BESIDES THE STANDARD NIOBIUM BATH CHEMICAL POLISHING

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Abstract

In the following we will illustrate our research about alternative recipes for Niobium chemical etching and electropolishing, that are as well effective than Standard recipes, less costly (therefore suitable for large scale production), but, above all, less-hazardous to prepare and to handle. In particular the paper is structured in four parts: i) our investigation about the standard Buffered Chemical Polishing (HF, HNO_3, H_3PO_4) in different ratios than the standard 1:1:1 or 1:1:2; ii) our attempt to substitute in chemical etching the Hydrofluoric acid with the less aggressive Ammonium Fluoride; iii) our method for automatically finding the right electropolishing parameters of any solution we desire to try; iv) our proposal for a novel Electropolishing containing the more "pacific" Oxalic acid and Boric acid instead than Sulphuric acid.

1 THE STANDARD CHEMICAL POLISHING

Standard Buffered Chemical Polishing (BCP) and Electrolytic Polishing (EP) for Niobium work remarkably for the surface treatment of Superconducting cavities. Nevertheless the presence of aggressive acids as the Hydrofluoric acid, Nitric acid or Sulphuric Acid makes their use both expensive and hazardous. If, ab absurdo, one could achieve 40 MV/m in a cavity polished by only kitchen salt and alcohol diluted in deionised water, this would be a real breakthrough in the history of superconducting cavities. The cost saving would result not only from the reduction in reagent costs, but also in equipment, tools, manufacture time, and precautions. We do not aspire to this, but we try to investigate the possibility to make use of less hazardous reagents than the previous mentioned. In order to get deeper in this topic, let us examine the standard treatments worldwide adopted in the scientific community dedicated to superconducting cavity R&D.

The Niobium chemical etchings, commonly called BCP 1:1:1 or BCP 1:1:2, are a mixture of Hydrofluoric, Nitric and Phosphoric acids, respectively in the ratio 1:1:1 or in the ratio 1:1:2. Nitric acid plays the role to oxide the Niobium surface. Hydrofluoric acid reduces the Niobium Pentaoxide into a salt that is soluble in water. Phosphoric acid acts as a moderator for the chemical reaction giving rises to a less turbulent and more controllable reaction. That's why often 1:1:2 is preferred to 1:1:1 for treating cavities. The main reaction happening at the Niobium surface is reported:

$$6\ Nb + 10\ HNO_3 = 3\ Nb_2O_5 + 10\ NO + 5H_2O$$

and

$$Nb_2O_5 + 10\ HF = 2\ NbF_5 + 5\ H_2O$$

then

$$3Nb + 5\ HNO_3 + 15\ HF = 3\ NbF_5 + 5\ NO + 10\ H_2O$$
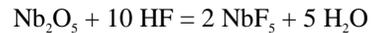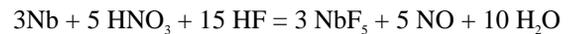
For completeness it must be mentioned the results proposed by Antoine et al. [1]. They have investigated the possibility to substitute phosphoric acid with sulphuric acid. The Niobium oxidation takes place as well, while in addition sulphuric acid has a brightening action.

2 THE BCP 1:1:N

The large statistics performed on Niobium cavity chemical treatments only refers to the BCP in both the percentages 1:1:1 and 1:1:2. Nevertheless, on our opinion, it is not clear if are just these the right percentages that give rise to the best surface quality. We even suspect that it is rather improbable that the lowest roughness corresponds to a composition in which Nitric acid is mixed in the same percentage of Hydrofluoric acid. In particular our idea is that a slower etching rate could be preferable because of a lower risk of solution self-heating, then a lower probability for hydrogen to diffuse into Nb. Moreover, whenever stirring of the etching solution is applied we do not see a priori any reason by which the surface roughness should worsen.

