

EFFICIENCY OF ELECTROPOLISHING VERSUS BATH COMPOSITION AND AGING: FIRST RESULTS *

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Abstract

Electropolishing experiments on niobium samples are carried out in Saclay:

- to study the bath aging, its origins and the consequences on the polishing performances,
- to highlight the influence of parameters such as temperature and acids concentrations (hydrofluoric and sulfuric).

Some mixtures with different concentrations have already been investigated. Intensity as a function of time, surface states and polishing speed were considered at different potentials.

INTRODUCTION

There are several electropolishing (EP) processes applicable to niobium [1], but the most efficient one was developed by Siemens in the 70's [2], in a mixture of sulfuric and hydrofluoric acids. Application to large cavities has been done at KEK during the 80's where a thorough work has been completed taking all the practical aspects into account [3]. This surface preparation technique has proven to produce record accelerating gradients and is now widely used for cavities. Meanwhile discrepancy of the results is still the main issue; as compared to classical chemical polishing.

We have tried to pursue the pioneering work done at KEK, by trying to understand the aging of EP solution. Two aspects can be taken into consideration: efficiency of the electropolishing process itself and role of impurities. This last aspect is treated elsewhere [4], and we shall concentrate here on the evolution of the efficiency of the process with aging. These experiments are an introduction to a more complete program involving design of experiments to find an optimal polishing mixture, with a higher lifetime, less impurities production and cost effectiveness whenever possible.

Experiments on sample

For simplicity we have decided to work out this study on samples. One has to keep in mind that adaptation to a RF cavity set-up will not be straightforward as the current distribution, the quality of the viscous layer (see next §) or hydrodynamics of the system will certainly be different than in the small set-up used for samples. This aspect of the question will be treated elsewhere [5].

Electropolishing basics

Several current-voltage behaviors can be expected for a

metal inside an electrolyte solution (cf Fig.1), among them, the most common are active dissolution (similar to chemical etching), or passivation (e.g. Nb or Al in pure water). Electropolishing refers to a phenomenon where a current plateau (about 50-100 mA/cm²) appears, usually attributed to a diffusion limiting phenomena. Polishing and brightening effects are attributed to the existence of a highly resistive viscous layer. [6-10]

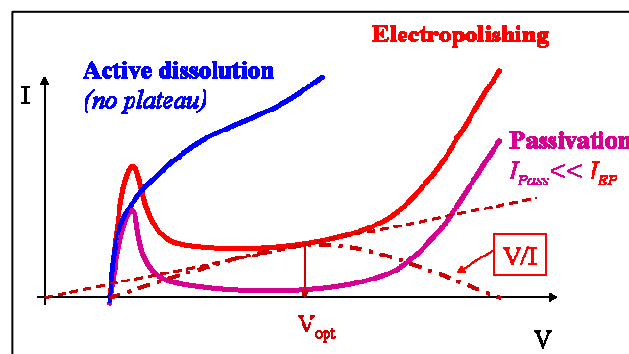


Figure 1: Schematic current voltage curves in various typical situations: active dissolution, when no viscous layer is formed and the metallic ions dissolve freely in electrolyte; passivation, where formation of a stable, insoluble film prevents further corrosion, and electropolishing, where an interface layer (viscous layer) is a source of limitation in current. In the absence of reference electrode, V figures $V_{\text{anode}} - V_{\text{cathode}}$ and includes ohmic losses inside solution.

Wagner made theoretical prediction of the rate of leveling of microprofiles at the limiting current, based on the Nernst diffusion layer [11, 12]. *Charge transfer overvoltage tends to reduce the rate of anodic leveling. A measure of the relative importance of charge transfer overvoltage is the Wagner number, $Wa = (d\eta/di)/(\rho_e \epsilon_0)$ where $d\eta/di$ is the slope of the current voltage curve, ρ_e the resistivity of the electrolyte, ϵ_0 the initial profile height [7]. This theory applies to anodic leveling (roughness $\sigma_{\text{rms}} \sim 1\mu\text{m}$) and not to anodic brightening ($\sigma_{\text{rms}} \ll 1\mu\text{m}$). The highest Wa , the more efficient is anodic leveling [7]. Choosing the voltage at the highest cell impedance as a functioning point answers to this criteria and is widely used as a practical application [13].*

Nevertheless, the process developed by Siemens for Nb, is based on the existence of oscillations at the end of the plateau, and the absence of stirring. Several authors claim that oscillations are mandatory to gain very good surface states, in particular in the case without any stirring [2, 14, 15].

