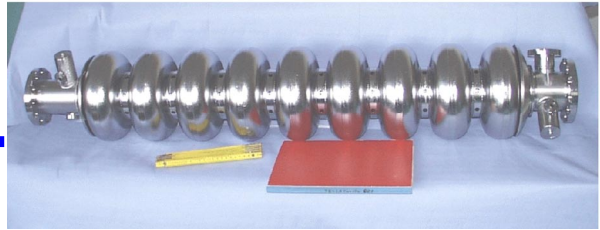




SRF



WP 5.1.1.4 : “Electropolishing of Niobium : best EP Parameters”

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Abstract

Particle accelerators are used by scientists in order to discover properties of matter at sub microscopic scales. Particles are accelerated in resonators (cavities). Superconductivity Radio Frequency (SRF) using niobium cavities is widely recognized as efficient to reach high accelerating gradients (E_{acc}) and this technology should fit out the next International Linear Collider.

Niobium cavities need surface treatment such as polishing in order to provide high gradients. Electropolishing is believed to be the most efficient technique because of the smooth surfaces that are obtained. A recipe has been proposed by Siemens in the 70's with mixture of hydrofluoric (40-45 w%) and sulphuric (95-98 w%) acids in the ratio 1 Volume – 9 Volumes. Electropolishing is a common electrolytic process; nevertheless, mechanisms that are involved remain obscure.

This work aims at understanding the niobium EP process and to propose a resulting optimization. Niobium samples are first treated and the study will go on with the polishing of single cell cavities in a device that is being implemented in our laboratory. We have put into evidence early aging of the electrochemical baths, conditions of sulphur production, and the preponderant role of fluorine ions. Directions of improvement are enlightened, but still need further exploration.

Key Words:

Particle accelerators, SRF technology, Niobium, Electropolishing, Cavity, Resonator, Electrolyte, , Aging.

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Introduction

Progress in particle physics is linked with progress in designing accelerators with higher performances. As a consequence the race for the highest energies has begun. Particles are accelerated into radiofrequency (RF) resonators, namely accelerating cavities, which performances are a key issue to get high quality particle beams at reduced costs.

A great improvement resulted from the use of Superconductive RF cavities in niobium, that allow less power dissipation and larger beam aperture compared with former copper cavities. This technology has been developed within the frame of an international collaboration (TESLA) involving mainly European, American, and Japanese laboratories. In August 2004, the International Technology Recommendation Panel (ITRP) of the ICFA¹ recommended that the next high energy physics facility, ILC, should be based on TESLA SCRF technology. ILC stands for International Linear Collider, which should provide 500 GeV energies and be upgradable up to the TeV range.

The surface treatments associated with cavities is a key issue towards the obtaining of high performances. Standard surface treatments involve mechanical polishing, chemical or electrochemical polishing, rinsing procedures and baking. Electropolishing is believed to provide the highest accelerating gradients (compared to chemical polishing). The application of this process to cavities has been developed in Japan by KEK in the 80's. Nevertheless, of chemical mechanisms are not yet well understood, and the bath composition needs to be optimized, which is the goal of this study. More precisely, two approaches will be investigated:

- Experiments on niobium samples with two devices ("Fixed Electrodes" and "Rotanodes", see § III 1) c))
- A single cell electropolishing device is being implemented in the laboratory. Next experiments will be carried out with this tool.

This work has been financed with the support of the European Community-Research Infrastructure Activity under the FP6 "Structuring the European Research Area" program (CARE, contract number RII3-CT-2003-506395) and of the Région Ile-De-France.

This report is divided into 5 chapters: the first chapter explains the context of the study. The second describes the state of the art concerning niobium and electropolishing. In chapter III, we will present electropolishing mechanisms concerning niobium highlighted during the research. The fourth chapter deals with impurities generated in the electrolyte and with the resulting aging. At last, the fifth chapter presents some information concerning the single cell electropolishing device implementation.

Some of these chapters can be found with more details the diploma thesis from one of us (F.E.) [55]

¹ ICFA, the International Committee for Future Accelerators, was created to facilitate international collaboration in the construction and use of accelerators for high energy physics. It was created in 1976 by the International Union of Pure and Applied Physics.

Chapter I Context

1) Particle accelerators and cavities

- Particle accelerators are devices used in fundamental research in Physics. They aim at accelerating charged particles. Energy ranges from some MeV to TeV, depending on the application, as well as the nature of the accelerated particles. There are two kinds of accelerators: linear accelerators which require very high accelerating gradients, and circular accelerators (synchrotrons and cyclotrons).

When energies above 1 MeV are needed, the most efficient way to get high electric field is to use radiofrequency resonators, also called accelerating cavities. The simplest examples are elliptic shaped cells (Figure 1).

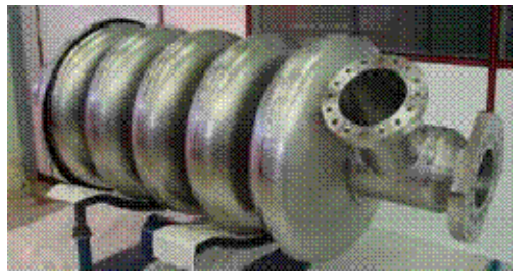


Figure 1: A pentacell proton cavity (CEA IPN collaboration). Cavities are used to accelerate particles.

We must distinguish two parts of a cavity: The iris where the electric field is the highest and the equator, where the magnetic field and current density are the highest (See Figure 2).

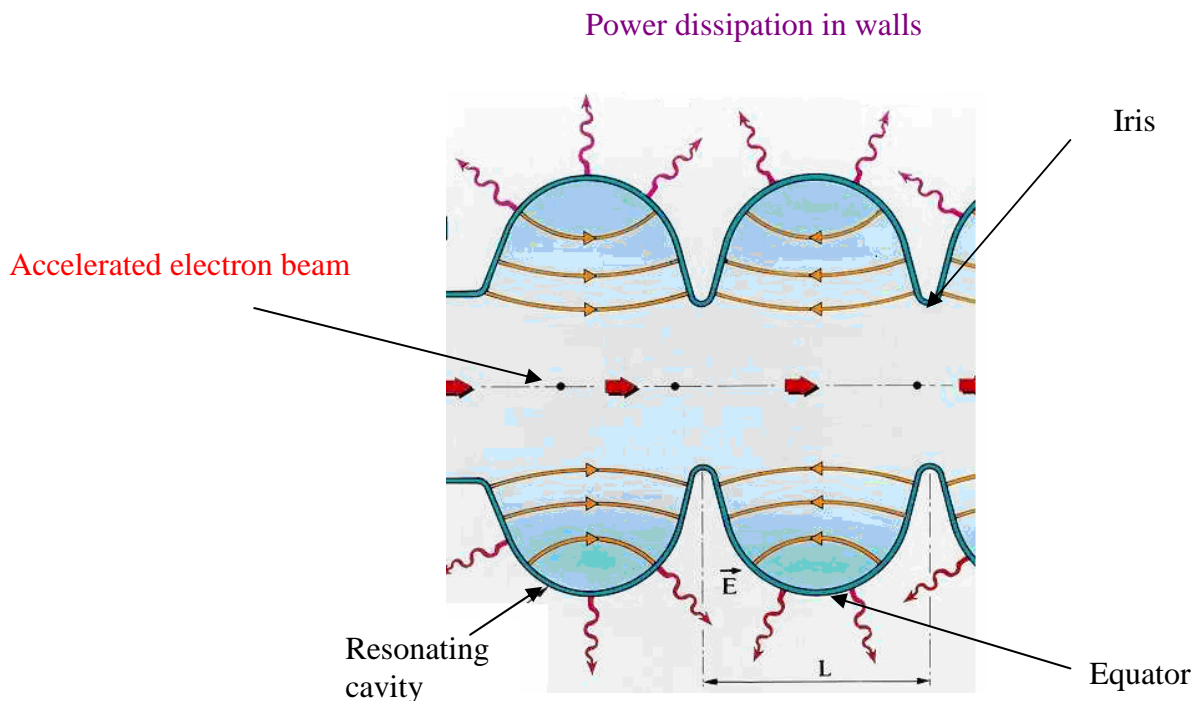


Figure 2: Cavity, accelerating field E_{acc} and electron beam. Electric field is the highest at the iris.

2) Cavities and superconductivity

Particles are accelerated in cavities which are designed to offer the highest accelerating field (or accelerating gradient) E_{acc} . Another figure of interest is the Q_0 quality factor that represents ratio between stored and dissipated energies. The plot $Q_0 = f(E_{acc})$ is commonly used to evaluate cavity performances. See for example Figure 3.

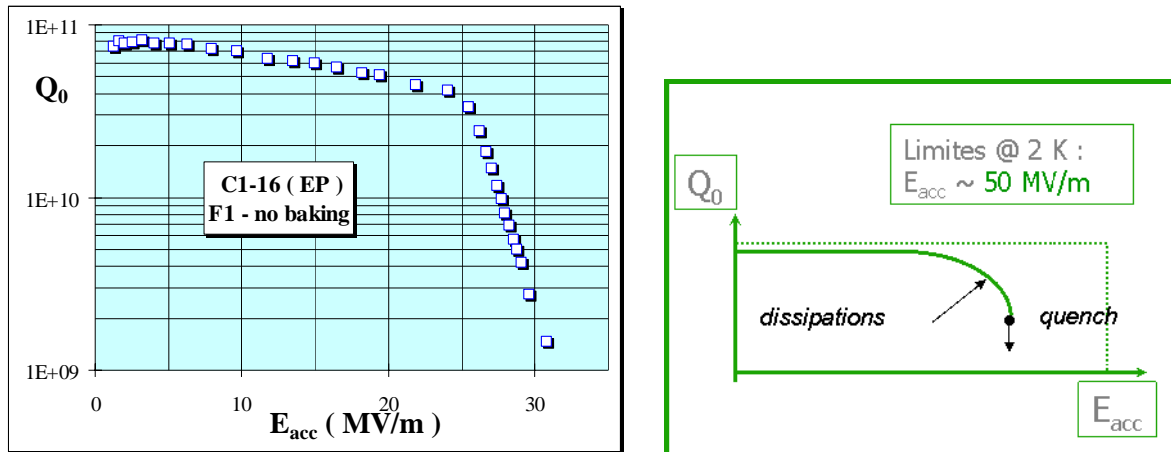


Figure 3: Q_0 vs E_{acc} plot for Nb cavity : at high field thermal dissipations occur, and eventually lead to the transition superconducting => normal, so-called “Quench”.

Cavities in copper can reach very high field E_{acc} , but with very low duty cycle due to the overheating by Joule effect. Superconductivity and the use of niobium cavities cooled down to a 1.8 K-4.2 K range provide high fields with high duty cycles, with a far better efficiency: most of the energy stored is given to the beam as the losses in the cavity walls are very low.

For TESLA, the requirement concerning E_{acc} was in a first step $25 \text{ MV}\cdot\text{m}^{-1}$ which was then upgraded at $35 \text{ MV}\cdot\text{m}^{-1}$ due to ongoing improvement of cavity performance. The aim for ILC is even more ambitious, about $40 \text{ MV}\cdot\text{m}^{-1}$. Such a value is reached currently at lab on single cells, but these results cannot yet be reliably obtained on accelerator multicells. In theory, the maximum accelerating field is $54 \text{ MV}\cdot\text{m}^{-1}$ at 1.8 K. Studies are also carried out in different laboratories in order to improve that limit by changing the cavity shape.

European efforts have been gathered within the CARE SRF, where a whole workpackage (W5) stands for surface treatments. The task WP 5-1 “Electropolishing on monocell” has been attributed to CEA and deals with optimization of that process.

3) Cavity preparation:

a) Presentation

In order to reach appropriate accelerating field and Q_0 factor, niobium cavities go through different surface treatments after their delivery by industry:

- Chemical or electrochemical polishing: $150 \mu\text{m}$ of niobium are stripped out.
- High Pressure Rinsing (HPR) with ultra-pure water.
- Baking (110°C , 48h).
- Final Assembly inside clean environment (class 10-100 cleanroom).

Chapter I Context

In order to achieve efficient cavity preparation (avoiding particle contamination of the inner surface), laboratories tend to implement at the same place treatments units and clean rooms, where they are rinsed and mounted. Cavities are then tested in a cryostat.

b) Chemical Vs Electrochemical processes

Buffered chemical polishing has been widely used to prepare RF cavities during several decades, as it is quite simple to handle. It tends now to be replaced by electropolishing, which allows to reach higher accelerating gradients [2], although it is less reproducible (Please find an example of distribution of performances in Figure 4).

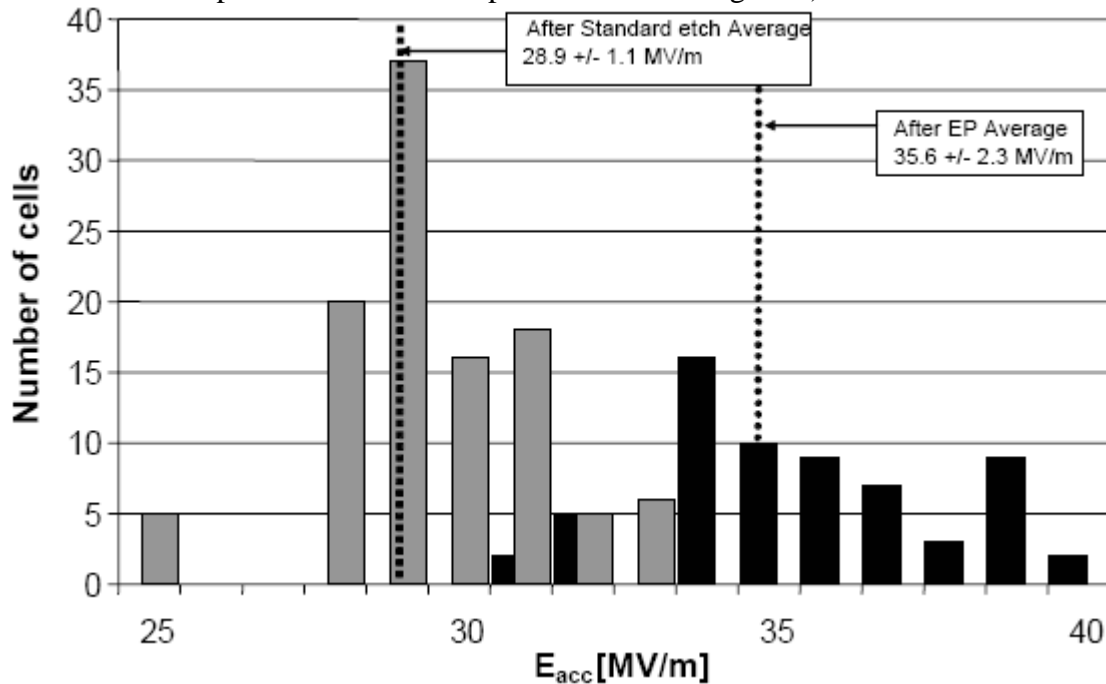


Figure 4: Accelerating gradient comparison between chemically etched and electropolished cavities (from[2]). Electropolished cavities reach higher gradients but the distribution is larger.

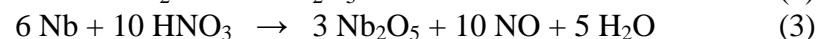
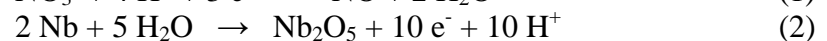
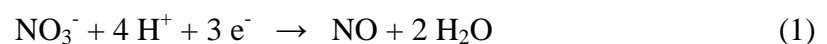
These two techniques are based on the oxidation of the niobium and its removal with a complexant.

b.i Chemical polishing:

Metal surface is treated with a mixture of nitric (oxidizing specie), sulfuric and phosphoric acids. Cavities might be plunged in an acid bath or treated internally thanks to a close circuit. This technique provides a fast niobium removal rate ($1 \mu\text{m.mn}^{-1}$ or higher) but the surface is etched at grain boundaries and is then not very smooth (R_a : some μm). The cavities chemically polished reach currently 30 MV.m^{-1} .

