

Observation of Q-Degradation in Superconducting Niobium Cavities due to Cooldown Conditions*

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ABSTRACT

In the past two years several laboratories around the world have observed degradations of the Q-value of superconducting niobium cavities made from high purity niobium under certain cool-down conditions. Severe degradations have been reported for larger systems, when they were slowly cooled down or warmed up to temperatures $< 200\text{K}$.

A systematic study of the influence of surface treatments like chemical polishing, anodic oxidation and heat-treatment as well as the cooling conditions on cavity performance of cavities manufactured from niobium of different purity has been conducted.

Possible reductions of the Q-degradations by anodic oxidation have been explored. Results of these investigations are reported and changes in material parameters as caused by the degradation are discussed.

INTRODUCTION

In 1989, R. R \ddot{o} th¹ observed a significant degradation of the Q-value of a 1500 MHz cavity made from high purity niobium after it had been kept at nitrogen temperature for several days after the initial test in superfluid helium. A temperature map indicated that these unexpected losses were distributed uniformly over the whole cavity surface. Other laboratories^{2,3} observed similar degradations in Q-value when cavities were kept for longer periods of time at temperatures between 200K and 50K.

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Because of the important impact of this observation on accelerator projects involving superconducting niobium cavities, a large number of investigations were carried out at various laboratories.^{4,5,6} The initial hypothesis expressed in¹ of precipitation of the Nb-hydride phase was supported by additional experimental data provided by other laboratories. The detrimental effect of hydrogen precipitation in niobium has been known for many years.⁷ It was experimentally verified that a hydrogen degassing of the niobium at temperatures above 800° C eliminated the Q-degradation phenomenon,^{3,4,5} but that extensive chemical polishing reversed the process. A summary of these investigations is provided at this workshop.⁸

At CEBAF a study is being conducted to first verify the Q-degradation under certain experimental conditions and secondly to find a possible cure for the increased losses, which could be easily applied to complex cavity systems. We chose to look into the process of anodic oxidation and this paper reports on the results obtained with several cavities.

CAVITY PREPARATION AND TESTING

For the investigations single cell and five-cell 1500 MHz cavities of the CORNELL/CEBAF-design were used.⁹ The cavities were manufactured of niobium from four different suppliers: reactor grade niobium with an RRR-value of ≈ 40 by Cabot Corporation and high purity niobium with RRR-values ≥ 250 supplied by W. C. Heraeus, Teledyne and Fansteel. After manufacturing all cavities were chemically treated and assembled in a standard way:

A. Buffered chemical Polishing

After degreasing in a caustic solution combined with ultrasonic agitation the cavities were chemically polished in a buffered 1:1:1 solution of hydrofluoric (49%), nitric (65%), and phosphoric (85%) acids at room temperature for several minutes resulting in the removal of $\approx 60 \mu\text{m}$ of niobium from the surface. The cavities were thoroughly rinsed with ultrapure water with ultrasonic agitation for one hour with several exchanges of the rinse water. A final rinsing with reagent grade methanol

was carried out in a class 100 cleanroom, where the assembly of the variable input coupler and the transmission probe took place. The cavities were then attached to a cryogenic test station using extreme precautions to avoid particulate contamination of the inner cavity surfaces.

B. Anodizing

After a cryogenic test with the cavity was completed, the niobium surfaces were renewed by removing 3–4 μm of niobium by buffered chemical polishing as described above, rinsed in ultrapure water and subsequently anodized with a solution of 10% ammonium hydroxide. At a voltage of 100 V and a current density of $\approx 0.8 \text{ mA/cm}^2$ an amorphous Nb_2O_5 - layer of $\approx 2000 \text{ \AA}$ was grown, after the current had decayed to 1/10 of its initial value at 100 V. In one case, the oxide layer was only grown to 1300 \AA (65 V).

Rinsing in ultrapure water and methanol as described above followed prior to assembly in the cleanroom.

C. Testing

Before cooldown to 4.2K the cavities were evacuated to a vacuum of $\leq 6 \times 10^{-7}$ torr. The standard cooldown (“fast”) took place in less than one hour and the static external magnetic field in the vicinity of the cavity was shielded to less than 10 mG by an active compensation coil in combination with two layers of μ -metal.

During the experiments (a) the temperature dependence of the surface resistance at low RF-fields ($E_{peak} \approx 2 - 4 \text{ MV/m}$) was measured between 4.2K and 1.7K and (b) data for the variation of the Q_0 - value with increasing peak surface electric fields were obtained.

For the experiments, during which the cavities were held at intermediate temperatures ($50\text{K} \leq T \leq 120\text{K}$), the cavity temperature was monitored by two Si-diodes attached to the outside of the cavities. Typically the natural warm-up from 50K to 100K happened in ≈ 20 hours in our cryostat.

EXPERIMENTAL RESULTS AND DISCUSSION

Examples for the temperature dependence of the surface resistance for “bare” niobium and anodized niobium are shown in Figures 1 and 2. Figures 3 to 8 show examples for Q vs. E for “bare” and anodized niobium cavities after “fast” cooldown and a warm-up to an intermediate temperature of 100K for ≈ 20 hours.