We have built the ternary diagram of fig. 1 by measuring the Niobium etching rate versus different percentages of Hydrofluoric, Nitric and Phosphoric acids. We can notice that the same etching rate of the 1:1:1 mixture can be obtained by decreasing the nitric percentage vs the hydrofluoric content if we increased the phosphoric percentage or vice versa. In other words, the reduction effect of Hydrofluoric acid is so high that a little fraction of the oxidant agent (Nitric) is needed in order to solute Niobium; more Phosphoric in this case is needed for smoothing the reaction. The numbered lines inside the triangle are the curves of equal etching rate (removed micron per minute) in the three-dimensional space determined by the three acids. The dot serials instead correspond to points obtained by varying the phosphoric percentage leaving unchanged the hydrofluoric-nitric ratios.
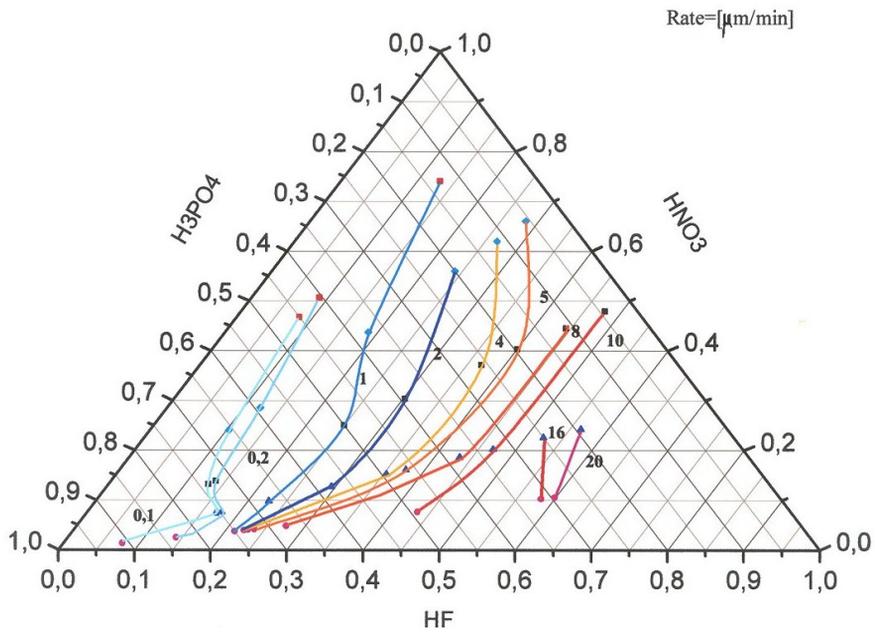
Figure 1: Curves of equal etching rate in the three-dimensional space of BCP. The number reported close to each curve corresponds to the etching rate (removed micron per minute)

In fig. 2 we report the effect on surface roughness we have detected on samples etched in the *HF : HNO$_3$: H$_3$PO$_4$* mixture versus the percentage of phosphoric acid. From our measurements, it seems that the roughness does no not change versus the moderator concentration when 20 microns are removed, while it has a slight increase when 200 microns are removed.

3 LESS HAZARDOUS REAGENTS FOR THE BCP

The recipes based on the mixture of hydrofluoric acid with nitric acid are well known for etching several type of steels. However, just for the same reasons mentioned above, the steel industry often prefers a less good finishing in spite of using so aggressive reagents. Therefore it is not rare to find NH_4F in substitution of HF and H_2O_2 as an oxidant instead of HNO_3, or ascorbic acid and acetic acid as complexants instead of phosphoric acid. We have investigated the role of the single reaction constituents and their combination on Niobium both at room temperature and at 70ºC. Among the several recipes we have tried, best results were found at room temperature by the following mixtures:

$$NH_4F + HCl + H_2O_2 + H_3PO_4$$
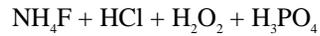
in the ratio 2:2:4:1 with (60g/lt) of NH_4F
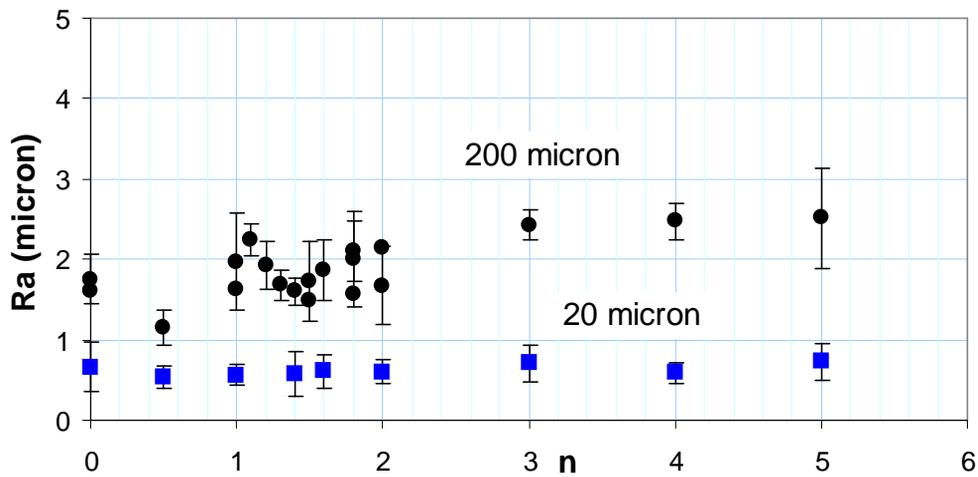
Figure 2: Surface Roughness of Niobium samples after 20 microns (blue squares) and 200 microns (black circles) erosion versus the percentage of phosphoric acid in BCP 1:1:n