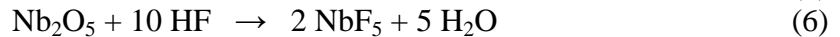
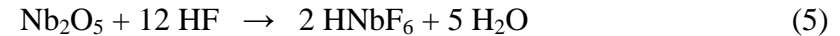
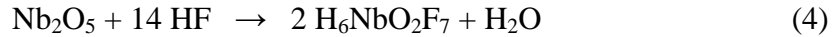
Basics concerning chemistry of a chemical polishing:

NO_3^- ion makes niobium oxidize into its state +5. NO_3^- is reduced into NO_x [4]:



In presence of HF, Nb_2O_5 is transformed into fluoride or oxifluoride species:

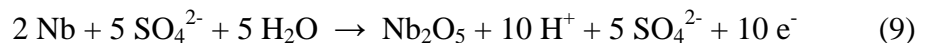
Chapter I Context

**b.ii Electropolishing:**

This technique that we will discuss in this report provides smooth surfaces with lower roughness (Ra: some 0.1 μm) and higher E_{acc} . Surface smoothness is believed to be the origin of the cavity performance. But that question is not totally elucidated. (see § II 4) a). The electrolyte that is used is composed of hydrofluoric (40 w%) and sulfuric (96 w%) acids in a ratio: 1 volume HF for 9 volumes of H_2SO_4 . The bath temperature is controlled in order to stabilize at about 30 °C leading current densities between 30 and 100 $\text{mA}\cdot\text{cm}^{-2}$. The cathode is in aluminum.

Basics concerning chemistry of an electrochemical polishing:

Niobium oxidation during electropolishing might be written:



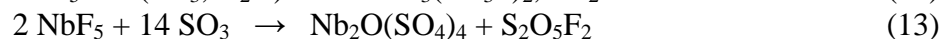
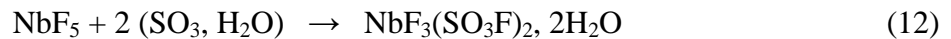
The reduction process is hydrogen formation at the aluminum cathode:



For a global and easier understanding, the oxido-reduction equation might be written:



Nb_2O_5 is then dissolved to form niobium fluoride, oxofluoride (see equations 4 to 8) species and fluorosulfate or oxysulfate and pyrosulfuryfluoride because of sulfuric acid considered as hydrated sulfur trioxide ($\text{SO}_3, \text{H}_2\text{O}$):



A device was developed at KeK (Japan) with a rotating anode in a horizontal position (See Figure 5). A lot of experimental results obtained with that technique were presented at the 4th Workshop on SRF superconductivity [5].

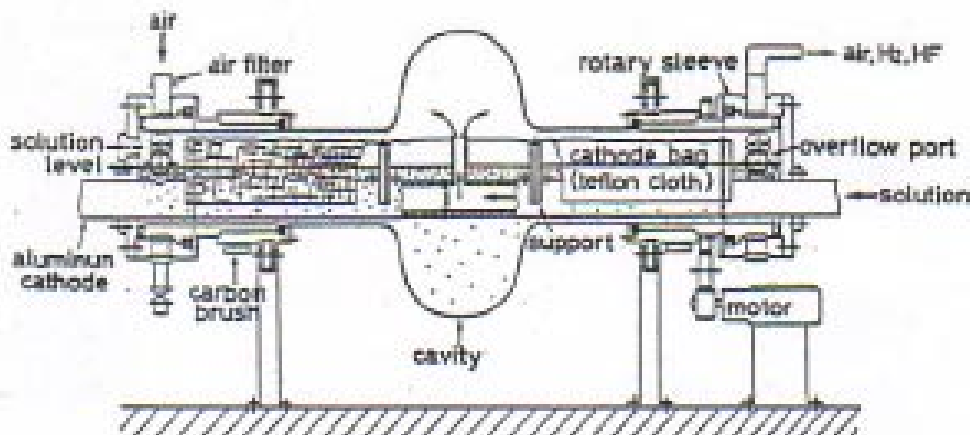


Figure 5: Horizontal EP set-up developed at KeK (from [6]).

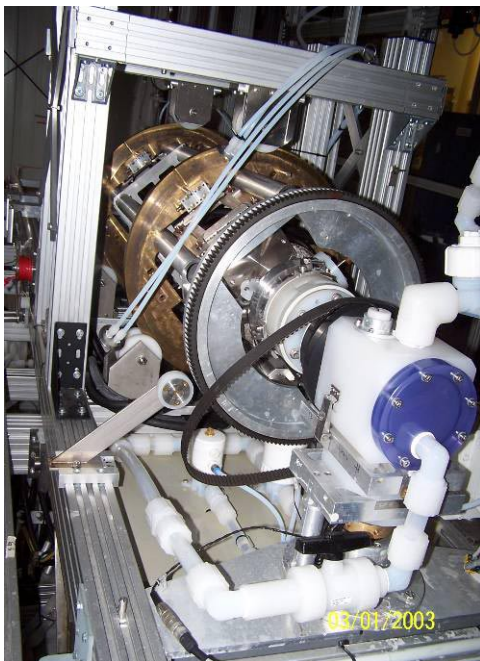
Chapter I Context

A similar technique is now largely adopted by the SRF community.

In spite of electrochemical process' superiority on the chemical one, a huge discrepancy in results is noticed. It could be explained by the presence of impurities remaining after High Pressure Rinsing. This aspect, as well as the aging of the bath and the effect of new electrolyte compositions will be discussed in chapter IV.

c) Example of niobium cavities electropolishing unit

A 9-cell cavities treatment unit (see pictures on Figure 6) has been implemented within the Tesla Test Facility collaboration. It aims at improving E_{acc} gradients in a reproducible process up to 40 MV.m^{-1} . Nevertheless this unit is dedicated to production purpose, and is running with a standard procedure as defined by KeK in the 80'. We have built an experimental electropolishing set-up which aims to study and to optimize this process and to propose new parameters to the community (see chapter V).



Nine-cell cavity in the EP treatment device



Cavity after EP being transferred into the clean room

Figure 6: EP at DESY. 9-cells cavities are treated and then transferred into clean room for rinsing.

Chapter II Niobium and Electropolishing : State of the Art

1) Niobium an its oxides

a) Niobium oxides

Niobium is a passive valve metal, which means that it is recovered by a thin, very stable oxide layer, namely $\text{Nb}_2\text{O}_{5-x}$. This oxide has a very particular structure, able to accommodate many stoichiometry defects, and to accept incorporation of large ions like PO_4^{3-} or SO_4^{2-} [7-12]. It loses its passivation properties in presence of F^- . It will obviously play a key role in the electropolishing process; therefore, it is important to describe it more into details. Two other less oxidized species are known: NbO_2 and NbO , which can stabilize under certain conditions.

b) $\text{Nb}_2\text{O}_{5-x}$ structure

In $\text{Nb}_2\text{O}_{5-x}$, the Nb^{5+} ion is surrounded by 6 oxygen ions, completing a NbO_3^- stoichiometry (see Figure 7 and Figure 8). In order to insure electrical neutrality, NbO_2 i.e. Nb in a tetrahedral environment distribute more or less regularly among the octahedral stacking, giving rise to a so-called “microcrystalline-amorphous” structure. The tetrahedral site tend to form, column (so called CSP, crystallographic shear planes), which present slightly different local properties, like an increased ionic and electronic conductivity [11, 13, 14].

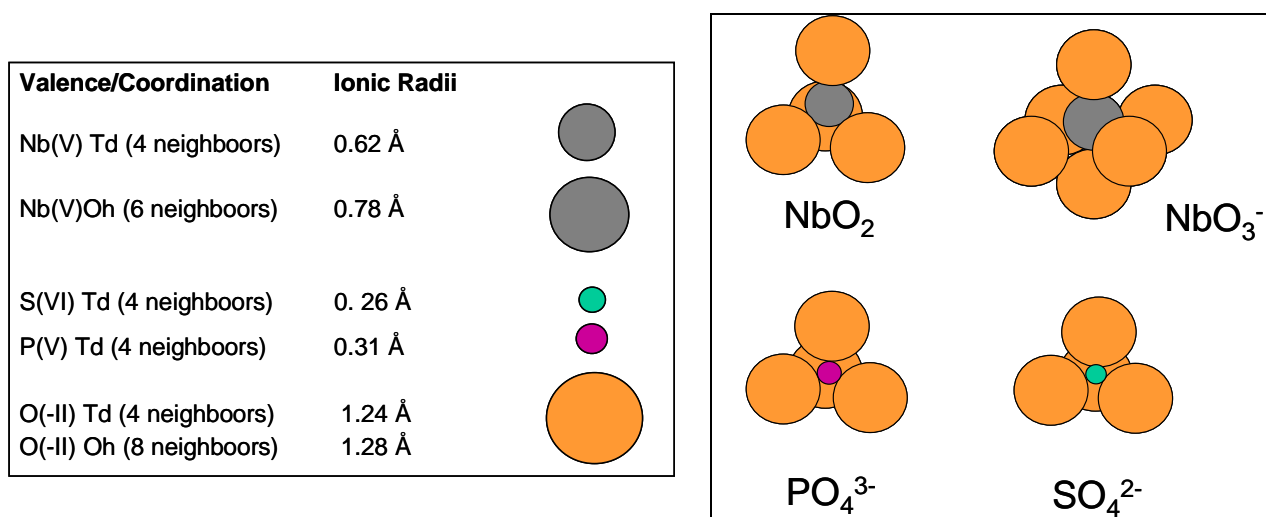


Figure 7: Comparison of the schematic steric volume for each species.

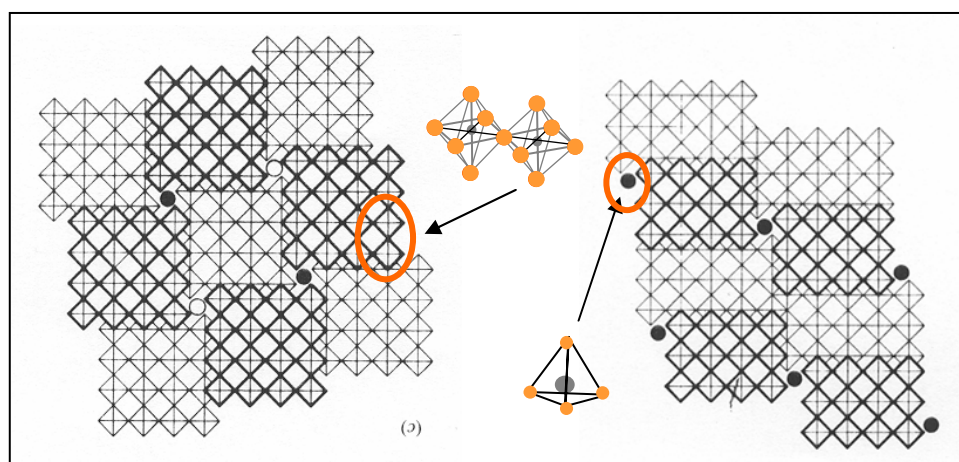


Figure 8: Two examples of possible arrangement between octahedral stacks and CSP.

Just by a slight arrangement of octahedral stacking vs. tetrahedral site, one can accommodate many slight variations around the equilibrium stoichiometry. Moreover the geometry of tetrahedral

Chapter II Niobium and Electropolishing: State of the Art

site is very close from the PO_4^{3-} or SO_4^{2-} ones, and incorporation of these electrolytes inside the oxide was often reported [7-10]. For instance, preparation of very good dielectric layers can be prepared by anodization of Nb into phosphoric acid, because incorporation of phosphoric ions is known to reduce both ionic and electric conductivity of this oxide [8].

Apparently, oxidation in wet condition produce more disordered pentoxide [10,14] , while oxidation condition also play a role on the growth rate, probably because the anion incorporation tends to stabilize one or another form [12].

c) Metal-oxide interface

Valve metals are usually considered to have a sharp transition between their oxide layer and the underlying metal. Evidence of the existence of a monolayer of NbO at the oxide have been found by XPS [11, 15], although it cannot be truly considered like an independent phase. NbO, and NbO₂ are also found upon a mild baking, similar to the one applied to RF cavities.

d) Oxides in presence of HF

Nb depassivates and Nb oxide gets dissolved in presence of HF. In presence of oxidizing conditions, there is still a competition between the built-up of the oxide and its dissolution, leading to a situation out of equilibrium. Anodization of Nb in presence of HF produces very particular structures, which can have a common origin with some observed effects during electropolishing, like oscillations. In [16], the formation of self organized Nb porous oxide is described in a mixture of 1M H₂SO₄ and 0.5-2 w% of HF, during anodization with an applied voltage of 20 V. Changing the concentration of HF will change the porosity of these “carpet-like” structures, which grow over a relatively thin compact film about 40-50 nm. In [17], other types of structures were observed, in aqueous solution of HF (0.25-2.5 w%) in various potential conditions (15-40 V) showing that both density and height of these structures vary with [HF] and voltage (see Figure 9). In [18], Monte Carlo simulations were conducted in order to model current oscillations with varying porosity of the oxide layer, and a distribution of oxide domains with the same thickness. This discussion will be resumed in § III 4) c).

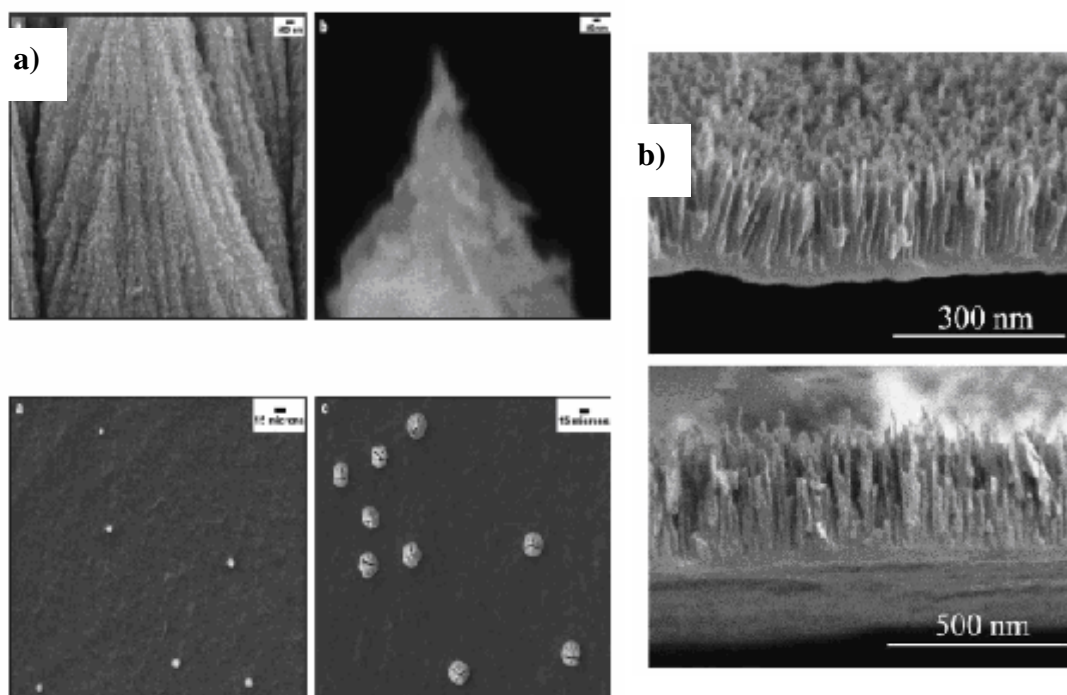


Figure 9: Examples of specific structured Nb₂O₅ observed upon anodization and in presence a) of HF (from [17]) and b) HF and H₂SO₄ (from [16]).