The results of our investigation can be summarized as follows:

- a). A cavity fabricated from reactor grade niobium with an RRR-value of ≈ 40 did not exhibit any degradation in Q -value due to warming up to intermediate temperatures $\leq 145\text{K}$ (see Figure 3).
- b). Severe degradations were observed in cavities fabricated from high purity niobium with RRR-values ≤ 250 , when the cavities were kept at temperatures between 50K and 120K for > 16 hours (see Figures 4 and 6).
- c). A warm-up to 170K from 4.2K and maintaining this temperature for 16.5 hours did not result in a Q -deterioration for a five-cell cavity (see Figure 7).
- d). A degradation can be fully recovered by warm-up to room temperature (see Figures 5 and 7).
- e). An electropolished cavity ($120\ \mu\text{m}$) was annealed at $710^\circ\ \text{C}$ for three hours and subsequently electropolished an additional $5\ \mu\text{m}$ as a final step; no Q -degradation was observed.¹³
- f). This cavity was subsequently chemically polished in a standard buffered solution resulting in a removal of $\approx 60\ \mu\text{m}$. A degradation of the Q -value was observed, but less severe than in a cavity, which did not have an intermediate vacuum annealing (see Figure 8).
- g). Anodic oxide layers of a thickness $\geq 1300\ \text{Å}$ reduce the amount of degradation to $< 50\%$; thicker layers of $d \geq 2000\ \text{Å}$ seem to be more effective. As an experimental result we observed somewhat higher residual resistances with anodic layers.
- h). $R_{BCS}(T)$ of a degraded surface (“bare” niobium) cannot be expressed by a

single superconducting phase in the temperature range of $4.2\text{K} \geq T \geq 1.9\text{K}$ (see Figure 1). Multiple phases are generated within the penetration depth and the residual resistance increases to 240 nOhm - 800 nOhm. Deviations from the BCS-behavior are most pronounced in the range $2.9\text{K} \geq T \geq 2.5\text{K}$ (see Figure 1) and the experimental data cannot any longer be fitted to the BCS theory as supplied by J. Halbritter's surface resistance program.¹⁰

- i). Anodized surfaces show single phase (exponential) behavior of $R_{BCS}(T)$ even after a warm-up to intermediate temperatures (see Figure 2). With material parameters for pure niobium, T_c , London penetration depth and coherence length, the experimental data can be fitted to the BCS-surface resistance with the mean free path ℓ and the band gap as a fit-parameter. The mean free path around the interface between the anodized film and the bulk niobium is increased by about a factor of two in comparison to a "virgin" surface.
- j). As mentioned above, with electropolished or anodized cavities no or reduced Q-degradations have been observed, when the cavities were kept at intermediate temperatures. However, the mean free path as a fitting parameter is greatly effected by the warmup and subsequent cooldown and can be reduced by factors ranging from 3 to 20 depending on the conditions. This might be interpreted as a precursor of hydrogen precipitation still weak enough for not effecting the cavity Q-values significantly.

We are speculating that the additional oxygen introduced into the surface layer by the anodizing process prevents the hydrogen in the bulk from precipitating into the niobium hydride phase; after all reactor grade niobium with a large concentration of interstitially dissolved oxygen does not show Q-degradations.

Multi-phase behavior of degraded surfaces has been reported in⁵ and the experimental data have been explained by a model of a thin surface layer of a poor superconductor on top of the bulk niobium. As discussed in⁸ a possible mechanism for the Q-degradation is the hypothesis that the hydrogen precipitates into "islands." A quantitative analysis of the experimental data based on this hypothesis would fol-

low a model as discussed in;¹¹ in this case the niobium matrix was “polluted” by oxygen/suboxide clusters, which resulted in a smearing out of the density of states. It is presently planned to try to apply such a model to the experimental data.

CONCLUSION

Our experiments provide some evidence that anodic oxide layers on niobium surfaces of high purity niobium are capable of significantly reducing Q-degradations due to precipitation of the niobium hydride phase. The benefits of an anodic layer should show up even more pronounced at lower frequencies, where the losses in a cavity operating at 4.2K are dominated by the BCS-losses. It is of interest to investigate the long term stability of anodic layers in the presence of field emission loading and such efforts have been initiated. Thicker Nb_2O_5 - layers seem to be more effective. This observation coupled with the fact that the hydrogen concentration in anodic layers are largely reduced¹² suggests that by diffusing oxygen into the surface by moderate “in situ” heating of an anodized cavity might further reduce the danger of Q degradations.

