40. In this case the hydrogen is shifted away from the surface [7,9] by suboxides and therefore hydrides do not form in the penetration depth regime of $\lambda_I \approx 50$ nm. The same mechanism can be accounted for the reduced Q–degradation observed in anodized Nb-cavities of high purity Nb: anodization causes a compressional strain at the surface, shifting hydrogen out of that region and reduces the probability of hydride precipitation in the penetration depth, as was found experimentally in Table 3.

What is the amount of additional resistance caused by such WL?

To estimate equation (2) for hydride weak links, we use $H_{c1J} \approx 10$ G at 1.7K, yielding $\lambda_J(1.7K) \approx 80 \cdot \lambda_I \approx 3$ µm.[5] The leakage current of such a SNS –junction in fields above H_{c1J} is quite low [5]:

$$R_{bl} \approx 10^3 R_{bn} \approx 10^3 \cdot 2 \cdot 10^{-12}\ \Omega\ cm^2$$

which yields

$$R_{res} \approx \mu \cdot 10^{-5}\ \Omega\ (f/GHz)^2$$

Thus the observed values of $R_{res} \approx n\Omega$ result in

$$\mu \approx 2 \cdot \lambda_I / a \approx 10^{-4}\text{, i.e } a \approx 10^{-2}\ cm$$

This mean distance decreases than to below a ≈ 1 µm for heavier hydride precipitation with time (see Tables 1 - 3).

VI. CONCLUSION

The experimental data obtained for the time, temperature and RF–field dependence of the additional resistance caused by slow cooldown of high purity niobium cavities can be qualitatively and quantitatively explained by weak links, which develop as hydride precipitations in the penetration depth region of the cavity surface. The linear dependence of the additional resistance on RF–field reported in this contribution gave new clues about the shape of hydrides and the residual loss mechanism. As found for Nb, NbN, Nb_3Sn and cuprate superconductors [5, 12], also hydride precipitates in high purity niobium show up as WL, i.e. as Josephson junctions with critical entry fields of $H_{c1J}^* \approx 10$ G. The distance of these hydride precipitates can be estimated to be of the order of about 100 µm, which decreases to ≈ 1 µm for heavy hydride precipitation. This model is an alternative to the "island" and "surface layer" models proposed in [2], which have difficulties to explain the observed T–and RF–field dependencies with known NbH_x properties. For $H_{rf} \geq 100$ G at 1.7 K NbO_x WL show up via fluxons preformed in NbH_x WL at 1.5 K. Whether these NbO_x WL exist always in niobium, e.g. in larger depth (≥ 1 µm) has to be studied in the future.

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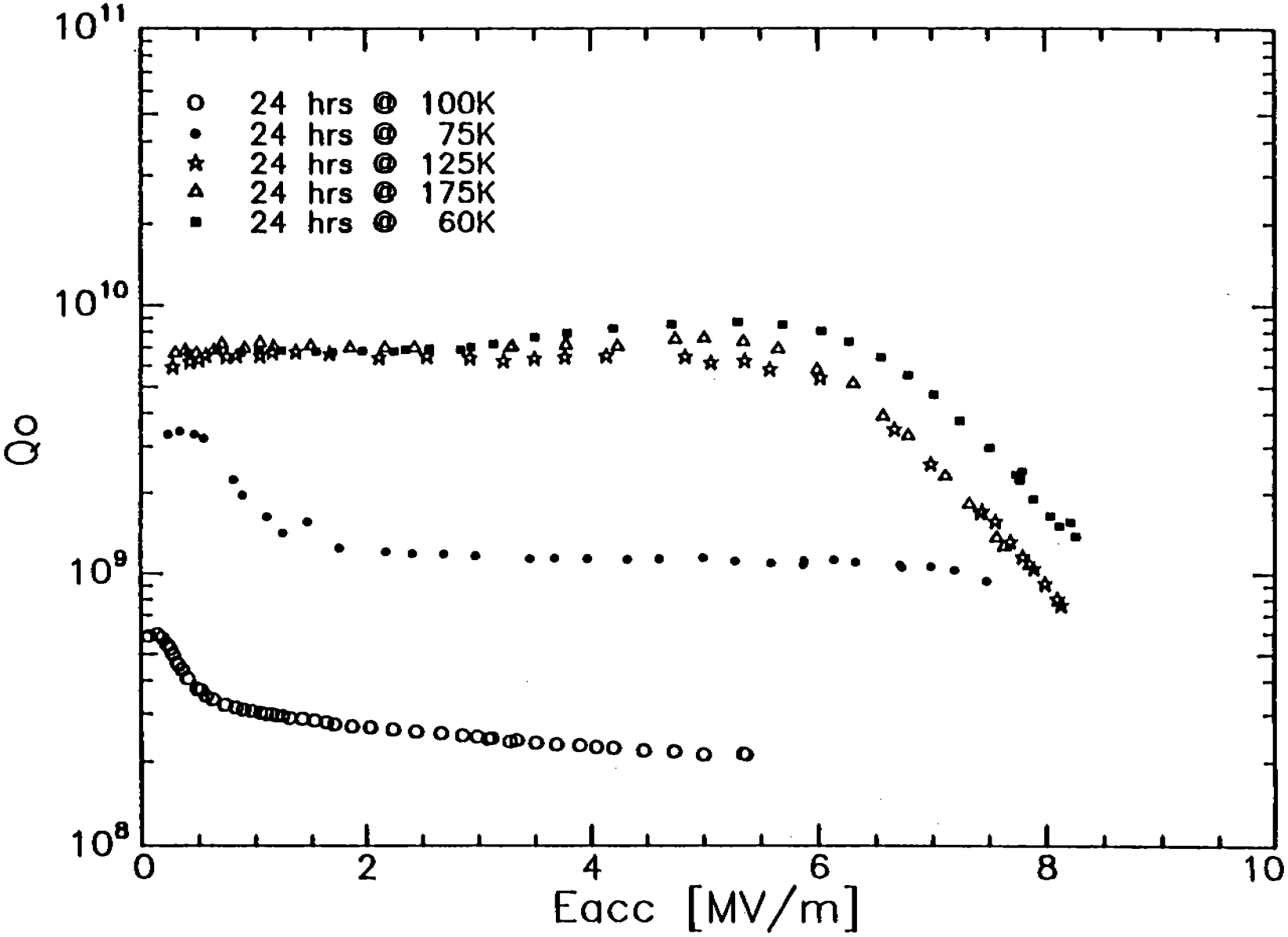

