

Proposal for an R&D Plan towards better Understanding of the Electropolishing of Niobium Cavities

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During the last year issues concerning the electropolishing of niobium cavities have been discussed at various meetings such as the TTC meeting at DESY in March 2005, the ILC Snowmass workshop, the SMTF workshop at FNAL in October 2005 and now at the TTC meeting in Frascati.

A summary report about Electropolishing activities worldwide will be published in the near future [1]

It has become very clear that the major problems have to do with contamination of the electropolished surfaces as well as with unpredictable hydrogen dissolution, resulting in some cases in “Q-disease”. Better “on line” monitoring of the process seems to be a desirable QA/QC activity.

A. Contamination and Rinsing studies

Already in 1971, when the electropolishing process was developed at Siemens AG in Germany [2], it was recognized that the electropolished surfaces were contaminated with residue from the polishing bath mixture of hydrofluoric acid (10 parts) and concentrated Sulfuric acid (85 parts) and that rinsing of the surfaces was a very important step in the surface preparation. At Siemens rinsing in a diluted solution of hydrogen peroxide was as well applied as a subsequent step/several steps of anodizing in ammonium-hydroxide solution and stripping the pentoxide in hydrofluoric acid under ultrasonic agitation (oxipolishing) The rinsing in peroxide solution had the effect of fully oxidizing reaction compounds on the surface to soluble chemical products.

Electropolished surfaces were investigated with XPS by Grunder [3] at the Kernforschungszentrum Karlsruhe and he found – besides various states of oxidation – sulfur in the form of sulfate and fluorine F^- . The sulfur contamination, which seems to be obvious by the odor of the surfaces (even after evacuation and exposure and after high temperature heat treatment), could be totally eliminated by oxipolishing, whereas boiling the samples in water reduced the sulfur contamination by a factor of 10 and converted the sulfate state to a sulfide state. The fluorine contamination could not totally be removed by either treatment, but was significantly reduced.

During the TRISTAN R&D and production phase K.Saito [4] developed – starting from the Siemens process – “continuous horizontal” electropolishing, which is the presently used technique for multi-cell elliptical cavities in most laboratories (exceptions are Cornell University, where vertical electropolishing is developed and at Argonne National Lab, where the Siemens intermittent electropolishing is applied). During the mass production, sulfur contamination of the bath was encountered at a rate of 4 mg/l of solution for a 80 micron material removal on a 5-cell TRISTAN cavity. It was promoted by the buffing abrasive contamination in the EP acid, which was applied to remove mechanically surface defects prior to the heavy EP (80 micron). Investigations showed, that the precipitation of sulfur in the bath could be reduced by rinsing the system with CCL_4 , CS_2 or acetone or by filtration with activated carbon. Consequently, KEK added a pre-EP (3micron) process before the heavy EP (80micron) in order to remove the contaminated surface layer from the buffing. The acid used for pre-EP was only used for this purpose. The TRISTAN cavities were treated in a batch of four cavities. EP acid was replaced every four cavities EP (80micron). The TRISTAN cavities apparently did not suffer from sulfur surface preparation, because KEK used new EP acid for the final EP (10micron) after the EP acid contamination problem and rinsed in peroxide solution. However, they observed a soft MP (2-point 1st order) barrier around $E_{acc} \sim 7MV/m$ in every cavity, which might still indicate a contamination problem.

Sulfur contamination in the electropolishing system at DESY has been reported since quite some time [5] and it is suspected that sulfur deposits on the surface are in some cases responsible for early onset of field emission at fields ≤ 25 MV/m. This suspicion is based on a comparison of repaired cavities from cryomodule 3, which were prepared by BCP in the same time period as the EP cavities and did not show field emission, excluding problems with the HPR system or during assembly. Sulfur can be dissolved in alcohol as initial tests have shown.

In the context of the CARE/JRA1 in work package 5.1, carried out at Saclay, optimization studies on electropolishing solutions and parameters are undertaken. In these studies it has also been found that sulfur is a contaminant on the polished surfaces and in the polishing system [6]. The generation of sulfur is inherent to the polishing mixture and the process.