Experiences at KEK, as well as some of ours, tend to show that oscillations are not a fundamental requirement

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to achieve good polishing [16]. This aspect is now under exploration but no clear conclusions have been drawn yet.

AGING AND EFFICIENCY OF THE BATH

Experimental set-up

Experiments are carried out in a teflon vessel. Cathode is in aluminum and niobium samples are 9 square centimeters. A separation divides the vessel into 2 parts and prevents the hydrogen bubbles formed at the cathode to migrate to the niobium sample. Bath is stirred with a magnetic stirrer and temperature is controlled by a coolant system. Acids mixtures are prepared with HF, 40% in weight and H₂SO₄, 95 % in weight, with possible addition of H₂O.

Evolution of surface state with time

In usual electropolishing (EP) experiment the following features can be observed with increasing time:

- Constant decrease in intensity and polishing rate.
- Long term deterioration of samples' surface.
- Changes in intensity oscillations.
- Aluminum corrosion.
- S and H₂S production

Usually, in the case of cavities preparation, EP solution is changed when the Nb content reaches ~9-10 g/l. Aging is thus not only an issue in term of efficiency, but also in costs as the acid mixture is quite expensive.

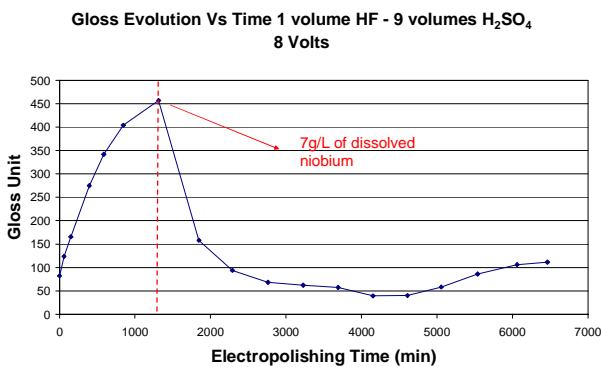
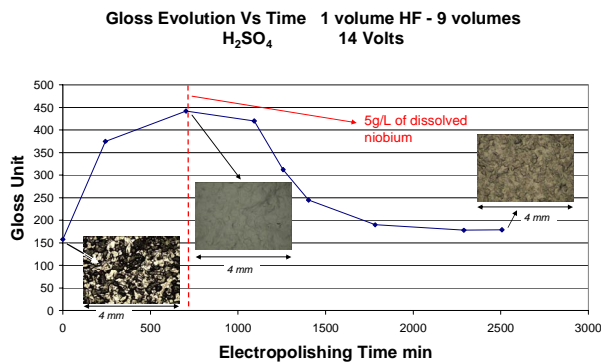


Figure 2: evolution of gloss and surface state vs. time at 14 V and 8 V ("1-9" bath)

Figure 2 shows the evolution of surface state and gloss for a usual bath at 2 different voltages. In both cases,

gloss increases for a certain time and then decreases. The maximum gloss is reached for different times at different potentials, and weight of dissolved niobium between 5 and 7 g/L.

Obviously, this result tends to demonstrate that some EP processes are conducted in conditions where the polishing is far from optimum, especially when $5\text{g/L} \leq [\text{Nb}] \leq 10\text{g/L}$.

Notes:

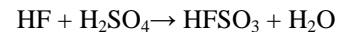
- After long time experiment solid sulfur is produced in appreciable amount and deposits on samples and experimental set up.
- Similar feature (a maximum on the gloss curve) can be observed in different mixtures. In a 0.5 vol HF – 9 vol H₂SO₄ mixture, bath renewal after the gloss maximum showed that surface was further improved until the same quantity of niobium was dissolved.

Meanwhile, changing the EP solution too often reveals very expensive and is not an appreciable issue. It is therefore interesting to vary bath composition, in order to increase solution lifetime. In the same time, decrease of production of solid S, would also be an appreciable improvement.

Aging and F⁻ concentration.