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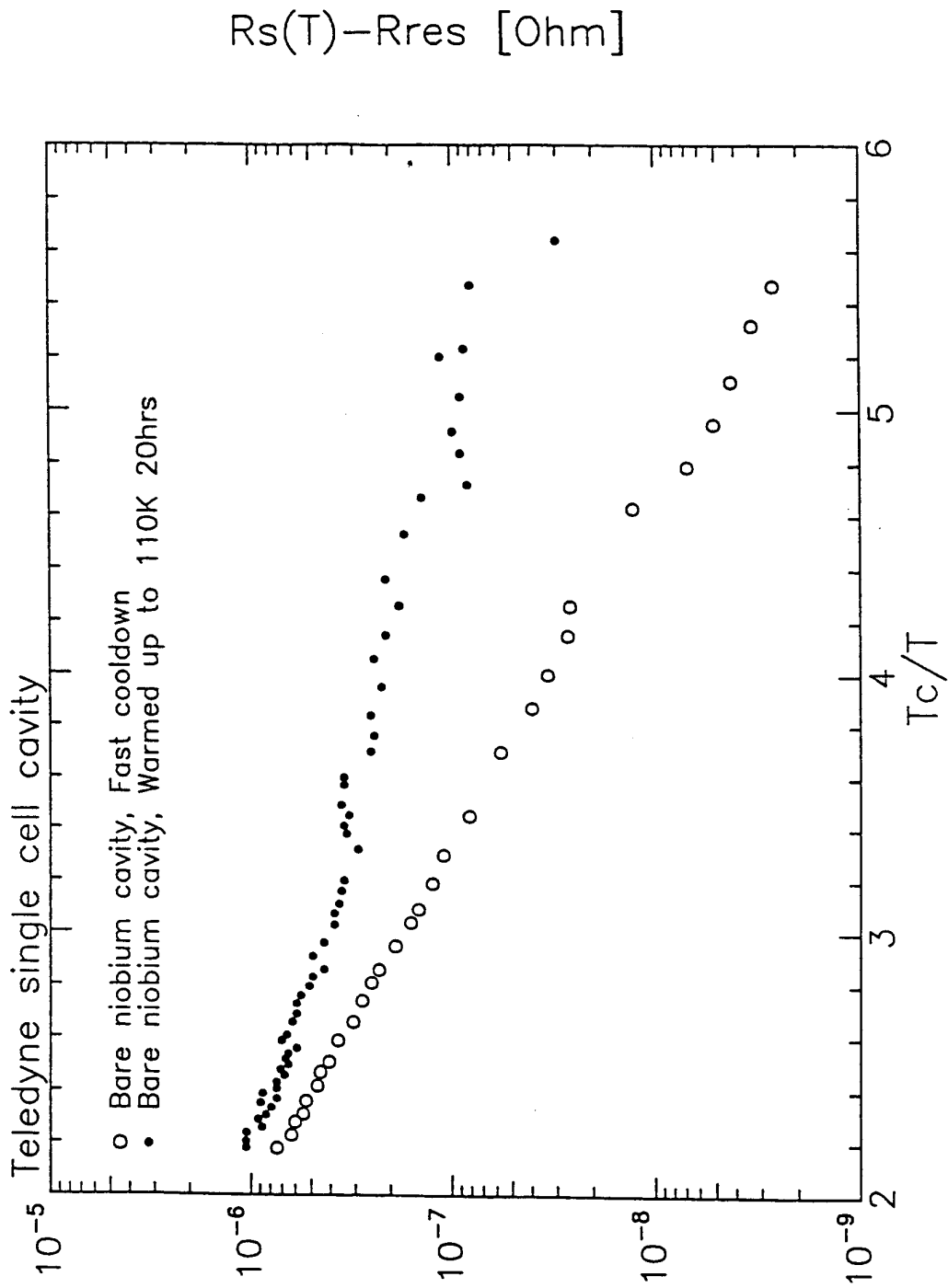


Fig. 1: Temperature dependence of $R(T) - R_{res}$ for "bare" niobium showing the non *BCS*-like behavior for cavity held at intermediate temperatures