Ammonium fluoride does not bring into the solution the same amount of Fluorine ions than Hydrofluoric acid, so Hydrochloric acid is added since Niobium Oxy-chloride is both stable and soluble in water too. We can get rid of Hydrochloric acid by increasing the concentration of NH_4F, even up to 700 g/lt . The etching rate in this way can be modulated up to 1 micron/min, giving rise to a brilliant surface.

4 THE ELECTROLYTIC POLISHING

Figure 3 reports a typical I-V characteristic for the electropolishing of Copper in Ortophosphoric acid solution in the case of planar and parallel face electrodes, when edge effects are negligible [2].

The following behaviour is observed at the voltages corresponding to different sections of the curve:

- Over section V_a and V_b the current increases as a linear function of the voltage. Material dissolution happens with a too low rate. The process is accompanied by evolution of Oxygen bubbles that sticking to the anode promote local pitting of the piece surface.

- Polishing effect is observed between V_b and V_c; the grain structure is brought into relief, as long as the process takes place. However roughness levelling and brilliant surface are obtained at voltages close to V_c. Here at the end of the plateau there is the minimum of Oxygen bubbles evolution. Even a minimum amount of bubbles can represent a limitation to the roughness smoothing action. Migrating toward the top they produce undesired vertical traces depending on the solution agitation.

- At a higher potential the gas evolution becomes stronger and the surface erosion is accompanied by pitting. A better surface quality, although mat, is obtainable at voltages well above V_c, since Oxygen bubbles have not time for sticking to the surface.
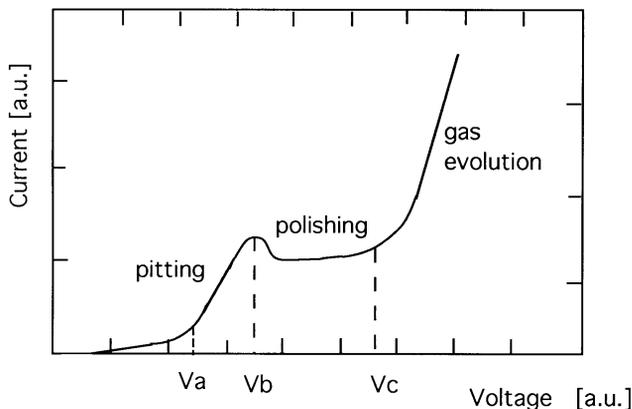
Figure 3: Typical I-V characteristic for electropolishing

The I-V characteristics for Niobium electropolished in the mixture HF-H_2SO_4 (by which massive investigation the Japanese group [3] has first achieved 40 MV/M) does not display the plateau, but a pocket of oscillations [4] corresponding to the growing and to the breaking of the oxide. However this does not modify what we will say in the following about our proposal to choose the working point. The method we propose here for controlling the electropolishing process is absolutely general, in our experience it can be applied to any kind of bath, even for baths where does not appear the plateau (e.g. EP of Aluminium in Chromic Acid). In such particular cases indeed we have even observed that our method is even more useful, because a guideline on how to operate, is normally more needed in the dark rather than in the light.

5 THE LNL PROPOSAL TO LOCK THE MINIMUM OF THE DIFFERENTIAL CONDUCTANCE

At LNL we have developed a method for controlling the electropolishing process. We try to minimize parasitic problems as gas evolution, by searching the best working point of the I-V characteristic and by following it during the whole process.