Chapter II Niobium and Electropolishing: State of the Art

2) Electropolishing Fundamentals

a) History of electropolishing

Beginning of electropolishing is attributed to Jacquet but its roots are older. Most of the following information can be found in a recent tutorial [19]. First electropolishing application results from a patent from the German Imperial Government for the finishing of silver in cyanide solutions. Copper was electropolished in 1935 and stainless steel in 1936 by Charles Faust. During World War 2, a lot of work concerning electrolytes formulas was carried out and results were published in the close post war period.

b) Generalities

Electropolishing belongs to the wide family of anodic electrochemical processes. In that case, the metal to be polished is in anodic position. A voltage is applied to the piece of metal to polish which dissolves and the counter electrode where reduction reactions occur. Electropolishing results then from the preferential dissolution of the metal's bumps. It might be done in potentiostatic or galvanostatic operating conditions. Magnitude that is commonly used to characterized polishing efficiency is the metal's reflectivity [20]. Electropolishing's superiority on mechanical polishing results from a main reason: it enables to associate macro and micro polishing.

Three factors are necessary to obtain an effective electropolishing [21]:

- An oxidising agent (anodic polarization that might be compared with the HNO_3 effect in chemical polishing).
- A depassivating specie.
- A diffusion layer promoter.

Electropolishing characteristics might be apprehended from $I(V)$ curves that generally include 4 regions shown in Figure 10:

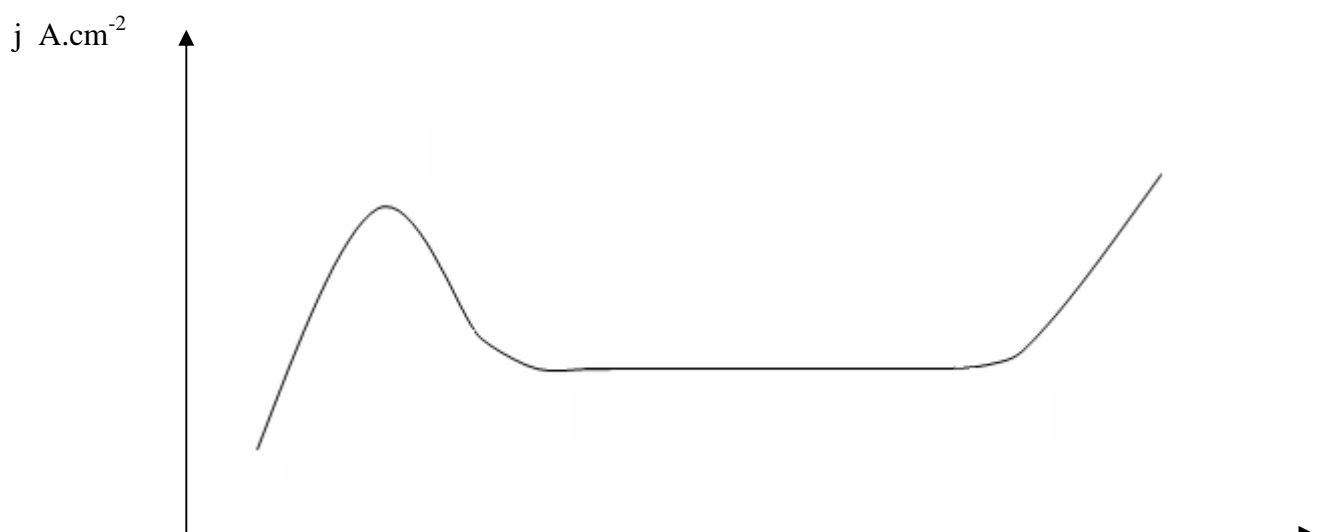


Figure 10: Characteristic $I(V)$ curve for EP. See text below for details.

Chapter II Niobium and Electropolishing: State of the Art

- Region AB: increase in current density.
- Region BC: instability.
- Region CD: “plateau” where are often found best electropolishing conditions.
- Region DE: gas evolution with O₂ emission provoking pitting.

Depending on the involved species, current oscillation might be noticed at different potentials on the I(V) curve.

c) First models: thin film and viscous layer

Beneath is apparent simplicity, electropolishing involves complex mechanisms. These mechanisms are particular to each couple electrolyte-metal. The couple Copper/Phosphoric acid is often quoted to describe involved phenomena at the metal surface. In fact, polishing efficiency is connected with the physico-chemical state close to the metal. Early publications mention the existence of a thin film and/or of a viscous layer.

c.i The thin film

Teggart [22] attributes micropolishing to this film. Nevertheless, the term remains vague and is both cited for a superficial layer of oxides or for a layer of precipitated salt films. Presence of an oxide layer is in some cases expressed in the oscillation of the current resulting from the competition between the growth of an oxide and its dissolution by a depassivant molecule. The existence of this film is thought to be indispensable for a brightening electropolishing. In fact, direct contact between the anode and the electrolyte must be avoided: otherwise preferential etching in high energies areas is to be expected.

c.ii The viscous layer

This layer [22] is much thicker than the thin film. Its forming results from the products of anodic dissociation. Moreover, nature of the interface depends on the electrode's potential and curve $V=f(t)$ after current relaxation might give some information about the stability of the species that might appear.

Some researchers have already investigated viscous layers' compositions for some metal-electrolyte couples. Thanks to XPS and AES techniques, Fang and Wu [23] established the composition from a viscous layer resulting from the polishing of copper in an electrolytic solution of 1-hydroxyethylidene-1.1-diphosphonic (HEDP) and phosphoric acids. The film was isolated maintaining the applied voltage during the sample's emersion and solidified immediately using a blast of warm air. The viscous layer is found to be constituted with a polymeric compound: $(\text{Cu}_4(\text{PO}_4)(\text{HEDP}))_n$.

d) First models explaining electropolishing

At the beginning of electropolishing, brightening was associated with non homogeneity of the thickness of the resistive viscous layer [22]. As it is thicker in the “valleys” of the metallic surface, unequal repartition of current leads the “peaks” to dissolve preferentially (see Figure 11).

Chapter II Niobium and Electropolishing: State of the Art

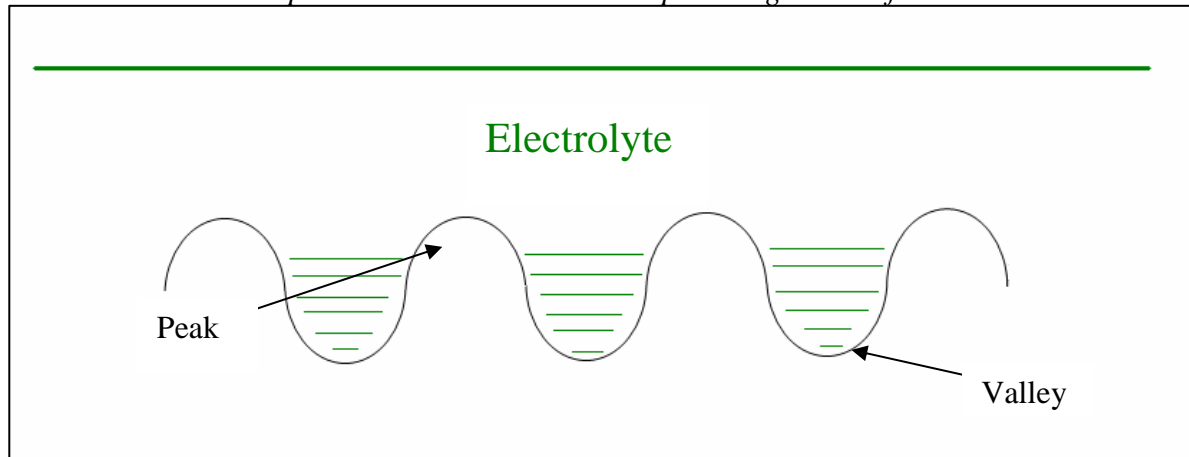


Figure 11: Principle of leveling process. Peaks dissolve preferentially because of the non homogeneity of the resistive viscous layer.

Elmore thought this model was incomplete because it did not take diffusion aspects into consideration. Leveling is then associated with a higher coefficient gradient at the picks because of the thinner viscous layer (reported by [19]). Wagner [24] even made theoretical prediction of the rate of leveling of microprofiles at the limiting current, based on a diffusion layer. *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 [Op. Cit.].* This model is also incomplete because it does not consider variations of diffusion coefficients and applies to anodic leveling (roughness Ra equivalent to 1 μm). This theory has been experimentally fulfilled [25]. The highest Wa , the more efficient is anodic leveling. Choosing the voltage at the highest cell impedance as a functioning point answers to this criterion and is widely used as a practical application [22].

e) More sophisticated models: Importance of the mass control transfer

As it was seen in §II 2) b), best electropolishing conditions are generally found along the “plateau” on the I(V) curve. With a Rotating Disc Electrode, an increase of the rotation speed causes a higher limit current density. It is a characteristic of systems controlled by diffusion phenomena. Depending on the system, several configurations might be encountered [26]:

e.i Limitation by the diffusion of metal cations from metal bulk into solution

This case corresponds to the precipitation of a salt film at the metal surface, and the concentration of the dissolved metal M_{aq} is equal to the saturation concentration. This film might be described as compact (ions migrate through it by high field conduction) or porous. The structure is sometimes believed to be more complex. In the case of iron into a FeCl_2 (4.0 M) electrolyte, R.D Grimm et al. [27] describe the structure has a “duplex film” with an inner compact layer, and an outer porous. The thickness of the inner part varies with potential whereas porosity is a function of agitation. This description is simplified and a continuous evolution from the compact to the porous layer is believed to be closer to reality.

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e.ii Limitation by the diffusion of an acceptor molecule from the solution to the metal (Acceptor-Limited Electropolishing)

This case might be found in the absence of salt film. The acceptor A^- is necessary for solvation of dissolving metal M_{aq} . As a consequence, this case is found when the transport processes are limited by the diffusion of A^- through the electrolyte diffusion layer. Concentration of the acceptor is then close to zero at the metal surface. For example, Matlosz et al.[28] believe anodic dissolution of Fe-13Cr alloys in 65% phosphoric-20% sulfuric acid electrolyte is limited by the transport of an acceptor.

e.iii Limitation by the diffusion of water molecules to the anode

This situation is a particular case of the acceptor-limited mechanism. In such a case, transport processes are limited by diffusion of water molecules through the diffusion layer.

These 3 possibilities generate 3 theoretical concentration profiles shown in Figure 12:

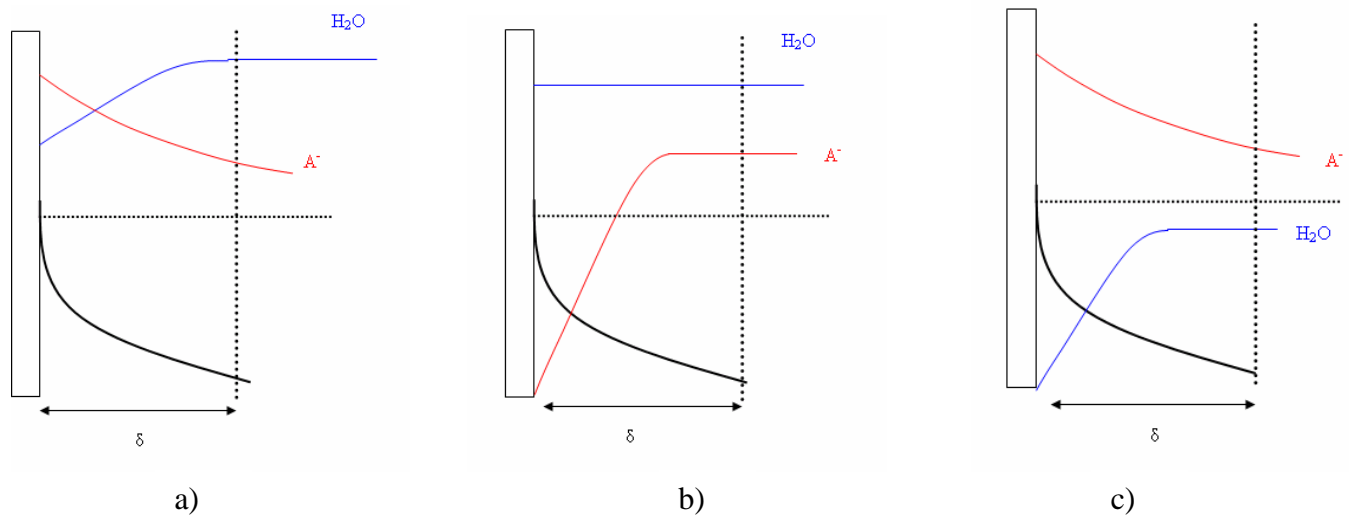


Figure 12: Concentration profiles in three cases: a) salt film, b) acceptor-limited diffusion, c) water-limited diffusion(from[26]).

Nevertheless, this view is simplified and reality may be conditioned by a mix of these effects. Furthermore, Landolt specifies that a plateau on the $I(V)$ curve is a necessary condition to obtain a good electropolishing. But it is not sufficient [29, 30]. Matlosz et al. [28, 31] simulated dimensionless steady state polarization curves for system under both diffusion and solvation considerations. Limitation might be due to a mix between diffusion and kinetic aspects (“conditions of mixed control”). Moving towards diffusion limitation is thus expected to lead to more efficient polishing conditions.

f) The contaminated oxide model

In this model described by T.P. Hoar et al. [32], brightening is attributed to the formation of a compact layer at the metal surface. This surface is not described as a plain oxide but as a “contaminated oxide” which has incorporated anions from the solution. This film has high cation conductivity: metal cations migrate through it at high rates and the layer dissolves as fast as it forms when steady state is established. Brightening and passivity are thought to involve same mechanisms and would simply differ in the magnitude of the limiting current plateau. (10^{-7} to 10^1 mA.cm⁻² for passivity and 10^1 to 10^3 mA.cm⁻² for brightening). This

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compact film avoids etching while brightening is dictated by random removal of metal atoms from the surface. The exact compositions of such films remains obscure, but as brightening conditions are generally found with very high acid concentrations, its stability must be governed by a high anion/O²⁻ ratio. Furthermore, this model is compatible with an outer part of the film that could be fluid.

Moreover, best polishing conditions are associated with high anode potentials. The authors provide a concise explanation for this phenomenon: *“the anions in the film must be forced against the metal as the interface recedes from the solution and into the metal; this is best achieved at the highest possible anode potential”* [Op. Cit]. This model shares similarities with the recent salt film model. Unfortunately, it is not clear if the random removal of the surface’s atoms should be governed by a mass transport limitation.

3) Electropolishing and oscillations

Niobium electropolishing is an unusual case. In fact, in potentiostatic conditions, current is found to oscillate for different potentials. Polishing in oscillating regions is accepted to be efficient and some laboratories use this principle as inherent to their process.

a) Siemens patents based on oscillations control

In this case the best operating conditions are associated with the existence of oscillations rather than a plateau [33-35]. Applied voltage is between 9 and 15 Volts, and there is no stirring. Oscillations form a characteristic “pocket” (see Figure 13) as they progressively fade, probably due to the formation of an insulating oxide layer. Once the oscillations have disappeared, voltage is shut down and stirring is set in order to dissolve the oxide layer. A new sequence is then started.