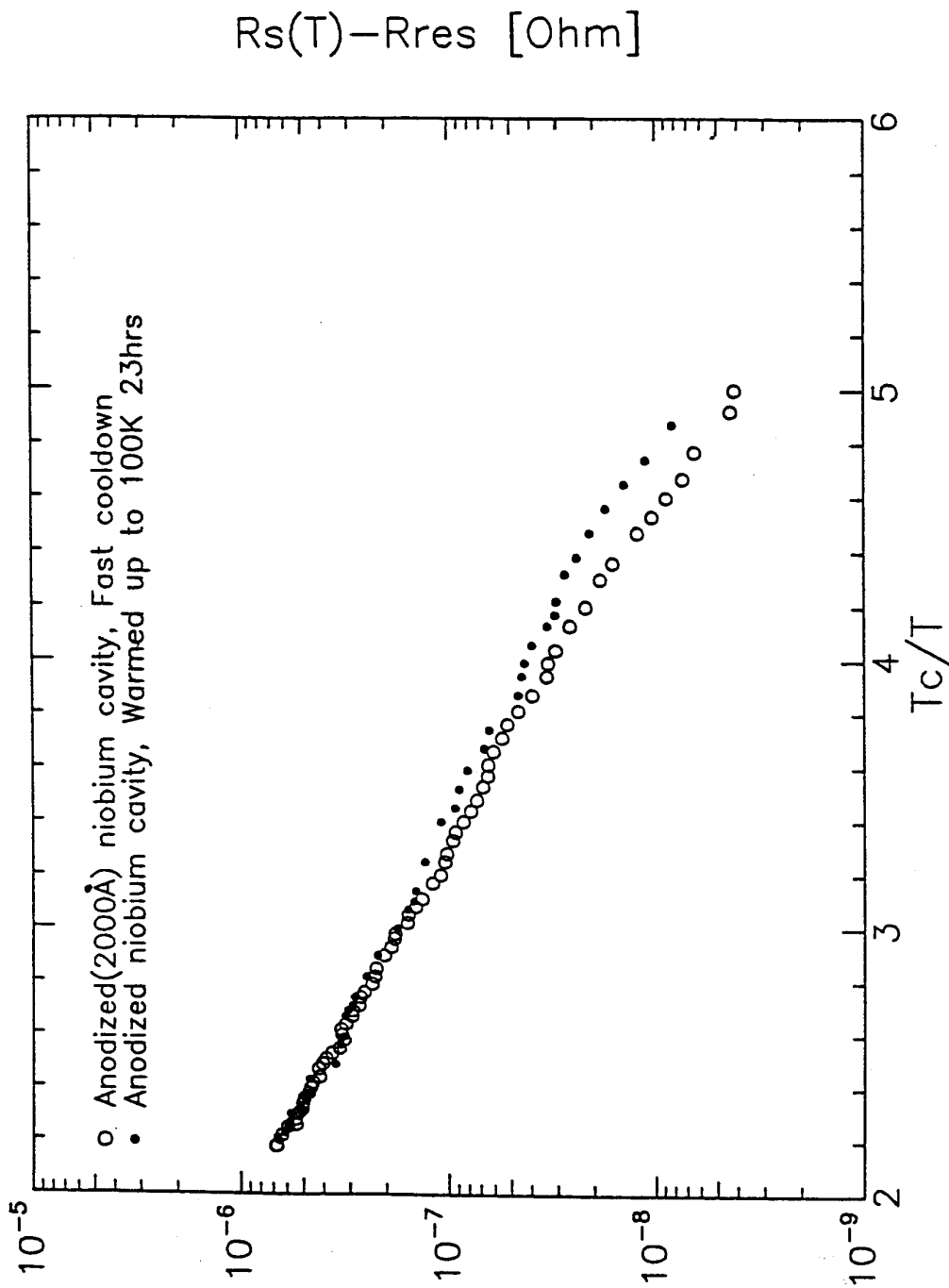


Fig. 2: Typical behavior of temperature dependence of $R(T) - R_{res}$ for anodized cavity between fast cooldown and warmup to 100K