The method consists in computer monitoring the I-V characteristic. The process is driven in voltage. An automatic program displays the numeric derivative of I versus V. The working point is chosen as the minimum of such derivative, i.e. the minimum of bath differential conductance that corresponds to the point of maximum resistance of the viscous layer.
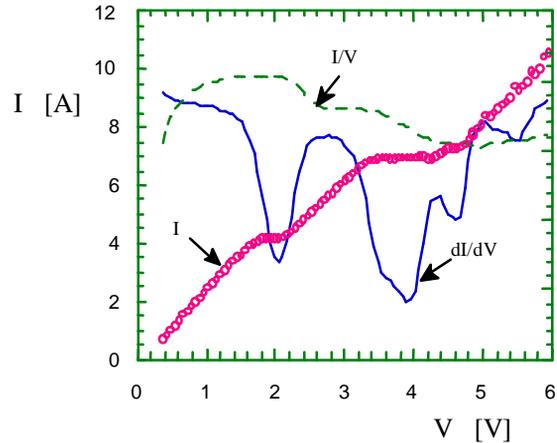
Figure 4: I-V characteristic for a standard electropolishing process (circles); The differential conductivity dI/dV (continuous line) and the ratio I/V (shaded line) are displayed versus voltage. We interpret the first minimum in differential conductance as due to edge effects and to the not uniform distance between electrodes

In fig. 4, we display the differential conductance compared to the ratio I-V and together with the I-V characteristic. Some literature approximates the minimum of dI/dV with the minimum of I/V. Already from fig. 4, it is visible that the two minima differ quite substantially in voltage. In any case that of an electrolytic cell is a non-linear circuit, hence the solution conductivity is a

differential quantity while, the ratio I/V has no any physical sense in such a case.

We have applied successfully such a method also for the electropolishing of materials such as Copper, Niobium, Aluminium, Steel and Titanium, each one in different solutions. However good results have always been obtained only by following the differential conductance, and not I/V that instead results into mat and sometimes etched surfaces.

The I-V characteristic evolves with time. Fig. 5 displays the evolution of the current *plateau*.
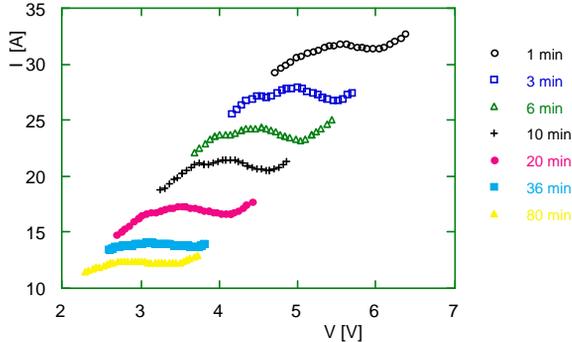
Figure 5: Time evolution of the I-V characteristic plateau

Figure 6 also shows the evolution of the working point. The reason for this is twofold. The leveling action decreasing the roughness, but also the surface area decreases. Moreover in the hypotheses of an anodic passivating oxide film, the longer is the process, the more stable is the film, the weaker is the etching. By locking the minimum of the differential conductance, we could lower the plateau up to very low values of Copper

dissolution rate. Hence the removal of large thicknesses cannot be obtained by simply increasing the process time. We have tried to electropolish Copper samples for 1, 3, 6 and even 12 hours. There is no difference in roughness between samples polished for 2 or for 12 hours. A serious drawback appears for long process times: there is nucleation of Copper Pirophosphate in large clusters at several points on the anode.
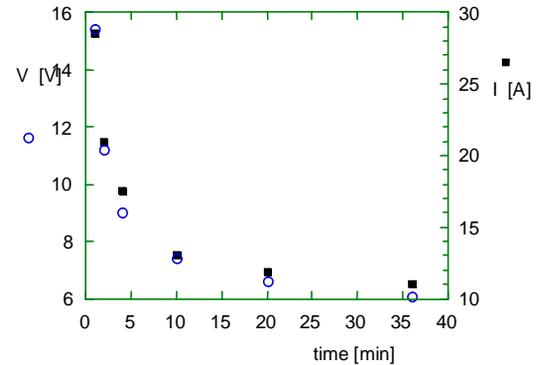
Figure 6: The voltage value corresponding to the minimum of differential conductance and the relative current value