- *Studies of surface contamination of EP surfaces with appropriate surface analytical methods are highly desirable and by applying different rinsing procedures one should be able to re-confirm the results from 3 decades ago.*

- *In parallel, rinsing studies on single cell cavities should be carried out to optimize cavity performance.*
As a reasonable procedure one can employ a reference cavity with a baseline performance, which will be in subsequent steps always electropolished by a chosen amount, eg. 10 micron, and rinsed differently. By carrying out at least 3 experiments per rinsing procedure, one should get some limited statistics.
An alternative procedure could be to use several different cavities for each rinsing activity. However, one has to bring each of these cavities to high performance, possibly multiplying the amount of effort going into this activity.

B. “Q – disease”

In 1991 it was discovered [7] that cavities made from high purity niobium can suffer from unexpected losses of several orders of magnitude, if they are exposed to temperatures between 150K and 75 K for longer periods of time. This increase in losses was in subsequent investigations at several laboratories identified as caused by precipitation of hydrogen in the form of the α -hydride; it happens, when interstitially dissolved hydrogen in the niobium matrix can cluster into this hydride. The hydrogen enters into the metal during the chemical surface treatment of the niobium either by BCP or electropolishing. Remedies against the uptake of hydrogen/Q-disease are a surface treatment at low temperature (<15 C of the acid bath) in the case of BCP, shielding of the cathode with a cathode bag and possibly adding a small amount of nitric acid [8] to the acid mixture in the case of electropolishing. In general, hydrogen can be degassed in UHV at temperatures $\geq 600\text{C}$ (hydrogen degassing procedures applied to RRR niobium range from 600C for ~ 10 hrs to 800 C for 3 hrs) , preventing Q-disease; also, a rapid cooldown of the cavity through the dangerous temperature region prevents the precipitation of residual hydrogen into hydrides. However, this procedure might not be applicable for large cryo-systems such as an ILC cryomodule. Therefore it is important to eliminate the possibility of additional losses caused by this phenomenon; a degassing heat treatment as has been applied e.g. to the cavities during the TRISTAN construction, would contribute to additional costs in the cavity preparation. It has been reported [9] that in some cases Q-degradations were encountered unpredictably on 9-cell TESLA type cavities, even though the electropolishing procedures had been applied identical to cavities, which did not suffer from degradation.

At KEK, where presently a very successful single cell program is being pursued with a modified surface treatment procedure consisting of centrifugal barrel polishing, heat treatment and electropolishing, no Q-disease has been identified. However, prior to this outstanding results, cavity performances were very mixed and only after the appropriate electropolishing conditions were re-established at the electropolishing shop have these excellent results been obtained [10]

It seems to be very important to understand the conditions, under which Q-disease is encountered. For this to happen, the following R&D activities are proposed:

- Each test of an electropolished cavity should be tested for Q-disease, meaning, that after an initial test, which might not show a Q-degradation because of fast cooldown, the cavity should be held for ~ 12 hrs at a temperature around 120K and then re-cooled again. Such a test sequence will give a baseline for the frequency of Q-degradations due to precipitation of hydrogen.

- Another possible source of non-reproducibility could be encountered during the rinsing procedure of the cavities at the end of an electropolishing cycle. The cavity surface is covered with an acid film (and possibly there is quite a bit of acid trapped in piping and fixturing volumes, which cannot be drained very well), which will react exothermically with the rinsing water and possibly raise the surface temperature. It is known from experiments with bcp [11] that a surface temperature above ~ 30 C increases the amount of hydrogen pick-up by the niobium. Single cell cavities, which usually do not show Q-disease (after fast cooldown) are easier to handle and might be less vulnerable to this potential source of hydrogen pick-up.

In addition, the niobium, when covered with a thin acid film containing hydrofluoric acid, has no protective oxide layer, which can prevent the pick-up of hydrogen. This situation is the same at the beginning of an EP cycle, where EP acid is put into the cavity without any voltage potential, which can prevent the hydrogen-ion from entering into the niobium material.