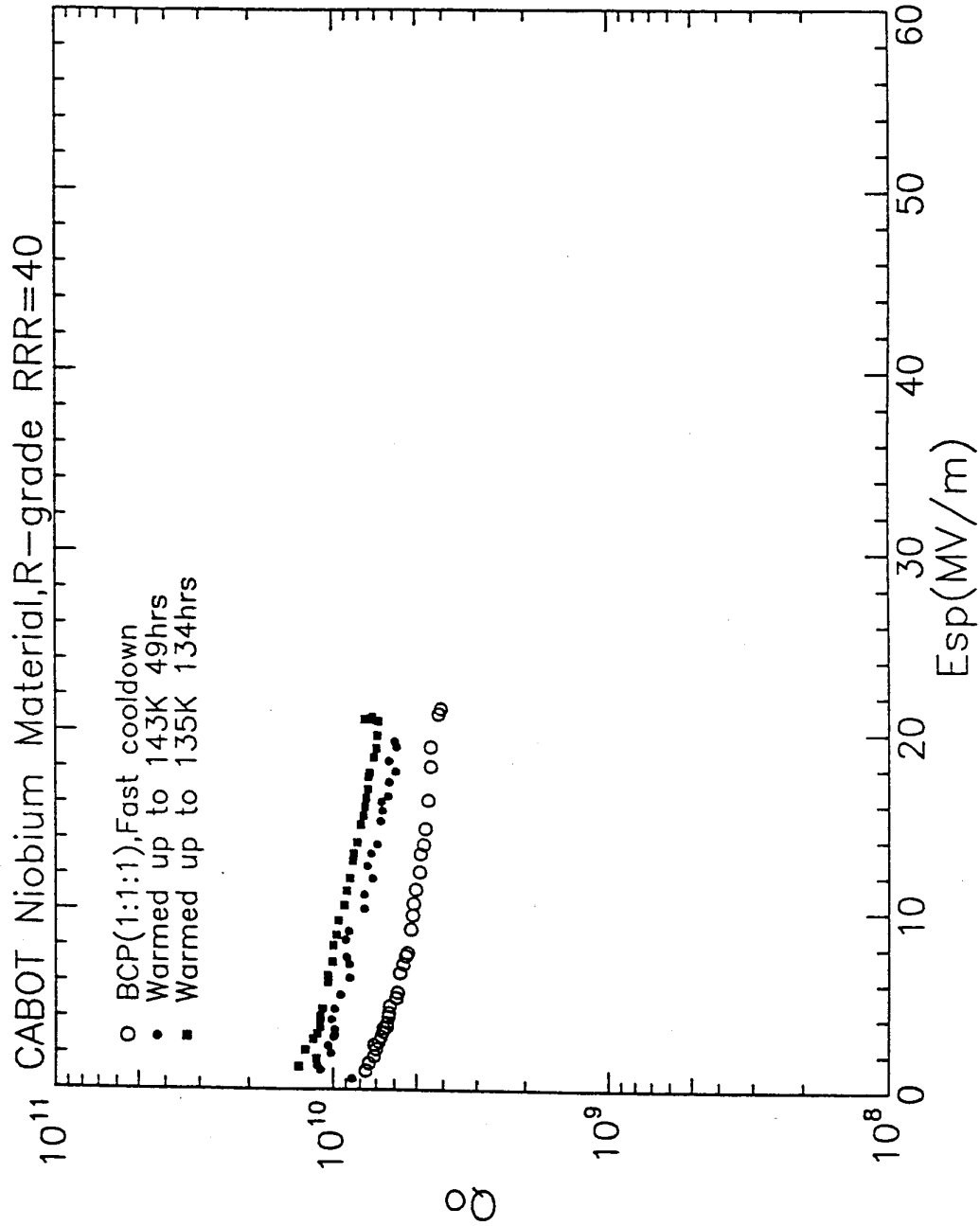


Fig. 3: Peak surface electric field E_{sp} vs. Q_0 for reactor grade niobium under different cooldown conditions

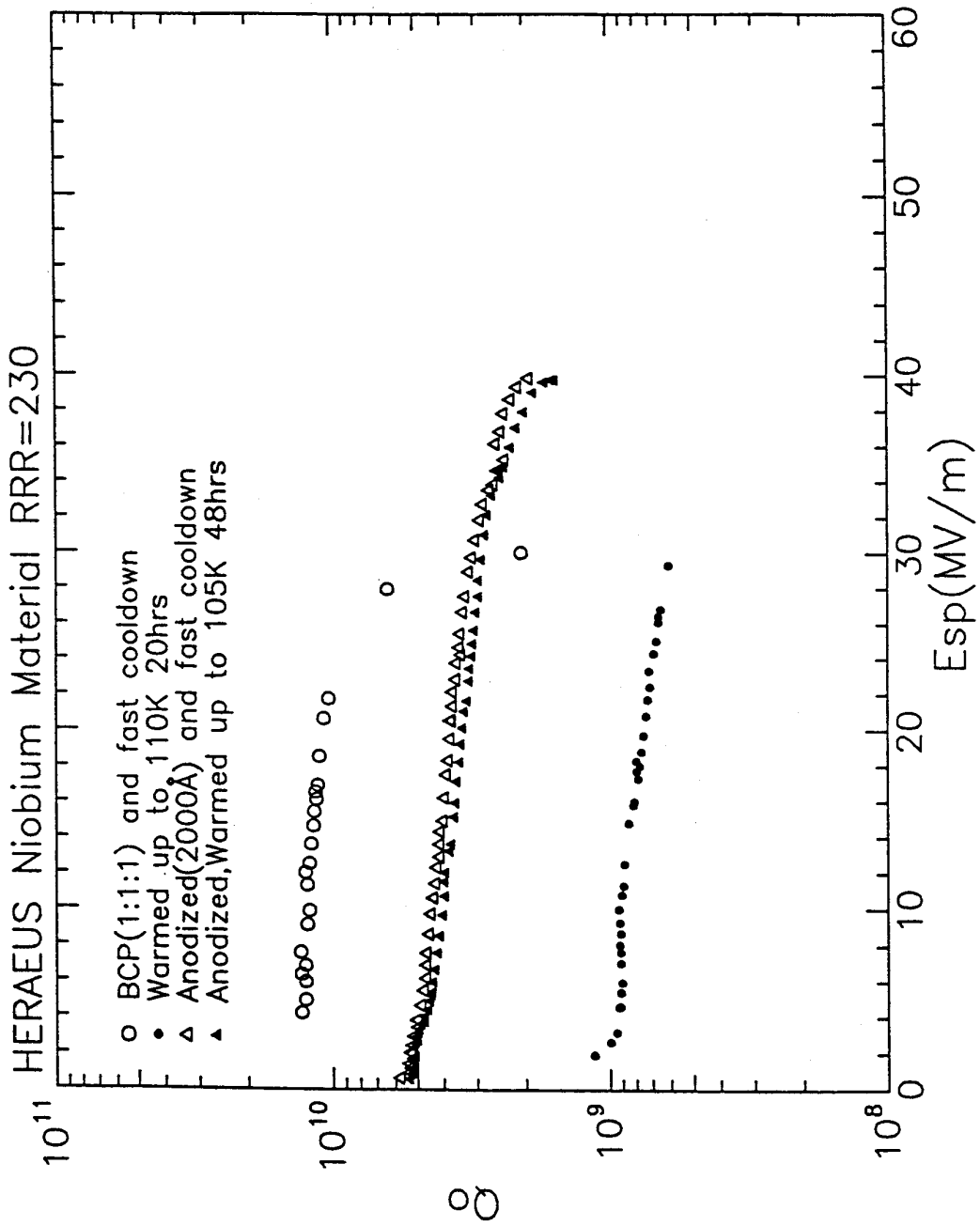


Fig. 4: E_{sp} vs. Q_0 for HERAEUS Nb material under different cooldown conditions