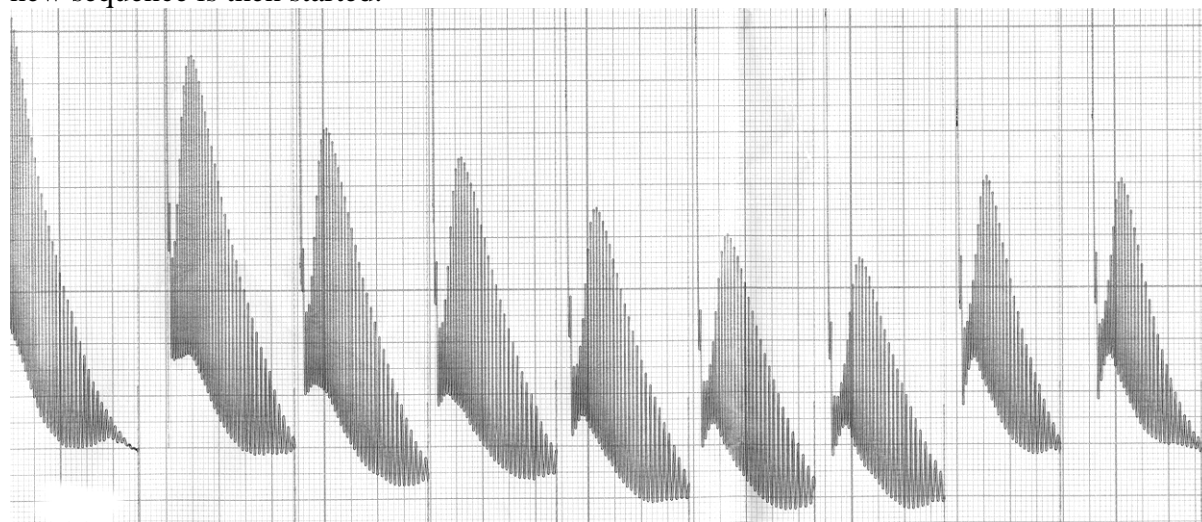


Figure 13: Example of « pockets » for EP in static condition. Each pocket sequences lasts 2-3 minutes. Stirring between each sequence is necessary. Note that the intensity of the pocket progressively decreases with time.

Cavity treatment at DESY is also carried out at potentials generating oscillations. During a sequence, oscillations might disappear. An increase in temperature or in potential enables to recover them.

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b) Other examples of electrochemical oscillating systems

Iron in sulfuric acid solutions

Geraldo et al. [36] studied iron dissolution in concentrated sulfuric acid solutions. Two areas of oscillations were detected, and the granular electrode surface is said to become smooth in presence of oscillations. Porous or non porous structures, colloidal dispersion of iron hydroxide or iron sulfate are cited as possible explanations for the phenomenon. Furthermore, oscillations have proven to start periodic, to move into non periodic and then finish periodic. Viscosity is suspected to impose periodic oscillations whereas hydrodynamics have little influence. Last, as the surface is uniformly accessible during the electropolishing, origin of the oscillations is rather sought in the electrolyte interface and not in the precipitation of a salt film. Effect of a viscous layer corresponding to a colloidal dispersion is in accordance with experimental results.

Nickel in H₂SO₄ 1mol.L⁻¹

This system is known to oscillate under galvanostatic conditions. It was studied under sinusoidal perturbation by F.Berthier et al [37]. In the transpassive zone, voltage increases with current intensity. For a certain value of current, potential begins to oscillate spontaneously.

c) Oscillations' investigation

M. I. Eidel'berg et al [38], investigated the oscillations area, believed to lead to the best polishing conditions. They used ellipsometry, illuminating the niobium surface with a helium-neon laser and recording light intensity variation. Changes were associated with a surface film thickness variation. Experimental observations were quite puzzling: In fact, light intensity oscillated with current oscillations at the beginning and then decreased and even disappeared whereas current kept on oscillating. A black film of deposition products was observed at the surface at the fading of light intensity oscillations. Once the film has dissolved, light intensity oscillations resume. This point will be further evoked in discussion in III 7).

Efremov et al [38] also investigated static EP and the formation of pockets, which they attributed to strange attractor.

4) Electropolishing Optimization

a) What aspects should be taken into consideration for cavities performances?

Electropolishing is widely used because it provides both micro and macropolishing. As a consequence, the treated surface is characterized by:

- Disappearance of initial waves on the metallic surface.
- Disappearance of grain boundaries.
- Very low roughness (less than 1 μm).
- High brightness.

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Nevertheless, there is no definite evidence of superiority of EP because of the polished surfaces at the microscopic scale. Some experiments are puzzling:

- From time to time, chemically polished cavities with a fairly high roughness reach same accelerating fields as electropolished best ones.
- New cavities have been built from monocrystals of niobium and polished chemically. In spite of their very low roughness, performance is not improved.

There are now models that show that magnetic field is enhanced at grain edges and can lead to a quench. Only one of such μm -sized defect is enough, and as large grains and preferential grain boundary etching can be found near the welding seam of the cavity (on the equator), whatever the surface treatment, it is difficult to foresee its existence. Electropolishing as it produces lower steps at grain boundaries appears more promising. Discrepancy of results is probably to find out in another issue than roughness. The responses that should be taken into consideration will result from tests that will be performed single cell device. The first challenge is then to reproduce on cavities surfaces obtained with samples. And, in a second time, our expectation is to establish a link between surface consideration and performance. If a large range of compositions leading to different surfaces are proven to reach the same RF efficiency, economical aspects should be taken into account. In that way, baths with a long lifetime and requiring low voltages are wanted. One should not forget that some new elements may appear during the research. For example, sulfur generation during the process has to be taken into consideration. It will be discussed in chapter IV and Appendix 2.

b) "Black Box method": Design of experiments.

As electropolishing involve complex mechanisms, some researchers use preferentially optimizing methods based on Design Of Experiments. This method enables to grasp the system minimizing the number of experiments. Furthermore, analyses of experiments might be of paramount importance for the understanding of the system. For instance Laurence Gasse used DOE ("plans de mélanges") [39] to optimize the composition of the electrolyte (H_3PO_4 , HNO_3) for the electropolishing of 308L and 316L steel alloys. This approach shall be very helpful to pursue the work presented here, once the general layout of the system would have been highlighted.

c) "Transparent" model

Another approach to optimize a process consists in understanding and quantifying physical phenomena involved in the considered system. Establishing of these phenomena often implies the use of electrochemical techniques such as, potentiostatic curves, potential decay, impedance spectroscopy [27, 28, 46, 47]. It is also possible to simulate any situation thanks to modeling, which allows to foresee the most influent parameters.

Electropolishing mechanisms have been established successfully for different metal-electrolytes couples. This study is incomplete in the case of niobium in $\text{HF-H}_2\text{SO}_4\text{-H}_2\text{O}$ mixtures. Determining of an adequate composition will result of this understanding. This report relates first conclusions drawn at Saclay concerning these mechanisms. A crucial point will result in the reproducibility of surface states with the monocell device. Furthermore, we will have to establish the link between surface state and RF cavity performance.

Chapter III Establishing of Involved Mechanisms

1) Experimental details

a) Preamble

This document deals with mixtures containing hydrofluoric acid (40 w%), sulfuric acid (96 w%) and additional water. Proportions in the mixture are then given in volumes. At the beginning, the notation is precise and is afterwards simplified. Components are always given in the order: HF, H₂SO₄, and H₂O.

For example: 1V-9V-1V corresponds to a mixture made of:

- 1 volume of HF (40 w%).
- 9 volumes of H₂SO₄ (96 w%).
- 1 volume of additional water.

Another example: 2V-9V stands for a mixture made of 2 volumes of HF (40 w%) for 9 Volumes of H₂SO₄ (96 w%). NB. Even without additional water, there is still constitutive water from the original acids.

During our experiences, we regularly checked surfaces with an optical microscope (zoom x50, x100, x200, x500, and x1000) and measured gloss (B60) with a DR-Lange REFO 3D reflectometer.

b) HF: Caution!

Hydrofluoric acid (HF) is indispensable for niobium electropolishing because of its depassivation properties. So the handling of the mixtures during bath preparations or samples processing requires a lot of care and the wearing of appropriate clothes (gloves, protective glasses, etc.). In fact, HF is one of the most dangerous acids because of its consequences on human health (serious attack of bones). Furthermore, it is first painless at skin contact. "Fortunately", as HF is mixed in the tested mixtures with concentrated H₂SO₄, skin exposure would result in a severe burn that would alarm the injured person (calcium gluconate must be quickly administered).

c) Electropolishing and reference electrode

Not only is HF corrosive for humans, it is also very aggressive towards glass. As a consequence, the use of classical reference electrodes is prohibited in such mixtures. We could not get to the anode electrode potential, but just to the potential difference between the niobium anode and the aluminum cathode. Niobium samples that are electro polished are parallelepipeds 30 x 30 x 4 mm³. Corresponding weight is approximately 30 g. Experiments were performed in two different devices:

c.i "Fixed electrodes"

This device is easy to handle but allows one sample per sequence. Experiments are carried out in a Teflon becher. The electrodes are set vertically (Please see Figure 14 and Figure 16). The distance between them might be chosen between 2.5 and 5.5 cm.

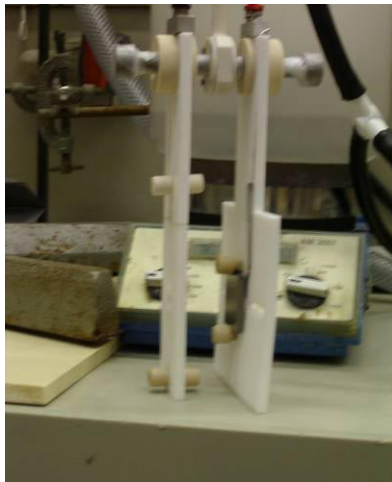


Figure 14: "Fixed electrodes" set-up.

Cathode is in aluminum. A Teflon cloth is necessary between the cathode and the anode in order to prevent the hydrogen bubbles formed at the cathode to migrate toward the niobium sample [40].

Bath temperature is controlled by a cooling system. Bath is stirred using a magnetic stirrer.

c.ii "Rotanodes" device

Rotanodes set-up is composed of a motor driven wheel in Teflon which handles up to 10 samples. The wheel rotates in a Teflon tank containing 1.5 liter of EP mixture. Samples are fixed to the wheel thanks to Teflon connections. Anodic contact is made with a niobium chip (see Figure 15 and Figure 16). Aluminum (purity 99.5%) cathode is cylindrical and brought into alignment with the centre of the wheel. Bath temperature is controlled thanks to a cooling system. Up to ten samples might be fixed on the wheel, at a distance between 31 and 101 mm from the border of the cathode.

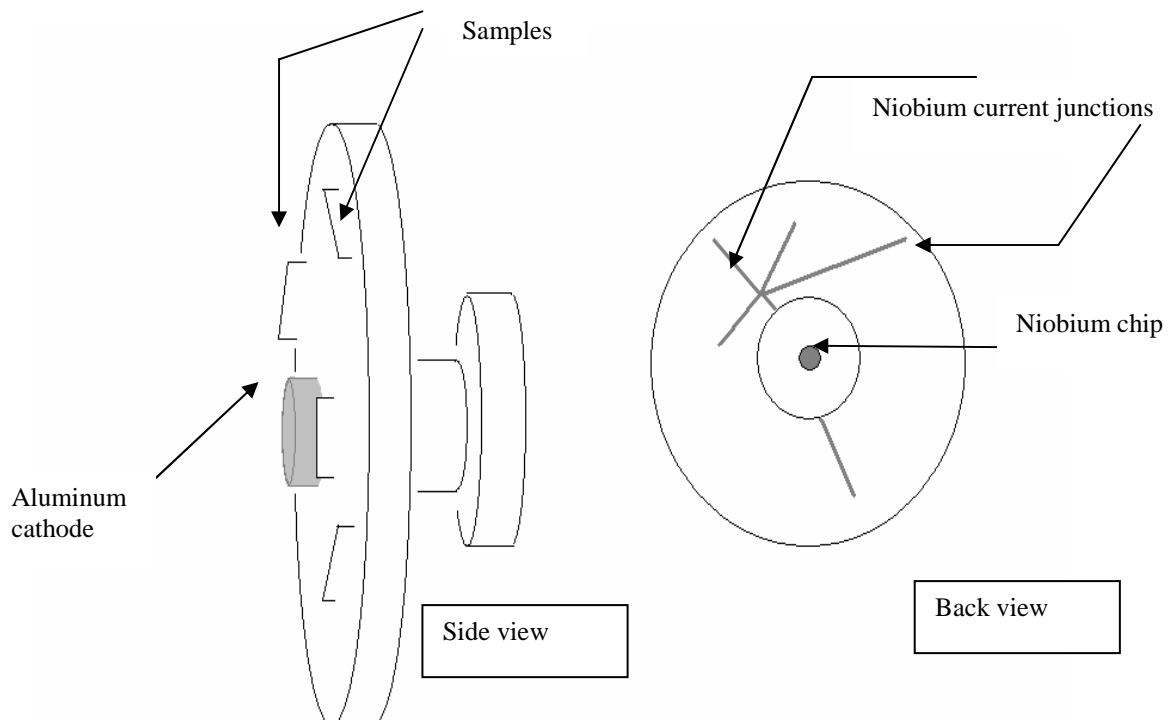


Figure 15: Rotanodes' wheel. Up to 10 samples might be fixed on the wheel. Their distance to the cylindrical cathode is between 31 and 101 mm.

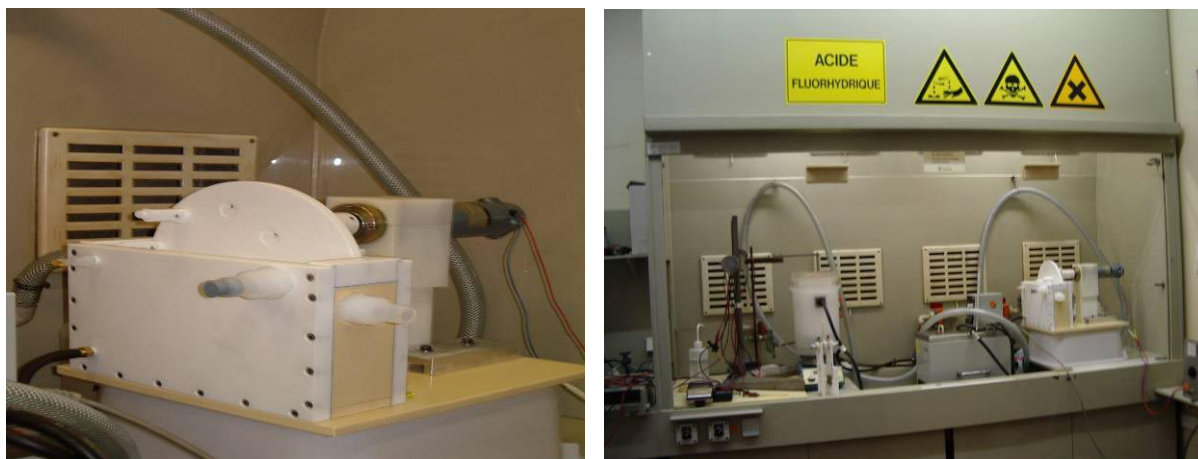


Figure 16: “Rotanodes” and “Fixed electrodes” set-up used in the laboratory.

NB. First temperature measurements were carried out with a laser sensor that revealed to be over dependent on the targeted surface. A teflonised Pt probe enabled us to improve our temperature measurements.

d) Data monitoring system

Previous measurement devices (multimeters, mechanical plotter) were insufficient to get precise information concerning the system. It is necessary to monitor following data with a program:

- Potential between anode and cathode.
- Current intensity.
- Temperature of the electrolyte.

We have benefited from the support of a technician who developed the program with Labview software. The program also commands the power supply and enables to plot I(V) curves.

2) Ohmic losses and their consequences

a) Ohmic losses in solution

Some $V(t)$ curves were monitored via this data monitoring system after the switching off of the voltage supplying. An example is given on Figure 17 for a 2V-9V mixture. $V(t)$ decreases by 77% in 50 ms. We may conclude that ohmic losses in the mixture are huge.