Figure 1 : Eacc – Dependence of Q – Degradation on "Holding"Temperature

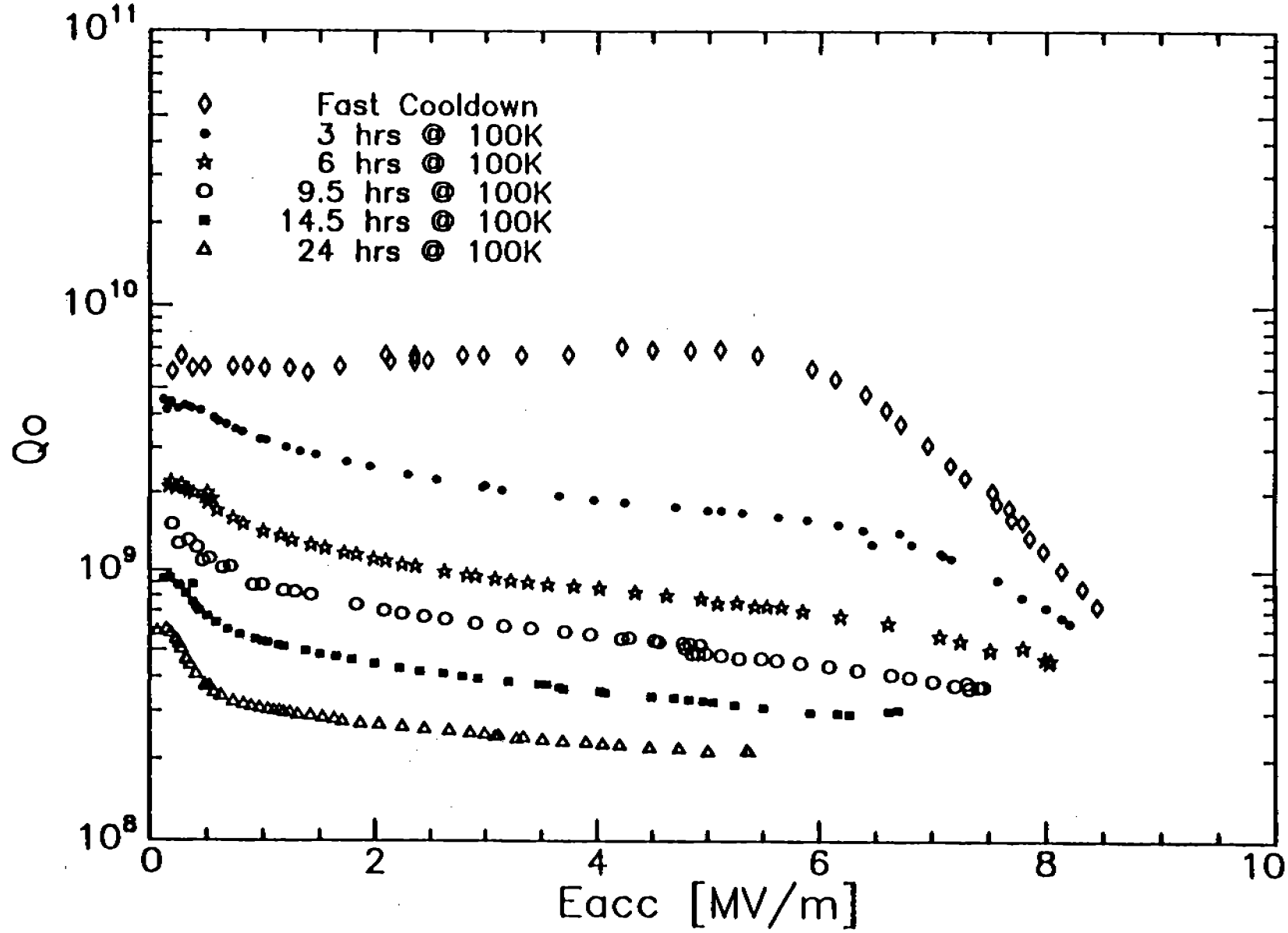

Figure 2 : "Holding" Time – Dependence of Q – Degradation

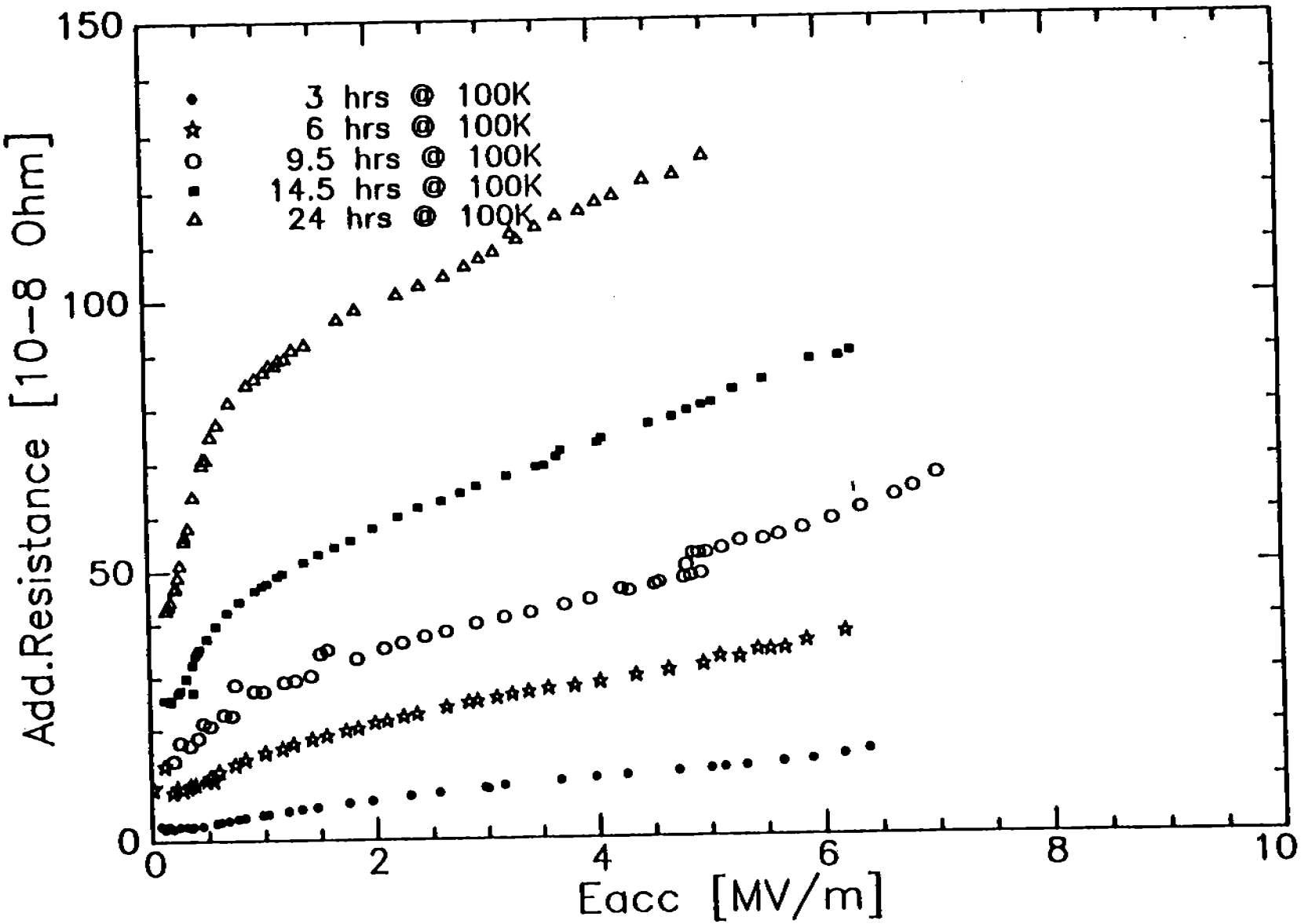

Figure 3 : Additional Surface Resistance Caused by Hydrogen Segragation