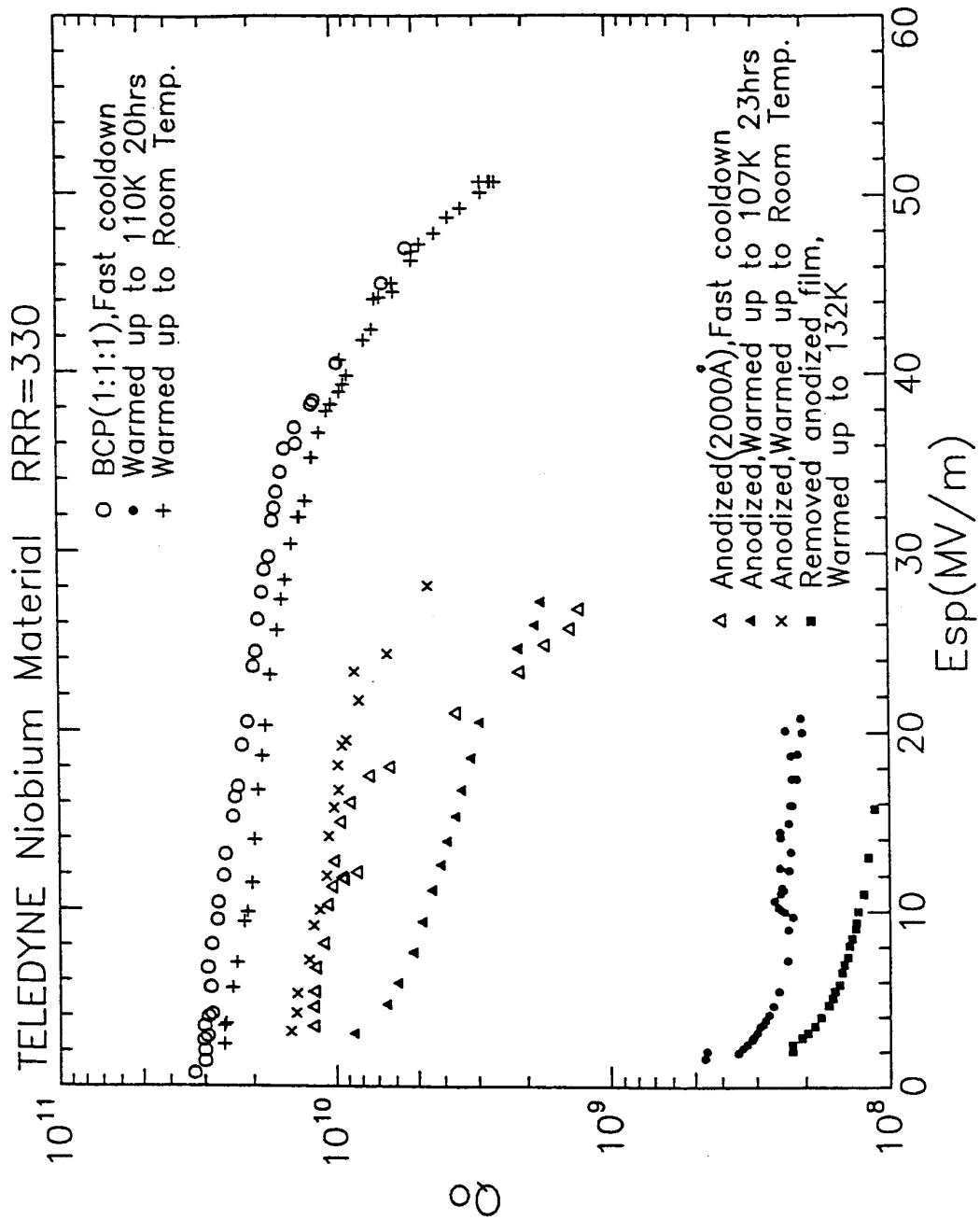


Fig. 5: E_{sp} vs. Q_0 for TELEDYNE Nb material under different cooldown conditions