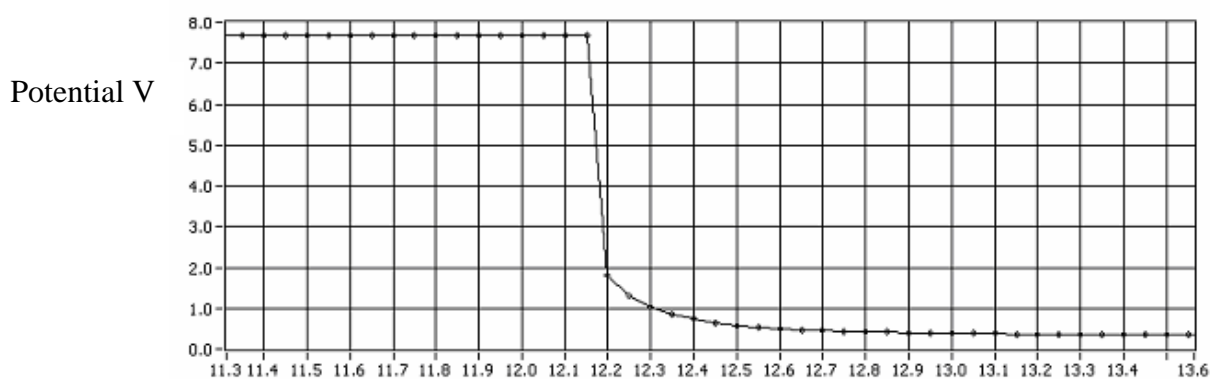


Figure 17: Discharge of the electrochemical cell in function of time 2V-9V mixture. $V(t)$ decrease by 77% in 50 ms.

Furthermore, details concerning heat production during 9-cell cavity treatment with 1V-9V mixture at DESY can be found in [41]: heat production is almost 67% of the applied electrical power. Thus, Joule effect is appreciable in such electrolytes and will have consequences on the cavities treatment.

b) Consequence: dependence of intensity on temperature

In order to quantify the dependence of temperature on current intensity, some experiments have been carried out with Rotanodes. Intensity has been recorded during the electropolishing of a sample at a distance $d_{ac}=101$ mm while temperature was increased from 20°C to 31.2°C. Results are displayed in Figure 18.

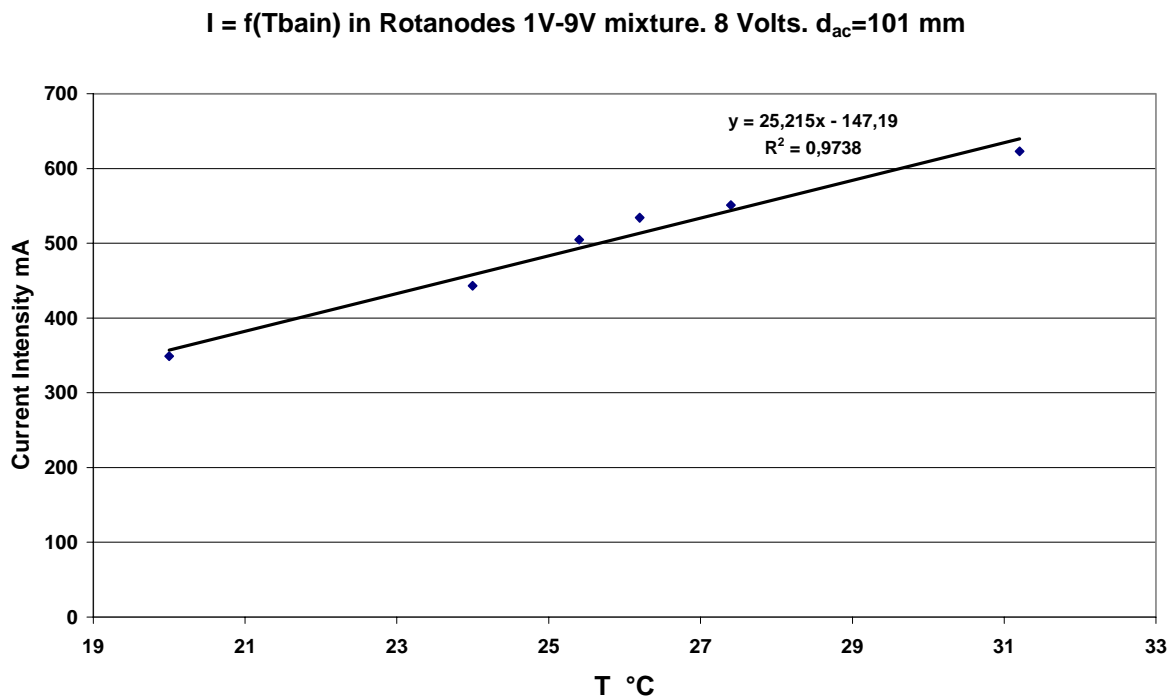


Figure 18: Intensity evolution as a function of temperature and linear fitting. 1V-9V mixture. Current intensity increases dramatically with temperature.

Intensity increases linearly with temperature. In this case, intensity doubles for a 11°C increase. As a consequence, it is crucial to control temperature at a constant value in order to compare different experiments: A drift in temperature will inevitably be followed by a substantial change in intensity.

3) First results with a 1V-9V mixture

The mixture that is commonly use to polish cavities is composed of 1 volume HF (40 w%) for 9 volumes of H₂SO₄ (95 or 98 w%).

a) Evidences of the existence of a viscous layer

Some samples were processed in a 1V-9V mixture with the Rotanodes setting at voltage varying between 10 and 16 Volts. The samples describe a circle. They are immersed during a half of the trajectory. As they go outside the bath, we notice a greenish film slowly dripping along the sample's surface and then dissolving into the bath. It is difficult to evaluate this film thickness. It looks to be almost 1 mm thick. Furthermore, another observation pleads in favor

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of a viscous layer. After electropolishing, we notice, a particular feature on the sample, like “hair”, with stripes starting at the fixing points of the sample and sliding down the surface (see Figure 19). This shape is probably due to the viscous layer sliding along the sample because of gravity.

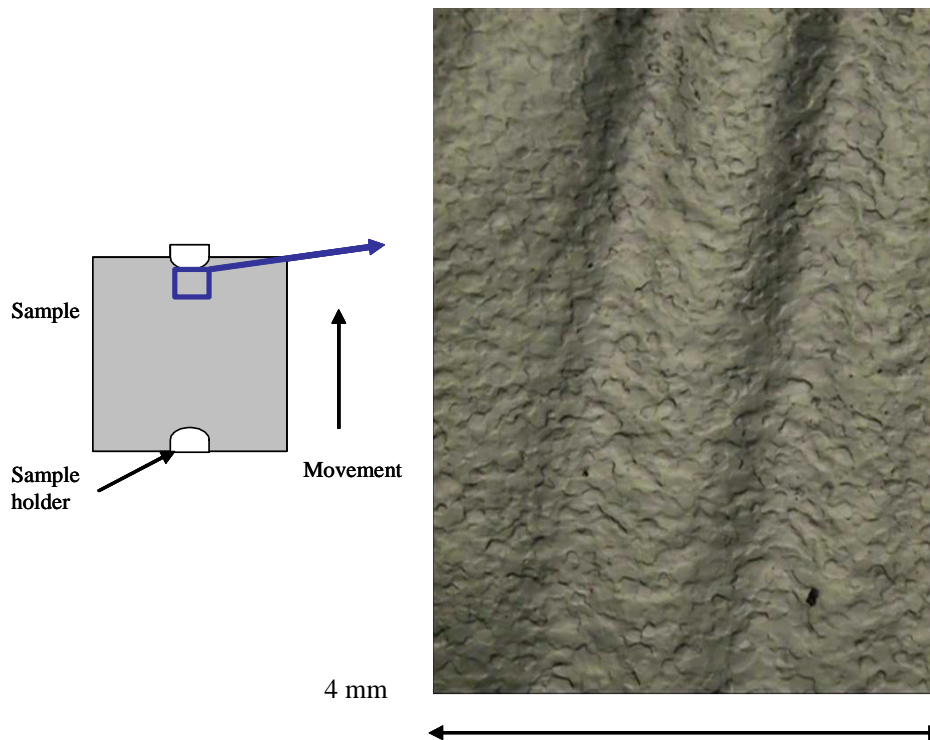


Figure 19: Sample’s surface after 703 min of EP 1V-9V mixture 14 Volts. Fixed electrodes set-up. Ripples are visible on the surface.

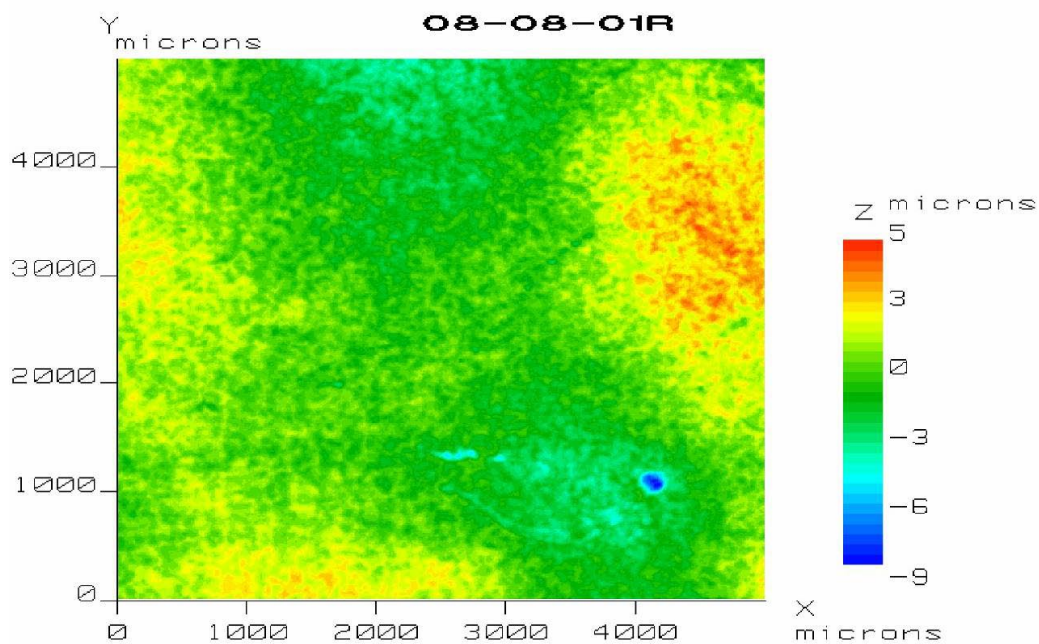
Roughness measurements also enable to point out this “wave” phenomenon on the sample. Some roughness measurements² were made and corresponding 2D-maps (Figure 20) might be plotted³. (Please also find 3D maps in chapter IV). Data are monitored in 5 mm x 5 mm areas with one point for 5 μ m. Maps below correspond to a sample processed with a 1V-9V mixture ($d_{ac}=5.5$ cm) after 300 min EP: The map a) corresponds to the upper part of the sample, and the b) to the lower. The waves are visible in part b). Furthermore, micropolishing seems more efficient in this part. In that case, waves are approximately 5 μ m high.

b) Hydrodynamics influence on intensity

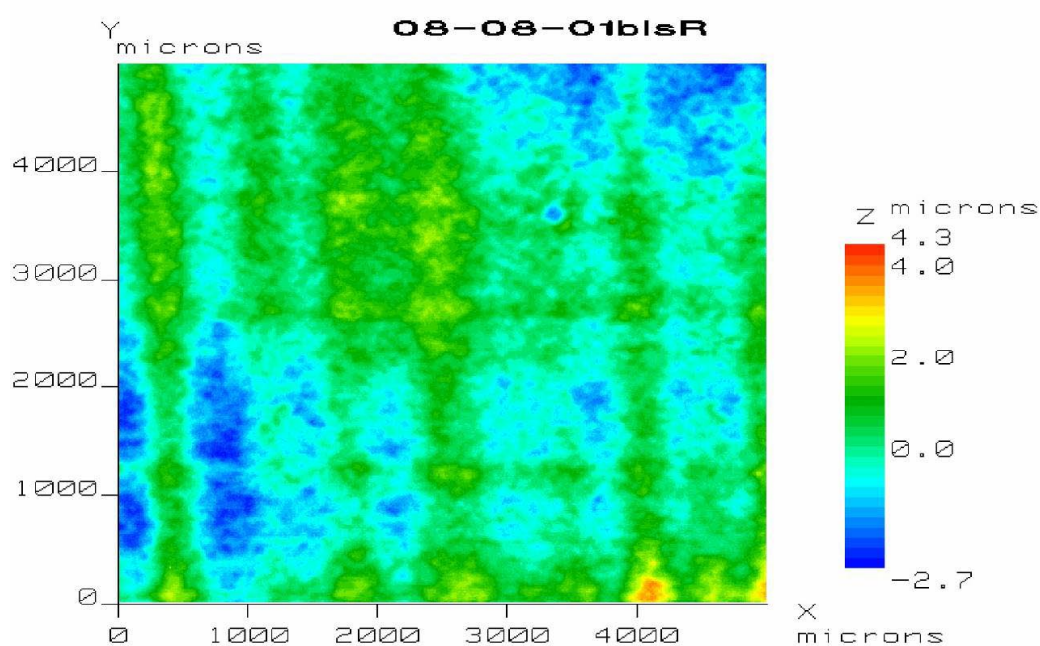
The Rotanodes setting enable us to polish a sample in various configurations. We decided to compare courant intensity for a sample in vertical or horizontal positions. Intensity was found to be 3% lower with the sample in horizontal position. Intuitively, it might be explained by the stagnant viscous layer discussed above whose resistivity is increased because of its higher thickness.

² FRW 750 Perthen Mahr and T10 Taylor Hobson probes

³ with MMB software (Akilog)



a)



b)

Figure 20: 2D roughness maps. 1V-9V mixture 16 Volts 300 min EP a) top of the sample b) bottom. "Waves phenomenon" is visible at the bottom.

c) *I(V) curve for a 1V-9V mixture*

Characteristic $I(V)$ curves were plotted with the Data Acquisition system for a 1V-9V bath at different temperatures. The graph for a 20°C temperature is given in the following graph (Figure 21):

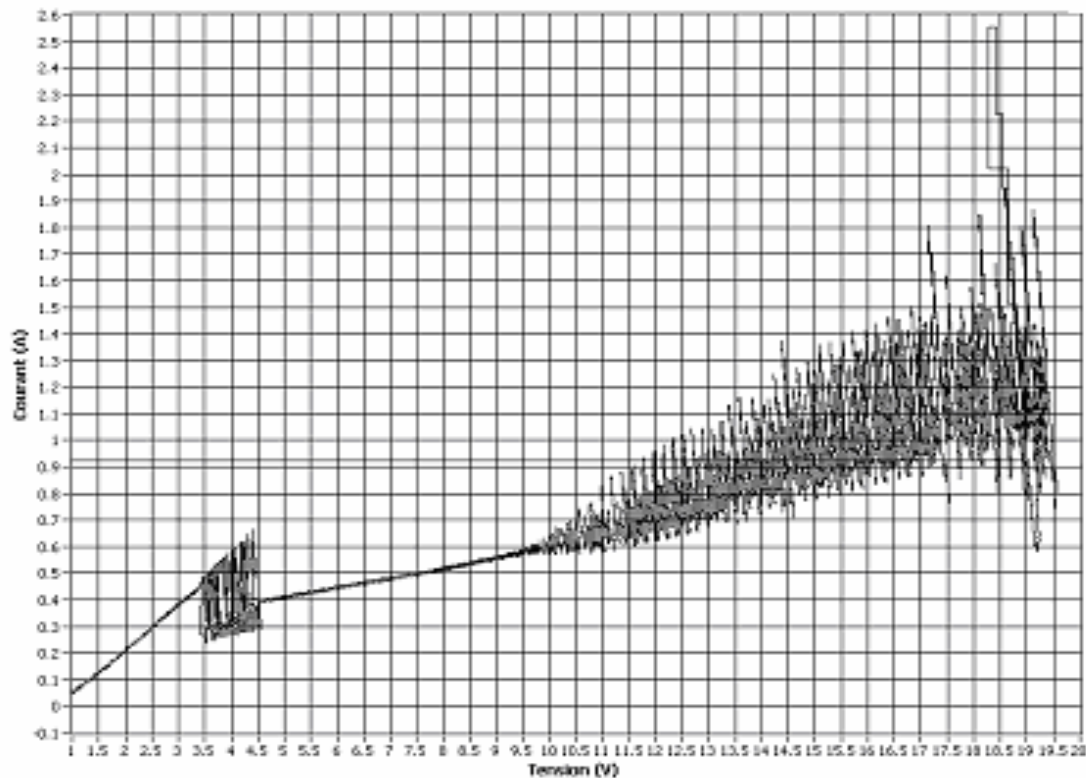


Figure 21: I(V) curve for a 1V-9V mixture. Characteristics of I(V) curves are observed. Moreover, the “plateau” is surrounded by two oscillations’ regions.