It is recommended that a series of tests be made, which explore these possible sources of hydrogen dissolution in the niobium.

- The electropolishing process as applied presently is done at an acid temperature of $\geq 30\text{C}$, a temperature, which for the bcp process is significantly too high. The hydrogen emanating from the process is being shielded from the non-exposed part of the cavity (–the part sticking out of the acid), however there is hydrogen generated in the

acid also. If the distance of the cathode to the anode (cavity) is insufficient, the hydrogen stream in the acid can reach the niobium surface and possibly can be dissolved in the material. This should not happen, if the set-up is optimized and the hydrogen is prevented from reaching the niobium surface, which is either inside the acid bath or outside (–the top part). As reported in [10], the appropriate adjustment of the cathode distance and hydrogen screen is a very important parameter for successful electropolishing conditions.

It is recommended that a series of electropolishing tests (most efficiently with single cell cavities) with modified cathode and cathode screen distances is undertaken and the cavities are checked for Q-disease

Hopefully, the result of these tests will be an optimized electropolishing configuration, which does not lead to hydrogen pick-up by the niobium surfaces.

C).” On-line” monitoring and control

It has been experienced that the material removal on a typical cavity surface is non-uniform. Even though the aluminum cathode is shielded at the irises and the major voltage drop supposedly happens close to the anode, there is nearly a factor of 2 difference in material removal between iris and equator of a cavity (the smaller amount is removed at the equator). Whether this difference is due to different polarization curves in the two cavity regions or due to temperature gradients or due to different acid flow patterns is not clear. It has , however, been established recently [12] that a shaped cathode leads to a more uniform polarization curve over the entire surface and should result in a more uniform material removal. Besides an experimental program, which can explore such improved conditions with cavity tests, DESY has recently acquired a computer simulation program from the University of Bruxelles, which can be used to simulate different polishing conditions and configurations as well as flow patterns.

During the electropolishing process the concentration of hydrofluoric acid, which is essential for good polishing conditions, is reduced and the polishing conditions are changing. For maintaining reproducible polishing conditions it seems to be important to implement in any EP

system an “on-line “ monitoring of HF concentration and of the polarization curve.

- *It is recommended to explore to its fullest the simulation program (this is happening already at DESY)*
- *It is recommended to implement in any existing EP system “on – line” monitoring and data logging of polarization curves and HF concentrations*
- *It is recommended to investigate with an experimental program the causes for the non-uniform material removal by e.g. modifying the temperature distribution, the acid flow pattern, the cathode shape, the cathode shielding or the location and number of current leads.*

D). Acid Composition

It has been reported at the TTC meeting in Frascati that at least one delivery of pre-mixed acid (“Honeywell Mixture”, 10 parts HF, 85 parts H₂SO₄) to DESY in summer of 2005 had an unusual composition [9] and behaved differently during the electropolishing. It has been “hypothesized”, that exposure of the mixture to hot weather during the delivery caused the modifications.

DESY is pursuing the industrialization of the electropolishing process with the company Henkel, mainly with single cell cavity preparations so far. Henkel is mixing the EP solution “in house” with nominally the same ratio of acids as in the “Honeywell mixture”, however, the company reports a much more ”active” mixture.

- *It is recommended that the subject of acid composition and different behaviour of nominally the same mixtures will be addressed; most likely, this can be done by chemical analysis and comparison of polarization curves measured on samples under identical conditions.*

The table below summarizes the proposed R&D activities:

Problem	Proposed Activity	Priority
Contamination Field Emission	Rinsing studies with samples (XPS,SIMS...) Rinsing studies with single cell cavities	1
Non-reproducible appearance of Q-disease	Test any electropolished cavity for Q-disease	1
	Can overheating during initial rinsing cause Q-disease?	2
	Optimizing studies for cathode/screening geometry	2
Monitoring and control	Implementation of “on line” monitoring and data logging of polarization curves and HF concentrations	1
	Exploitation of EP simulation program	1
	Investigation of the cause for non-uniform material removal	2
Acid composition/ decomposition	Chemical analysis of acid mixture (nominally equal)	2
	Polarization curves on samples	2

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