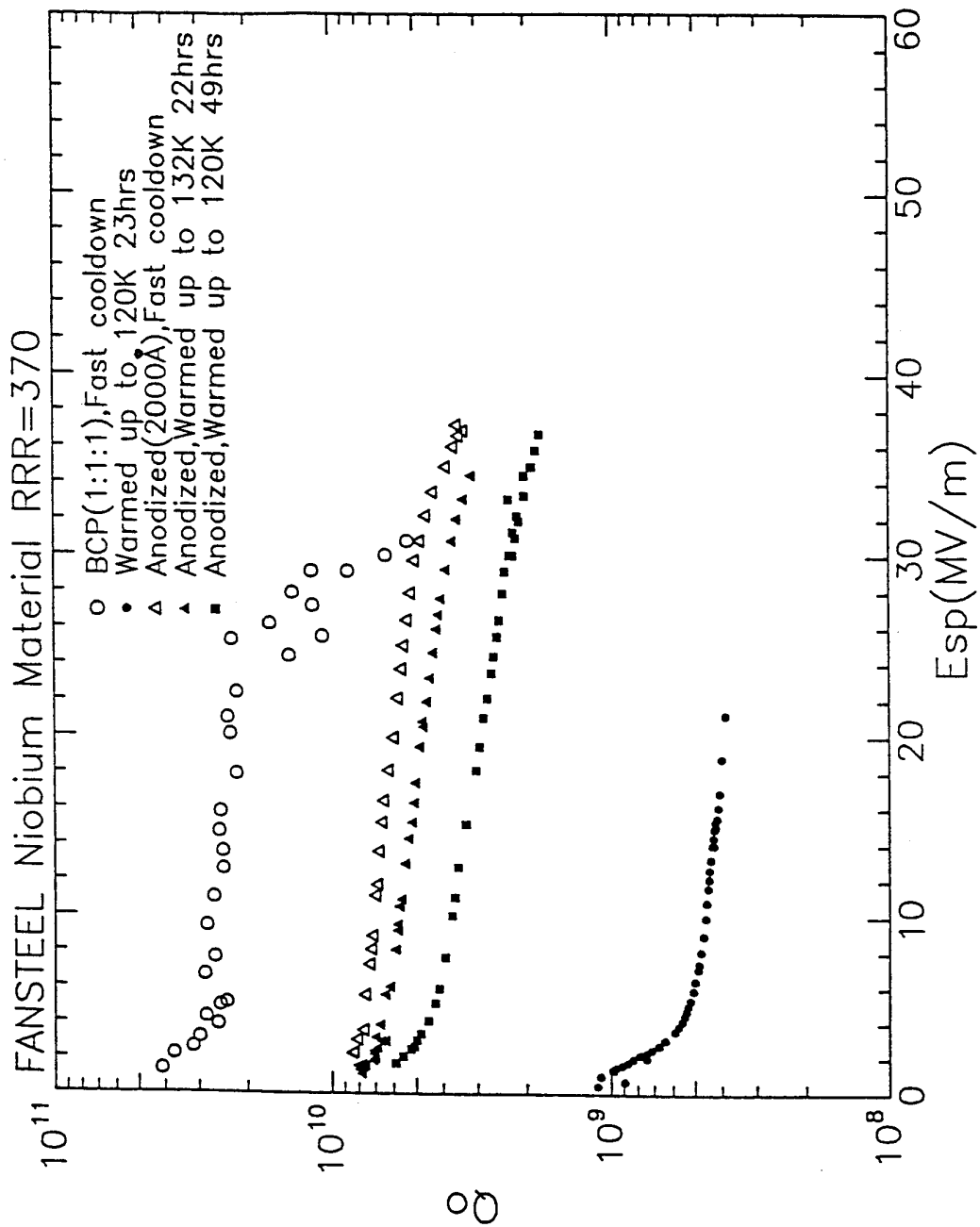


Fig. 6: E_{sp} vs. Q_0 for FANSTEEL Nb material under different cooldown conditions