The shape of the curve is true to what is generally noticed for electropolishing. Nevertheless, the plot reveals two potential areas of instability:

- At low potentials (3-5 Volts): Regular evolution. Current is oscillating at fixed voltage with a steady period. This phenomenon is common and is explained by JP-Diard [42].
- At high potentials (above 16 Volts). Intensity fluctuates a lot but in a "irregular" way.

4) Concentration variations

a) Tested mixtures and ternary diagram

The EP Bath is formed from HF and H₂SO₄ mixtures containing water. As a consequence, concentrations that can be experimentally reached only cover a part of the ternary diagram given in Figure 22. Most studied mixtures were made without additional water. Thus, representative points are localized on the A-B straight line.

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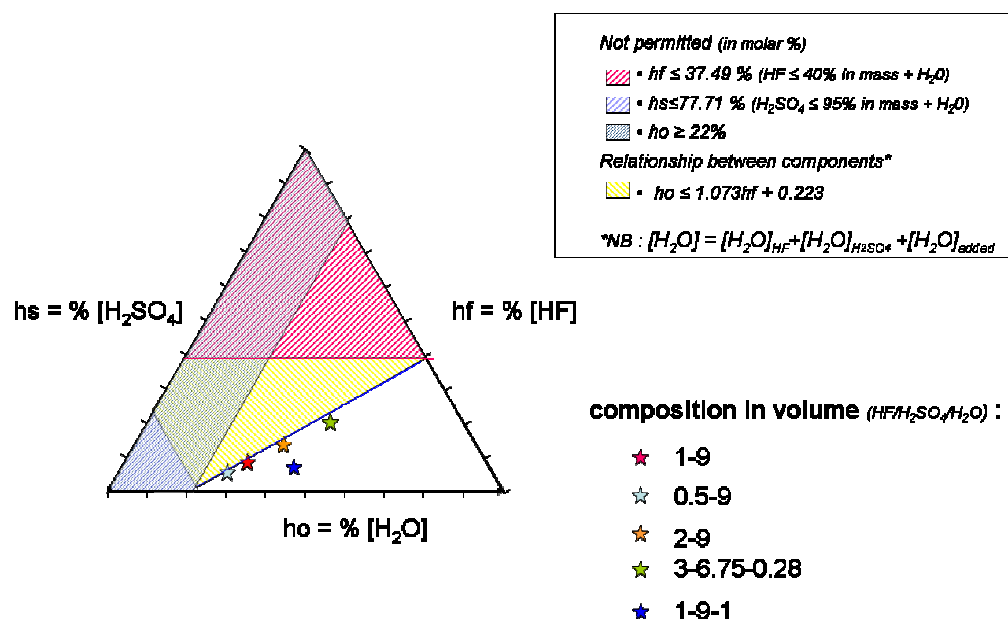


Figure 22: Ternary diagram for our chemical system and tested mixtures. Possible compositions are contained in a triangle.

b) HF effect on the system

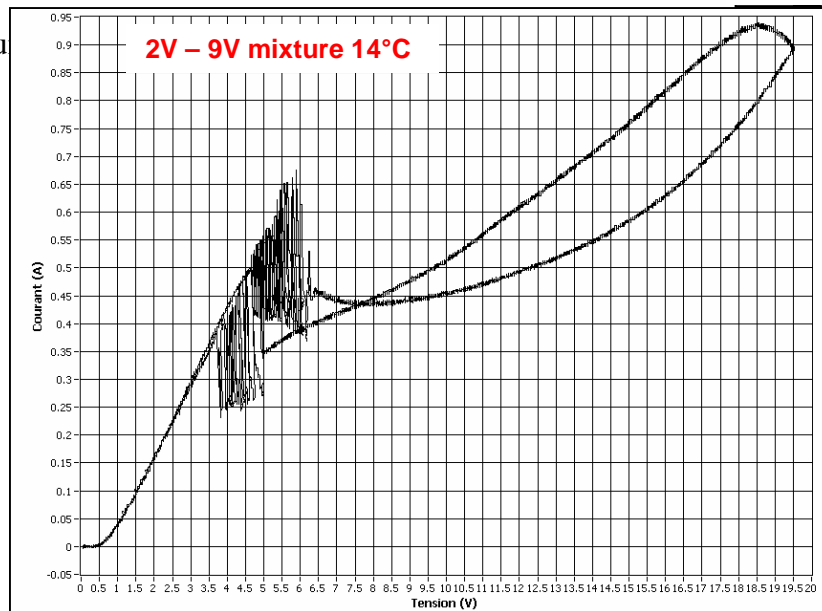
I(V) curves have been plotted for different mixtures, increasing gradually HF concentration. The curves were obtained for a potential range between 0 and 20 Volts. Potential is applied as a crenellation function whose step might be adjusted. A 50 mV step with an interval between 1 and 2 seconds has been chosen. A step whose duration is lower than 1s leads to unexploitable curves because of the oscillations. Tested electrolytes are 1V-9V, 2V-9V, 3V-9V and 4V-9V mixtures. Composition in concentration is given in Table1.

Table1: Compositions for tested mixtures.

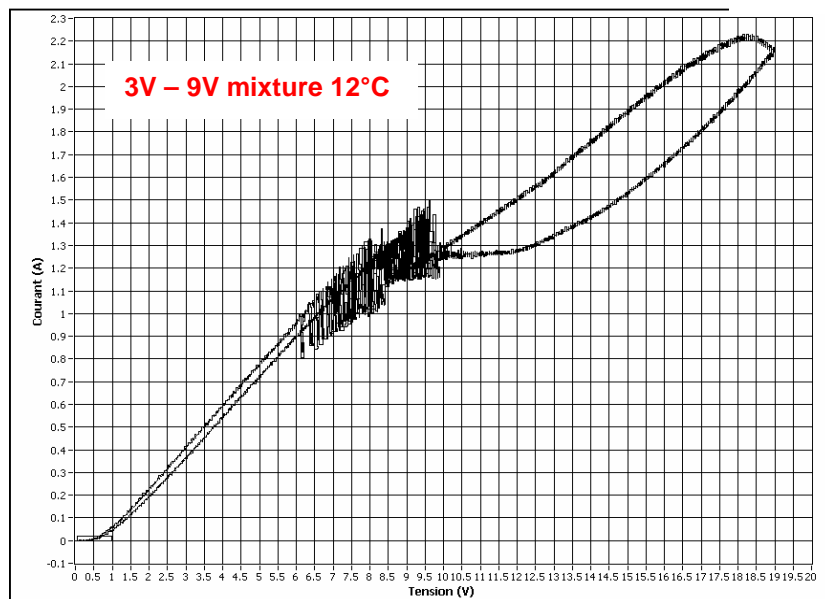
Composition	[HF] mol.L ⁻¹	H ₂ SO ₄ mol.L ⁻¹	H ₂ O mol.L ⁻¹
1V – 9V	2.26	16.15	7.43
2V – 9V	4.11	14.68	10.18
3V – 9V	5.65	13.46	12.47
4V – 9V	6.95	12.42	14.41

The corresponding I(V) curves are displayed next page (Figure 23).

a)



b)



c)

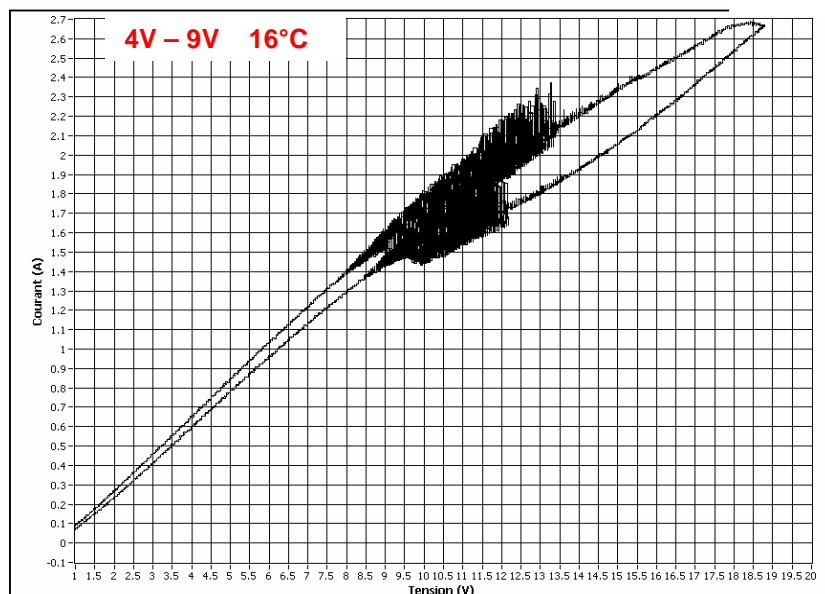


Figure 23: I(V) plots for: a) 2V-9V, b) 3V-9V and c) 4V-9V mixtures. Width of the plateau decreases with HF concentration and even disappears for the 4V-9V mixture. Oscillations are observed for all mixtures.

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Two points might be highlighted:

- The more the HF, the higher the removal rate at a chosen voltage.
- When HF concentration is increased, the length of the “plateau” decreases, and the second set of oscillations fades. For example, for a 1V-9V mixture, the plateau spreads between 4.5 and at least 13.5 Volts whereas there is just a 4 Volts window (between 5.5 and 9.5 Volts) for a 2V-9V mixture.

This decrease in plateau width might be related to this statement: HF does not favor the elaboration of a viscous layer at the metal surface. Furthermore, a 4V-9V mixture has been tested on Rotanodes to evaluate the influence of distance on removal rate (see § III 5) a)). No viscous layer was noticed to naked eye. Unfortunately, because of solution warming by Joule effect, only a low voltage (1.5 Volt) could be applied.

c) H₂O effect on the system

Water was added to a “classical” EP bath. The studied mixture was in 1-9-1 proportions. Shou [43] already tested a mixture with additional water in terms of removal rate evolution. Water was found to increase this removal rate. This point was attributed to a higher dissociation of acids⁴. The conclusions in this part will differ substantially. Figure 24 presents the I(V) curve for a 1-9-1 mixture at 20°C.

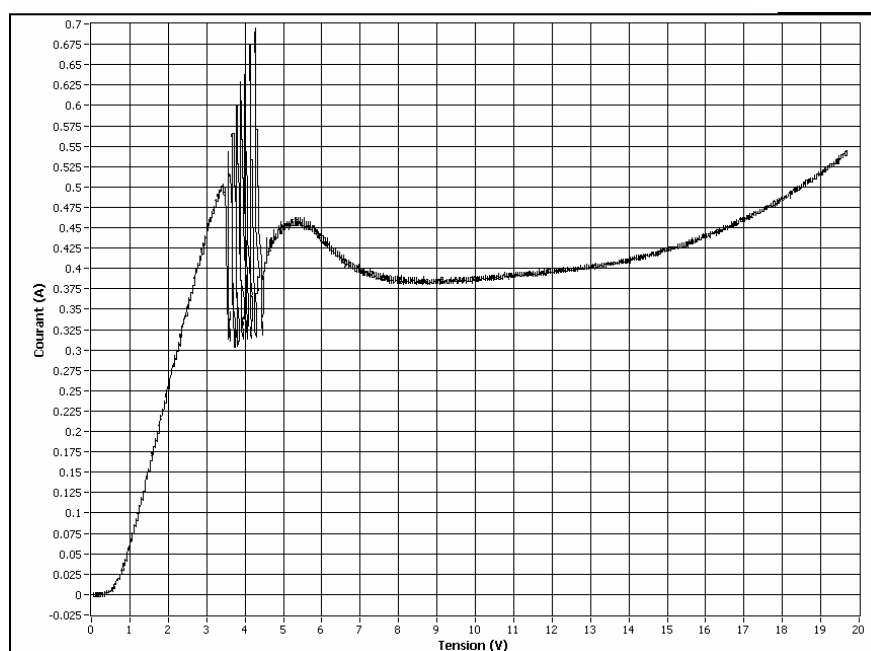


Figure 24: I(V) curve for a 1-9-1 mixture at 20°C. Higher water concentration does not lead to an intensity increase. Oscillations at high potentials disappear.

The current plateau exhibits a slightly lower intensity compared to the classical 1V-9V mixture. There is a 7% decrease but it has low signification as temperature was not exactly the same. Furthermore, one might notice that there is no instability (oscillations) at high potentials. As it will be described in chapter IV, a sample has been processed during long sequences with this bath. Brightness and surface were continuously monitored. The obtained

⁴ In this case [H₂SO₄] was decreased while [H₂O] was increasing, tested composition were : 1V-8.5V-0.5V; 1V-8V-1V; 1V-7.5V-1.5V.

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surface was quite unusual, compared to those analyzed with 1V-9V mixtures. In fact, surface does not become smooth but generates small irregularities still distinct with a x1000 zoom. Figure 25 shows the surface after 1445 min electropolishing at 14 Volts for x50 and x1000 zooms. The same sample was studied by SEM (see Figure 26). They exhibit some kind of grey scales, obviously insulating in nature, which hinder to get nice pictures, but tend to confirm the “thick oxide” hypothesis. This surface reminds us of some works presented in chapter II performed on niobium oxide growths [16, 17]. In such cases, these growths were prepared in HF-H₂O mixtures, with few amounts of hydrofluoric acid. As the 1V-9V-1V mixture contains additional water and a decreased HF concentration, we might associate this surface degradation with the generation of a self organized oxide layer. Moreover, we have observed that aged solutions, which contain few amount of HF because of evaporation and oxide dissolution, are more likely to develop these surfaces. Another observation argues in favor of an oxide growth. After 1445 min of EP, the sample is likely to be covered with blue spots, signature of thick Nb₂O₅ presence.