The observed behavior when refreshing solution tends to indicate that aging is related to the decrease of one component rather than Nb oxide modification. Thus we have monitored F⁻ and SO₄²⁻ content vs. time by ionic chromatography (see Figure 3).

Chromatographs pointed out three peaks for anions. Additional analyses with pure HFSO₃ tend to prove that the third anion is FSO₃⁻ in accordance with the equilibrium:



As the balance between F⁻ and FSO₃⁻ ions depends on the water dilution, and kinetic aspects, it is impossible to distinguish precisely F⁻ and FSO₃⁻ contributions in the mixture. Although it is possible to determine evolution of each species, it is safer to consider quantitatively fluorinated elements altogether.

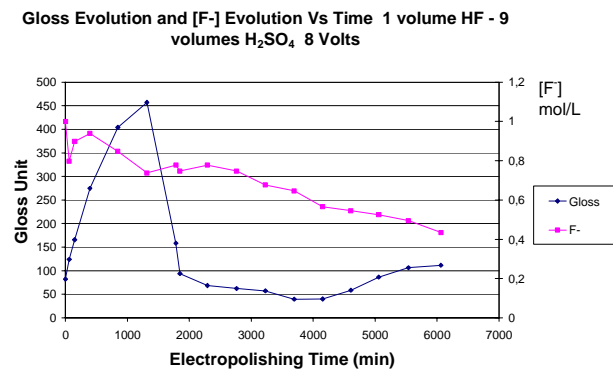


Figure 3 : evolution of F⁻ content and gloss vs. time during electropolishing of Nb sample. In the original solution, only half of the expected F⁻ concentration is found, the reminding fraction being probably in the FSO₃⁻ form.

Figure 3 shows $[F^-]$ evolution during a long EP sequence. The F^- concentration decreases very slowly during the first 2000 minutes. During this time gloss is improving. Afterwards the decrease of F^- accentuates, while gloss is also decreasing.

From this behaviour, we can infer that $HFSO_3$ acts like an F^- “reservoir” and that gloss can improve only as long as one keeps enough F^- into solution. Further experiments are of course needed to confirm that scenario but we can henceforth point out the Fluorine concentration influence.

CHANGING BATH'S COMPOSITION

Several compositions have already been tested. As can be observed on Figure 4, because of the initial concentration of acids, possible concentrations are contained in a limited domain. We have tried to enhance HF concentration operating at $\sim 15^\circ C$ with a 3 vol HF – 6.72 vol H_2SO_4 – 0.28 vol H_2O mixture. As a result, water

content is higher, acids dissociation is improved, and viscosity decreased. It should affect the viscous layer, and the diffusion limitation might be modified. Indeed, in the last tested composition, the I(V) curve looks more like active dissolution than true electropolishing.

Aging is dramatically changed with $[HF]$ increase. The gloss maximum is reached quicker, and keeps on a plateau before decreasing. Brightening still effective at low etching rate and high Nb content and moreover S is not found at high HF content (see e.g. Figure 5). The optimum voltage seems also to be lower, although current and etching rate are enhanced. Increasing HF concentration appears to be a favorable issue since we can gain time (current!) without supplying much more electrical power, without overheating of the solution and/or too much HF evaporation. Lifetime in increased and samples appear very shiny.