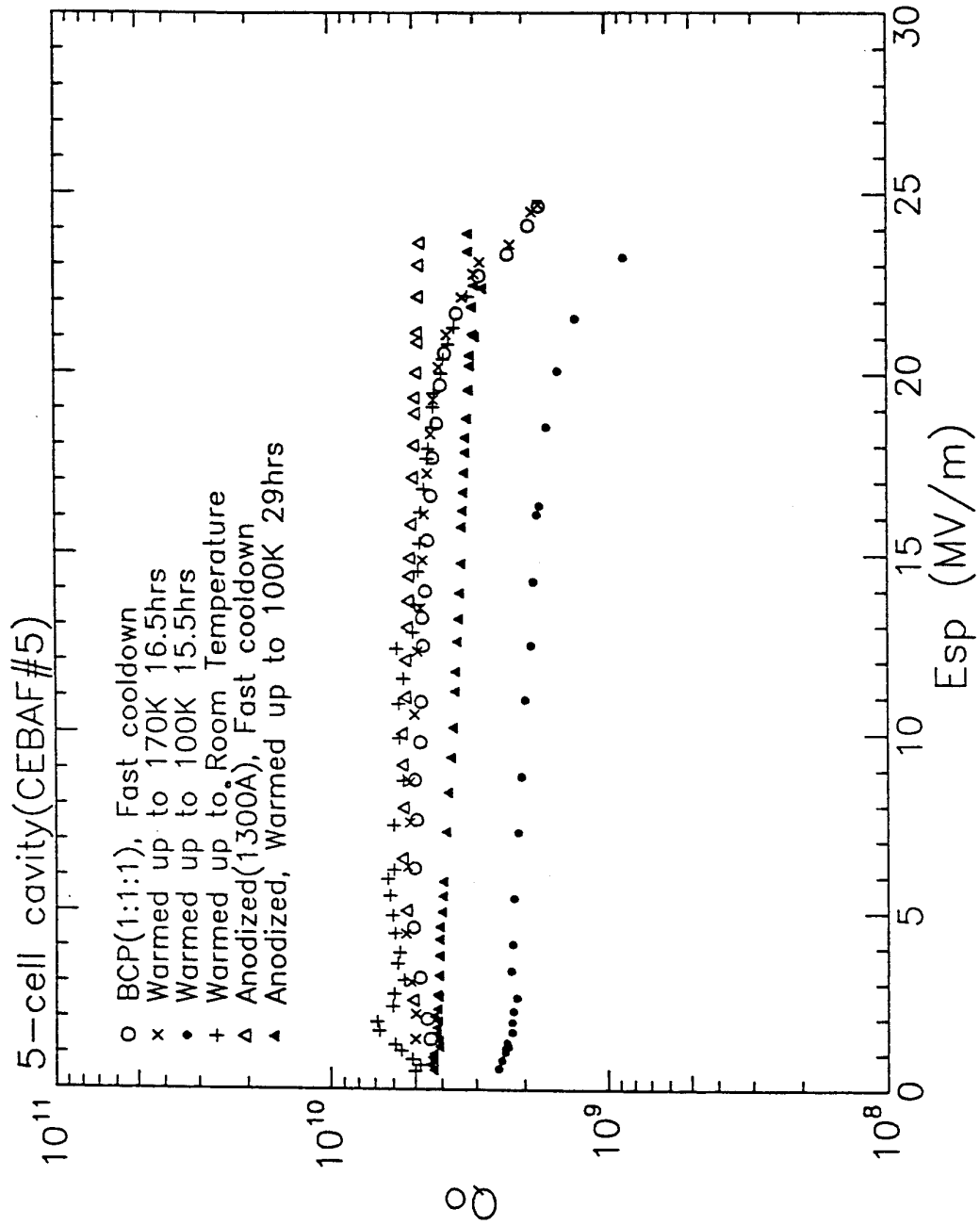


Fig. 7: Experimental Q_0 vs. E_{sp} dependences measured on an anodized 5-cell cavity

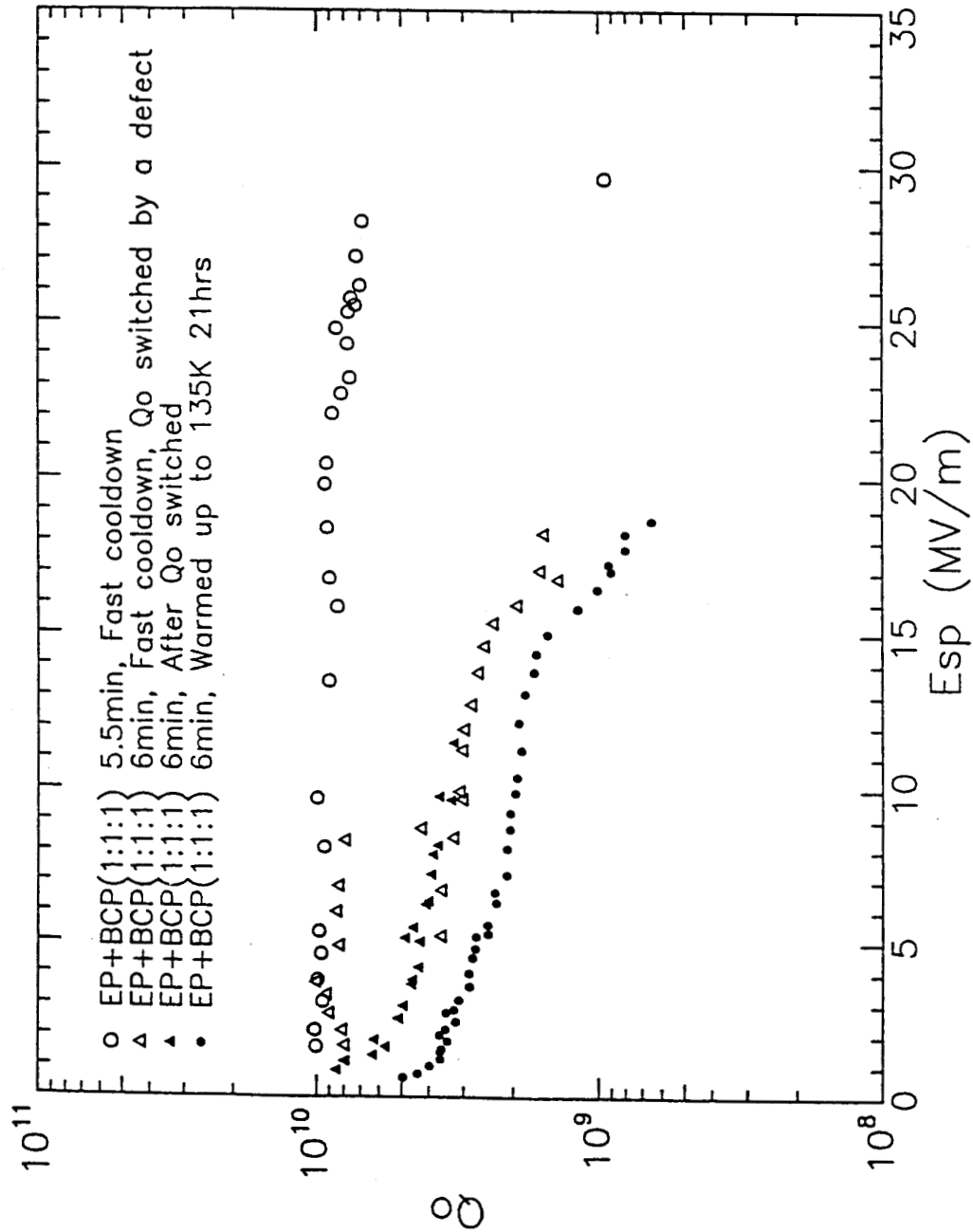


Fig. 8: Q_0 vs. E_{sp} for an electropolished, single cell cavity after various chemical treatments. After chemical treatment in a buffered solution for several minutes, Q-degradation was observed for the originally uneffected cavity