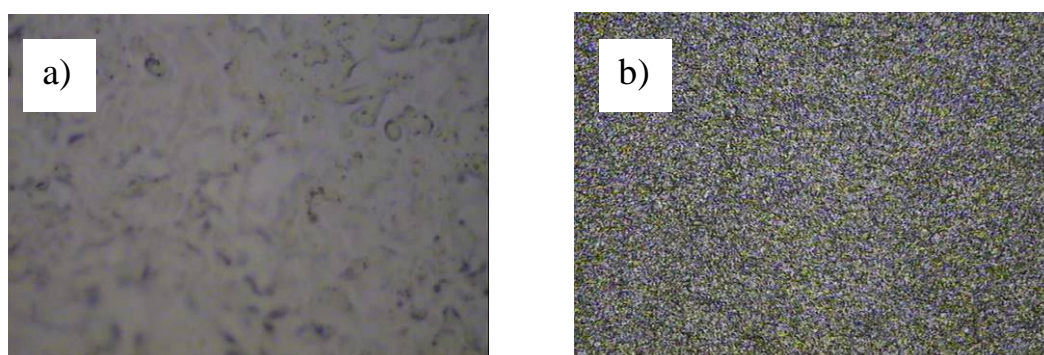


Figure 25: 1-9-1 mixture a) Surface after 1445 min EP x50; b) Surface after 1445 min EP x1000

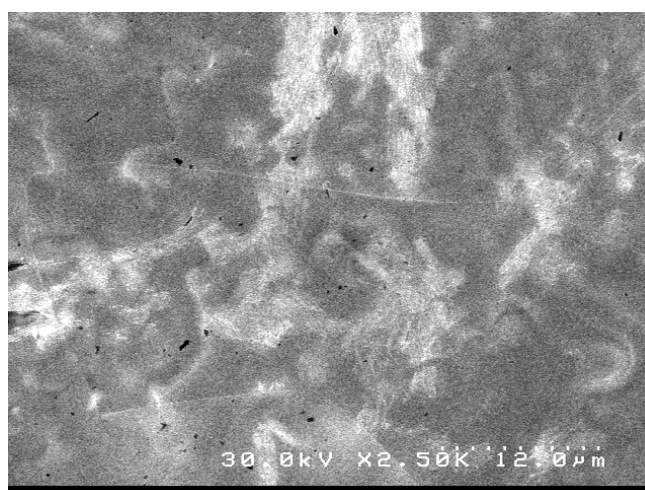


Figure 26: SEM Picture x 2500. 1-9-1 mixture 14 Volts, 1445 min EP. See text for comments.

For the electropolishing of Nb in HF-H₂SO₄-H₂O mixtures, the rate limitation step can not be water diffusion. In fact, the more the water, the lower the limiting current. Moreover, bath stirring does not or little affects current intensity although surface is very sensitive to bath hydrodynamics: waves due to agitation can be observed on electropolished samples in 1V-9V-1V mixtures.

d) H_2SO_4 effect

As it will be presented in § IV 7), a 0.5V-9V mixture has been tested, with a higher sulfuric acid concentration. Intensity as a function of applied voltage was investigated with a mechanical graph plotter. Each mark on Figure 27 corresponds to a pulse in potential with a 1 or 0.5 Volt increase for each pulse. One might distinguish 5 regions in the plot:

- Region 1: The current remains steady after a potential increase.
- Region 2: Oscillations area at low potentials.
- Region 3: Beginning of instability. Intensity oscillates with decreasing amplitude and then stabilizes.
- Region 4: Sustained oscillations are noticed with multi periods.
- Region 5: Irregular oscillations.

Observations concerning intensity are similar to those established for the 1V-9V mixture. Nevertheless, current density is lower. This should be related to the lower HF concentration in this sulfuric concentrated bath.

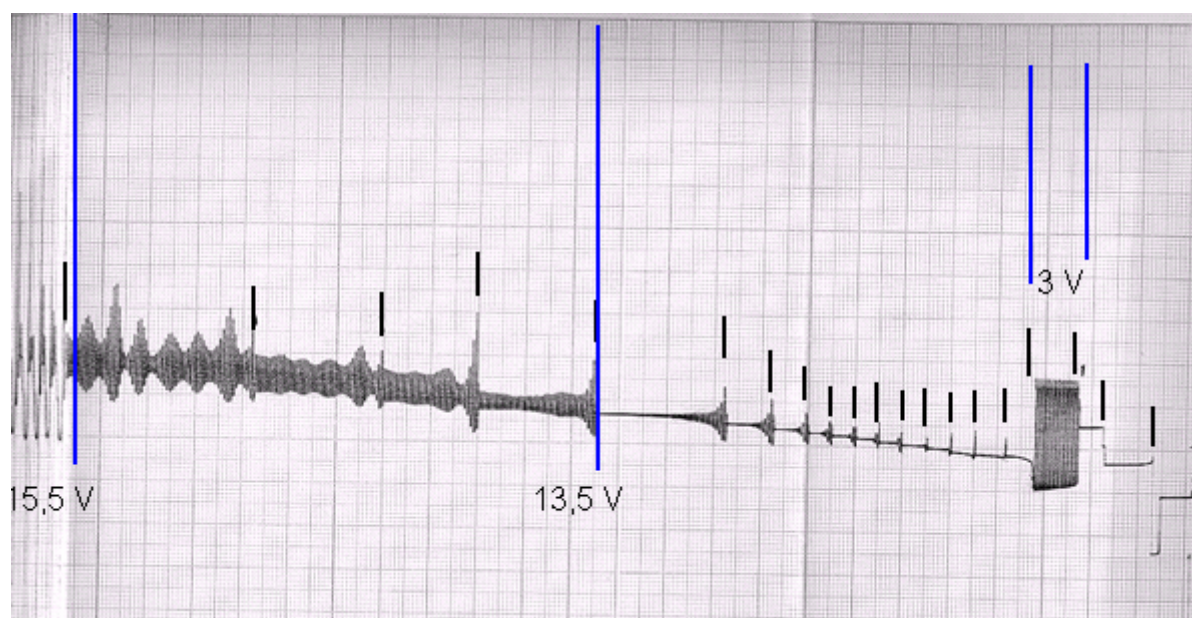


Figure 27: Intensity as a function of time at different voltages, 0.5V-9V mixture. Each black mark corresponds to a potential increase. 5 areas might be distinguished increasing the potential: 1: steady current, 2: regular oscillations, 3: beginning of oscillations with fading, 4: sustained oscillations with multi periods, 5: irregular oscillations.

More details concerning this bath will be given in chapter IV.

e) Removal rate and dissolved ions

In order to check if EP was controlled by niobium mass transport, we have tried to dissolve Nb_2O_5 and NaF in the EP solution. Indeed, as described in [26], if the dissolution of Nb is the limiting step, then a decrease of current density on the plateau should be observed upon adding Nb^{5+} into solution.

On the other hand, if the limiting step is the arrival of F^- at the metal interface, adding F^- should improve the process. In fact, we have observed higher etching rate with increasing HF

content, but this could also be attributed to the higher dissociation of the electrolyte. Adding NaF should provide information without fundamentally changing the nature of the solution.

Experimentals:

Unfortunately it was not possible to dissolve appreciable amount of powder neither of Nb_2O_5 or NaF inside 1V-9V the solution. In the case of Nb_2O_5 , the difficulty to dissolve the dehydrated form of this oxide is mentioned in literature [44]. And in the case of NaF, we can infer that this salt is poorly soluble in this solution constituted mainly by concentrated sulfuric acid. We are now intending to reproduce these experiments with a careful evaluation of the exact content of ionic species, either by chromatography or NMR.

5) Influence of the anode – cathode distance

Electric (Voltage) distribution depends on the geometry scale. I(V) curves will also depend on the cathode and cell shapes. It is vital to consider the influence of the distance between anode and cathode on electropolishing. In fact, because of the shape of the niobium cell, this distance is different for the iris and the equator (Figure 2). A uniform removal of niobium on the surface is expected for cell electropolishing. We will show the influence of distance in the two following cases:

a) In the presence of resistive surface layer

It was shown in paragraph III 3) c) that the I(V) curve for the 1V-9V mixture revealed a plateau for voltage above 6 Volts. As a viscous layer is visible to the naked eye, because of diffusion limitation, ohmic drop in the solution is not expected to affect current intensity. In order to ascertain that consideration, 6 sequences have been carried out with Rotanodes with a 1V-9V mixture for voltages between 10 and 16 Volts. Five samples at five different distances from the cathode (31 mm, 47 mm, 74 mm, 93 mm, and 101 mm) were processed. Corresponding results are shown in the Graph in Figure 28

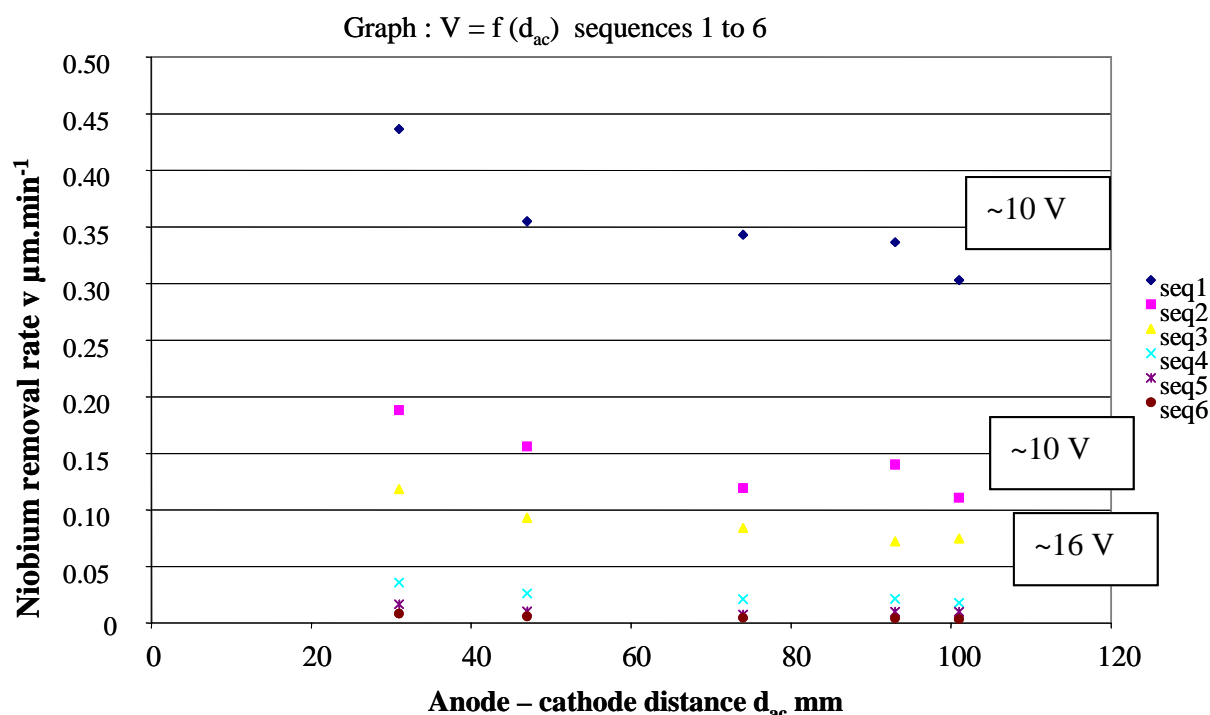


Figure 28: Niobium removal rate as a function of anode-cathode distance. 6 sequences have been carried out with different potentials. For distances between 47 and 93 mm, d_{ac} has low influence on removal rate.

Chapter III Establishing of Involved Mechanisms

The tendency is reproducible for the 6 sequences. The plot reveals a range of distance characterized by a steady removal rate between 47 and 93 mm. At 31 mm, the etching rate is roughly 20% higher than the average while it is 15% lower at 101 mm, which is still acceptable for practical applications. These experiments confirm that uniform removal rate with distance is achievable.

b) Influence of distance in “active dissolution”

The same experiment was carried out with a 4V-9V mixture. As it was seen in paragraph III 4) b), the I(V) curve reveals no plateau. Intensity increases substantially with applied voltage. In order to maintain temperature at a constant value, a low potential was chosen: 1.5 Volt. Results are displayed in Figure 29. Obviously, removal rate decreases linearly for the four first samples whose distance from cathode is between 31 and 93 mm. Surprisingly, the removal rate at 101 mm increases compared to 93mm. This point is not understood yet.

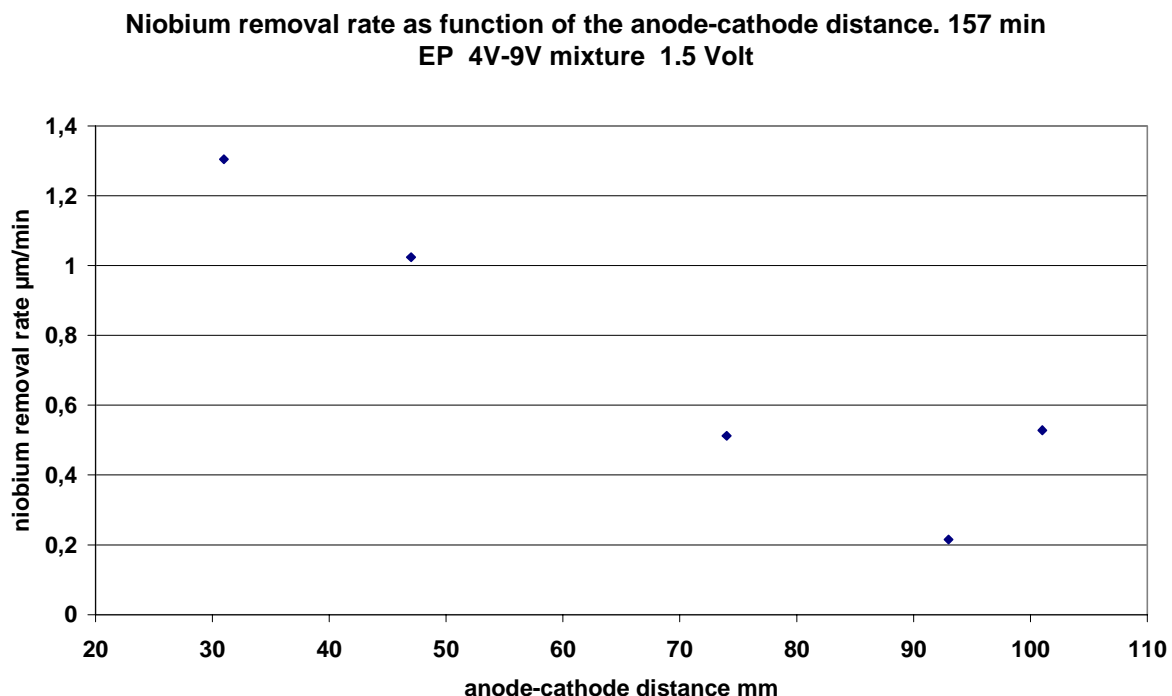


Figure 29: Niobium removal rate as a function of anode-cathode distance 4V-9V mixture, 1.5 Volt. A strong decrease in removal rate with distance is noticed for the 4 closer samples.

c) Conclusion: A « plateau » is necessary to get rid of the impact of the distance but is not sufficient.

In a nutshell, HF, contrary to water, favors high niobium removal rates and electropolishing might be linked to F^- transport limitation. Nevertheless, a too high HF concentration is harmful to the stability of a viscous diffusion layer at the metal surface and leads to active dissolution. Niobium removal rate is then over dependent on anode-cathode distance. On the other hand, in presence of a highly resistive viscous layer, influence of ohmic losses becomes less sensitive. Increased water concentration leads to a plateau on the I(V) curve. Removal rate is then stable with distance but surface deteriorates quickly, probably because of an oxide growth. Thus the existence of the plateau is highly desirable for application to cavities with a low impact of the cathode-anode distance, but it is not a sufficient condition. This first set of

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experiments also shows the importance of the F^- concentration in the process. This aspect of the question reveals to be a key issue for EP and will be further discussed hereafter.

For a better understanding of the above observations, we are using the Finite Elements Method (FEM) to study the steady states of the transport equations of our EP reactive system. The idea behind is to pursue the above analysis further and to investigate to what extent those critical factors (inter electrodes distance...) can effect first order changes in the viscous layer stability.

Modeling presents several advantages; one can for instance model precisely electrochemical conditions that are hardly experimentally achievable. For instance it will be possible to compare different experimental conditions (distance, stirring...) at given temperature. In practice, it is very difficult to compare precisely various experiments because of oversensitivity of measurement to slight temperature variations. Thus we should be able to highlight which parameters are the most influent.