Therefore whenever we need removing hundreds of microns of Copper, we use to apply the method of locking the minimum of differential conductance for one hour, than for few minutes we work at a much higher voltage in order to destroy the passivation layer, then we restart locking the minimum for another hour and so on.
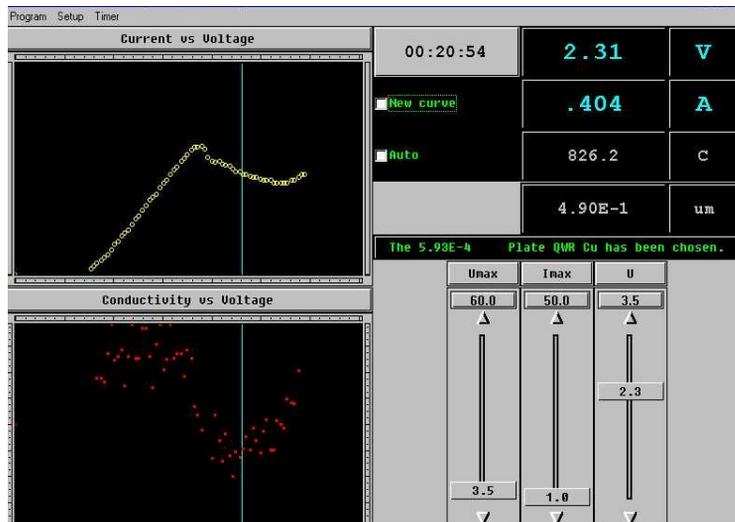
Fig. 7: Typical table displayed on the computer screen controlling the electropolishing processes. The curve on the top left is the I-V characteristics; the curve on the bottom left is the derivative of current versus voltage. The numbers on the top-right are the process parameters; the knobs at the bottom-right are needed for settling the starting point

At the minimum of the differential conductance there is already low gas evolution. However as soon as the process is started and the plateau starts to get lower, at a certain voltage threshold, gas evolution can even disappear.

We have built a computer program (fig. 7) that automatically locks onto the minimum of the bath differential conductance. In this way not only the process is constantly driven according the best parameters, but also we can directly find the best electropolishing current density, without need to know them a priori.

This leads to the great advantage that whenever we desire to test new recipes, just by drawing the I-V characteristics, we find by ourselves the current density at which to work.

6 OUR NEW ELECTROPOLISHING RECIPE

By means of our method based on the automatic following of the minimum of the differential conductance of an electrolytic bath, we have checked the goodness of several ideas, testing several EP recipes. Therefore we got the possibility to investigate the role that Oxalyc acid, Boric Acid, Phosphoric acid, Ascorbic acid and Ammonium Fluoride have on the electropolishing of Niobium.

By means of this study we have arrived to a new recipe, that gives a mirror like finishing on Niobium. Then our proposal is:

HF + OXALIC ACID + BORIC ACID + H_3PO_4
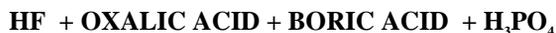
We have chosen the following percentages 30% HF, 15% H_3PO_4, 30 gr/lt Oxalic acid, 10 gr/lt Boric acid; the current density and voltage are found automatically by setting the process on the minimum of differential conductance.

We have tried in several ways to get rid of Hydrofluoric acid from this EP solution, but at the moment the results are not those we are searching for. Our work on the subject is constantly under progress, but further investigation is needed.

8 REFERENCES

[1] Antoine C.Z., Aspart A., Berthelot M., Gasser Y., Poupeau J.P., Valin F., Proceedings of the Ninth workshop on RF Superconductivity, November 1-4, 1999 Santa Fe', NM LA-13782-C, p. 295.

[2] Jacquet, P.A., Metal Finishing, 48, 1, 2 (1950).

[3] Saito K., Inoue H, Kako E., Fujino T., Noguchi S, Ono M., Shishido T., Proceedings of the Eighth Workshop on RF Superconductivity, October 1997, Abano Terme (Padua), V. Palmieri and A. Lombardi Eds, LNL- INFN (Rep) 133/98, vol. 4, p. 795.

[4] Sevryukova L.M., "Proceedings of the 5th Workshop of RF superconductivity" DESY, Hamburg, August 1991, D.Proch ed., DESY M-92-01, (1992) p. 433.