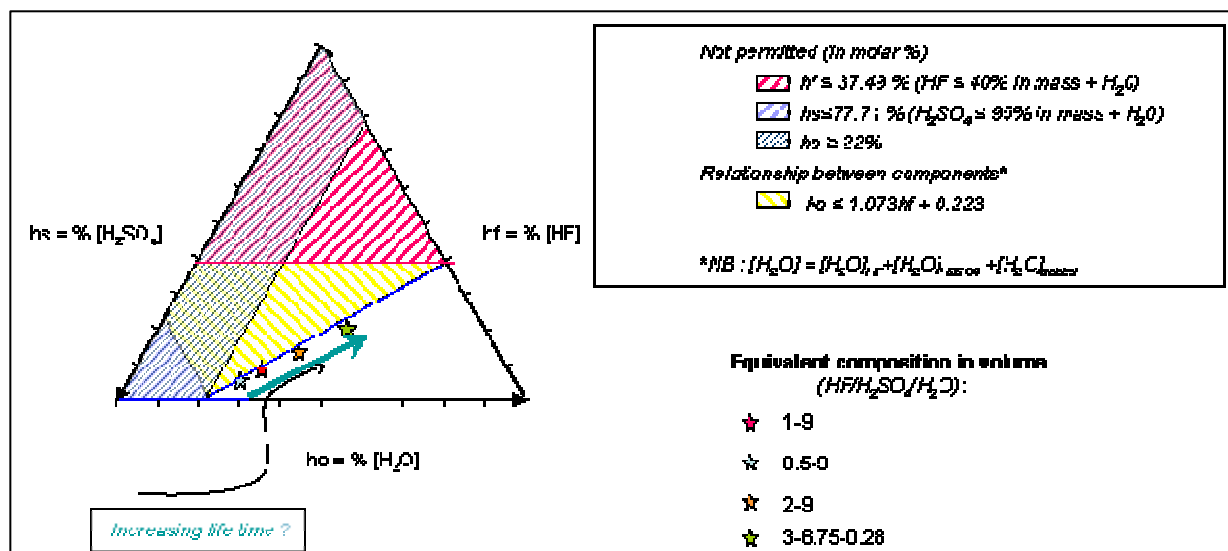


Figure 4: Possible domains of concentrations (in molar %) for any mixture of HF (40%), H_2SO_4 (95%) and H_2O .

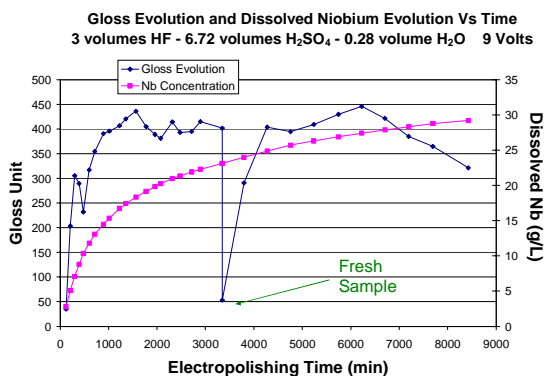


Figure 5 : evolution of gloss (blue curve) and dissolved (cyan curve) during electropolishing at 9 Volts of Nb in a HF (3 vol.), H_2SO_4 (6.72 vol.) and H_2O (0.28 vol.) solution. Gloss remains satisfactory even at low etching rate and high Nb content.

DISCUSSION

Enhancing the HF proportion inside the EP solutions seems to bring a lot of advantages: mainly the etching rate as well as lifetime of the solution is increased, but in detriment to the viscosity of the solution. Active etching at $50-100 \text{ mA/cm}^2$ has proven to produce very flat surfaces ($\sigma_{rms} \sim 10 \text{ nm}$) on steel [17], and one has to consider if this is acceptable for Nb, and easily applicable to cavities.

One of the main issues when passing from sample to cavity is the anode-cathode distance variation introduced by the cavities' shape. Indeed, when distance/shape is changed, parameters like ohmic drop inside the solution, or current line distribution are affected, and the initial I(V) curve as determined in a sample set-up doesn't apply any more. In theory one should determine a local “I(V) curve” and the best bias parameter for each point, which

of course is impossible from a practical point of view. Nevertheless one can consider that increasing the anode-cathode distance enhances the ohmic losses into the solution. Advantage of getting a large current limited plateau, is that changing a little the potential within the plateau doesn't influence much the current density. Thus the range of available potentials to operate with good polishing conditions is wide. On the other hand if the slope of the I(V) characteristic is high, a slight change in potential will lead to a large variation of current density.

Very large difference of etching rates observed on cavities between cut off tubes and equator might simply arise from the fact that the local potential is too high and that we are not any more on the plateau, but in the transpassive side of the I(V) curve.

Note: in practice, an increase in potential is often chosen to compensate bath's aging [2, 3, 18].

CONCLUSION

Increasing HF obviously enhances rapidity of electropolishing process and lifetime of EP solutions, which presents an appreciable advantage in term of easier handling and costs. Nevertheless, application to cavities is not straightforward, and improvement of the EP process will be necessarily a compromise between antagonistic effects. Many other aspects have to be further explored, like the impact of water content, HF evaporation, temperature or cathode corrosion... And of course, tests on cavities are still the only way to determine the effectiveness of such improvements.

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