This part of the work will be published later on.

Chapter IV Aging of the Bath

Mechanisms involved in EP were described in the previous chapter. We will now study the evolution of EP efficiency for long sequences and different mixtures.

1) Introduction

Long term experiments with a simple sample set-up can give useful hints about the involved mechanisms acting in aging. Once the general trends have been observed, precise determination of the amplitude of these effects must be studied on the cavity set-up. As it will be explained in next paragraph and in Appendix 2, aluminum and sulfur impurities form in EP baths. This parameter has to be taken into account in this chapter.

2) Impurities

a) Sulfur generation

Sulfur impurities forming in EP baths were put forward by KEK [4]. They are undesirable because they accumulate in pipes and might explain the huge discrepancy in results noticed in EP. As a consequence, this aspect must be taken into account in order to evaluate benefits of baths with modified composition. At Saclay, Aspart et al [54] gave quantitative results concerning impurities forming in baths containing both sulfuric and hydrofluoric acids for different concentrations. Experimental details and quantitative results are given in [54, 55]. Evidence of the impurities was also recently found at DESY on the nine-cell cavities EP plant. Moreover, new rinsing procedures with ethanol are now tested there to evaluate effective impact on RF performance of sulfur and aluminum.

Conclusion of the study is given below:

- Sulfur is synthesized in sulfuric concentrated baths, with or without applied voltage. Two contributions have to be taken into account: the standard corrosion process and an additional half reaction at the cathode when voltage is applied.
- Applied voltage radically favors sulfur generation. An obvious explanation lies in SO_4^{2-} ions reduction at the cathode:

$$\text{SO}_4^{2-} + 8 \text{H}^+ + 6 \text{e}^- = \text{S} + 4 \text{H}_2\text{O} \quad (19)$$
- Enhancing [HF] inhibits sulfur generation but is more likely to corrode aluminum cathode.

b) Aluminium corrosion

Corrosion of the cathode can be prevented by avoiding the use of aged baths. As found in literature, Aluminum corrosion is inhibited in HF – H_2SO_4 acids mixtures, but it is probably not due to the formation of a passive layer, but rather to the fact that AlF_3 is poorly soluble in concentrated HF – H_2SO_4 acids mixture: as H_2O concentration is low, acids are less dissociated.

Acidity of HF – H_2SO_4 mixtures decreases quickly with time. It is mainly due to HF evaporation and consumption (see [54]). This loss firstly reduces Al dissolution because of H^+ ions disappearance. Thus when HF content decreases, along with enhancement of the water content the bath becomes mainly “sulfuric” and inhibition due to HF vanishes. Corrosion recovers and leads to S and H_2S generation. It is worth noticing that Nitrogen flow used in cavities during ElectroPolishing will speed up HF losses in the bath.

*Chapter IV Aging of the Bath**c) Conclusion*

Corrosion of the cathode can be prevented by avoiding the use of aged baths. Nevertheless, one should notice that aluminum salt are little likely to transform into metallic particles, and they are easily rinsed with water. They should not be an alarming issue in our case.

On the other hand sulfur form solid particles that stick to surfaces and are hardly rinsed with water. It appears very early during the process and it is likely to go worse with aging of solution. Prevention from S formation is an important issue, along with the improving of rinsing procedure. As these impurities could explain undesirable effects noticed on cavities, this aspect must be taken into account in order to evaluate benefits of baths with modified composition.

3) Protocol

Experiments were carried out with the “fixed electrodes” set-up for long EP periods. Each period corresponds to several sequences. Generally one sequence is launched per day. The following parameters were monitored for each sequence:

- Current intensity evolution.
- Niobium removal rate (by differential weighing).
- Surface state observations (by optical microscope).
- Gloss (or brightness) (by glossmeter). On metallic surface the figure of merit is specular reflectance, measured by reflectivity for a 60° angle (notation: B60).

Other measurements, because of their constraints (they induce a long stopping of the experiments), have been more sporadically conducted:

- Roughness measurements.
- Composition analysis (by ionic chromatography or NMR).
- SEM analysis.
- Sulfur extraction.

Temperature during these experiments was stabilized between 26 and 30°C, excepted for the experiment with the 3V-6.72V-0.28V mixture (20°C) (§ IV 5)) and the last sequence of the experiment with the 0.5V-9V mixture (10°C at the last sequence of the experiment) (§ IV 7)).

4) Results with the 1V-9V mixture at two different potentials

Two experiments were carried out with the same mixture (1 Volume HF - 9 Volumes H₂SO₄) at two different voltages: 8 Volts and 14 Volts.

a) Brightness and dissolved niobium into solution

Brightness was considered as a function of time:

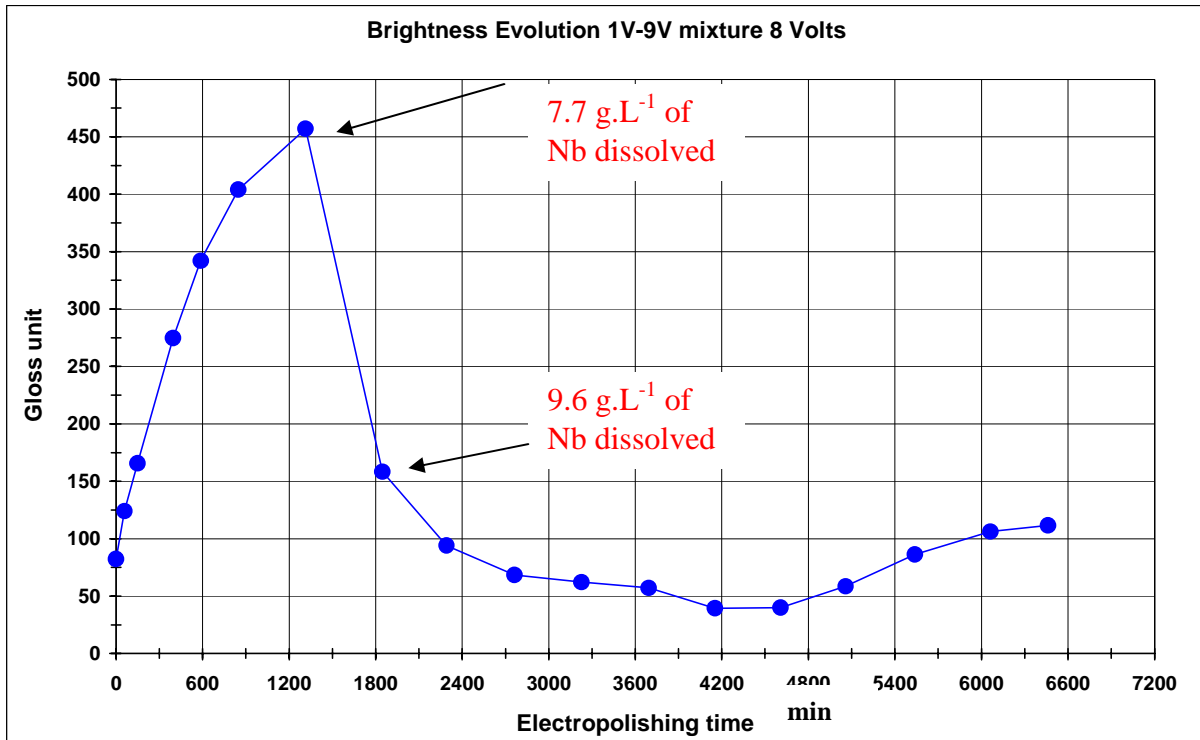
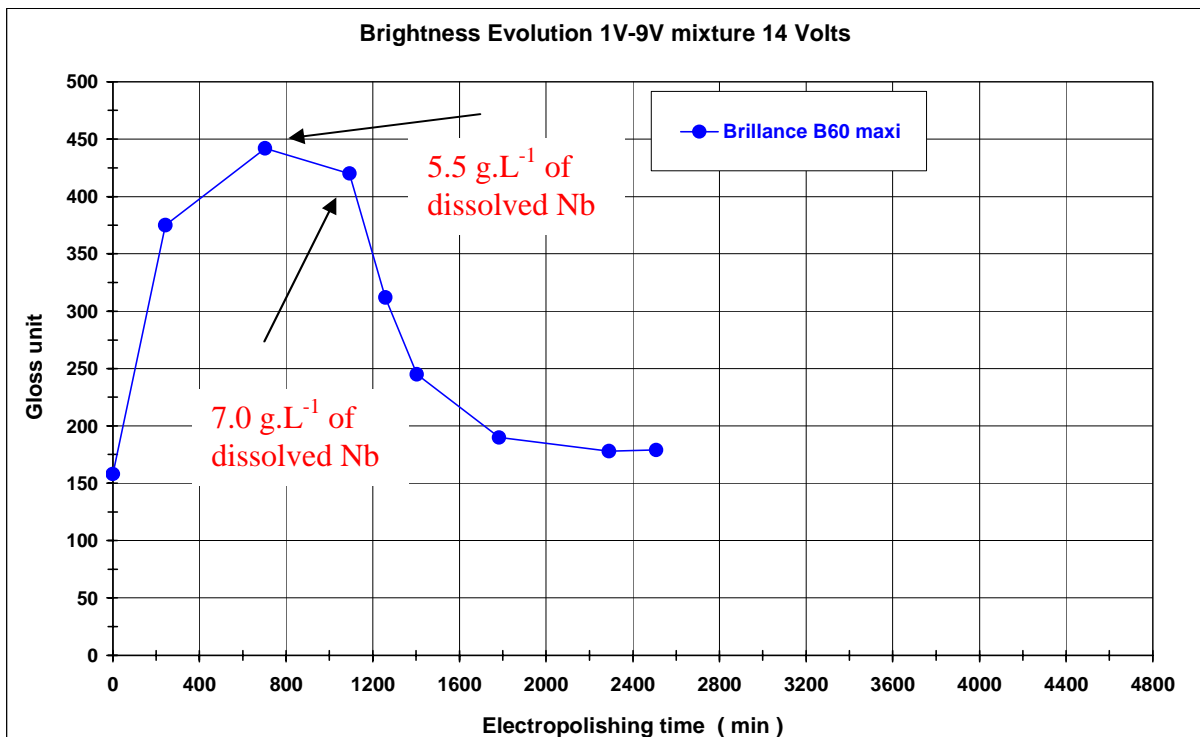


Figure 30: B60 evolution for EP with 1V-9V mixture 8 Volts and concentration of dissolved niobium after brightness decrease. Brightness first increases with time and then decreases after 1314 min EP.

The curves (see Figure 30 and Figure 31) show the same evolution: Initially, niobium samples are mechanically polished. Brightness is very low and surface is rough. During the first EP sequences, brightness continuously improves, reaches a maximum, and then decreases. The decreasing of the brightening efficiency appears when dissolved Nb exceeds 6-7 g.L⁻¹. In both cases, this concentration is lower than the specification applied to cavity treatment where the bath usually renewed when [Nb] > 9-10 g.L⁻¹.



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Figure 31: B60 evolution for EP with 1V-9V mixture 14 Volts and concentration of dissolved niobium during the brightness decrease. Brightness first increases with time and then decreases after 703 min EP.

Further experiments with other mixtures (2V-9V) have led to the same brightness evolution, with different niobium concentration at the max.

For the applied potentials (above 8 Volts), intensity is generally oscillating with a fresh mixture. Brightness and surface improve as long as we stay in the oscillations regimes. Oscillations amplitude decreases with time and leads to a steady current. The maximum is reached for different Nb contents when the composition of the bath is changed, but this could be correlated with the difference of solubility of NbF_5 in different HF concentrations. Aging of the bath is not directly or simply linked to niobium concentration in the mixture. The main challenge rests on the understanding of HF concentration and dissolved niobium contributions to aging. Some understanding will result from ion analysis in bath (IV 8)).

b) Evolution of etching rate with time

It decreases dramatically with aging of the bath, as it is observed on Figure 32. There is no obvious relation between surface deterioration and a value of the niobium removal rate.

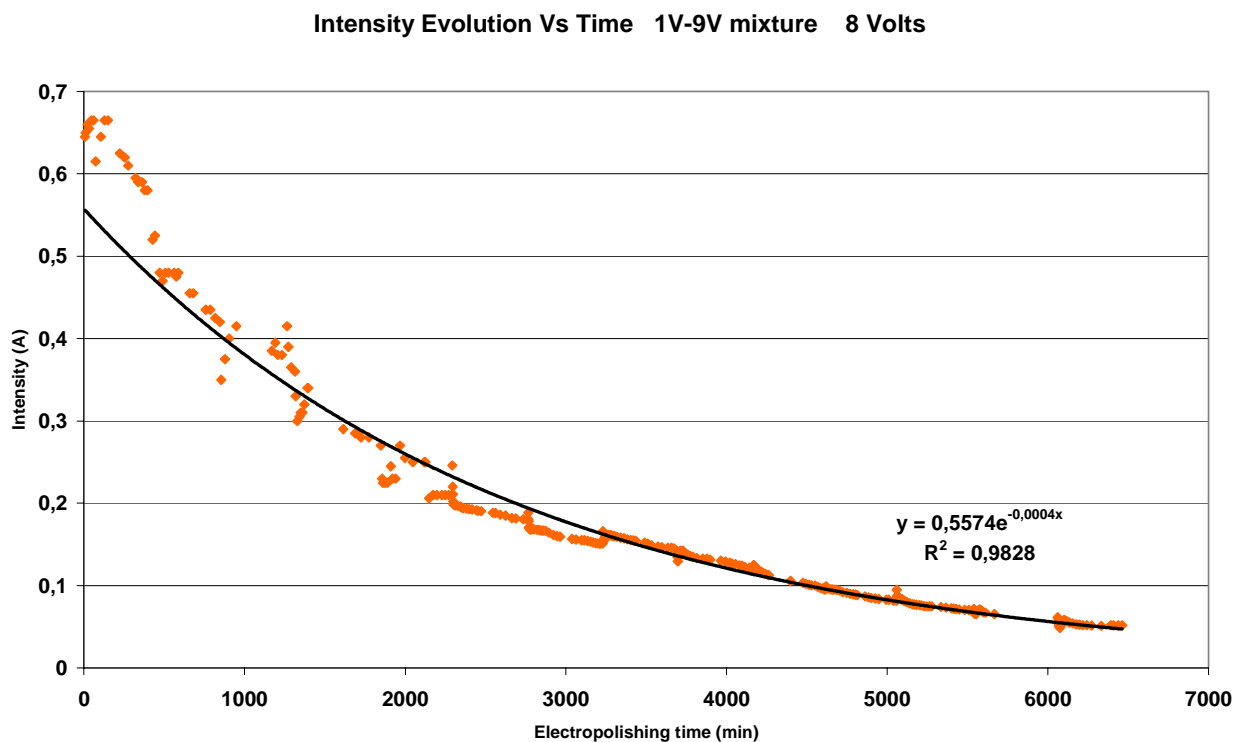


Figure 32: Intensity evolution for EP with 1V-9V mixture at 8 Volts and a fit with exponential decay.

c) Sulfur generation

Furthermore, as it has been explained in Appendix 2, electropolishing in this bath leads to sulfur and H_2S synthesis.

5) Tests with a hydrofluoric acid concentrated mixture: 3V-6.72V-0.28V

a) Brightness evolution and sulfur generation

Chapter IV Aging of the Bath

The removal rate is very high. As a result, it is necessary to operate at lower voltage and temperature. The voltage was 9 Volts and temperature around 20°C. This experiment enables to obtain quickly satisfactory brightness and surface states (see Figure 33). Furthermore, these results are still available for large quantities of dissolved niobium. After 25 g of dissolved Nb, we changed the sample for a fresh one. At this stage of the electropolishing process, the etching rate has decreased a lot, but the gloss improves back within about 500 min and keeps on a plateau around 400. At the end of the experiment, Nb concentration exceeds 29 g.L⁻¹.

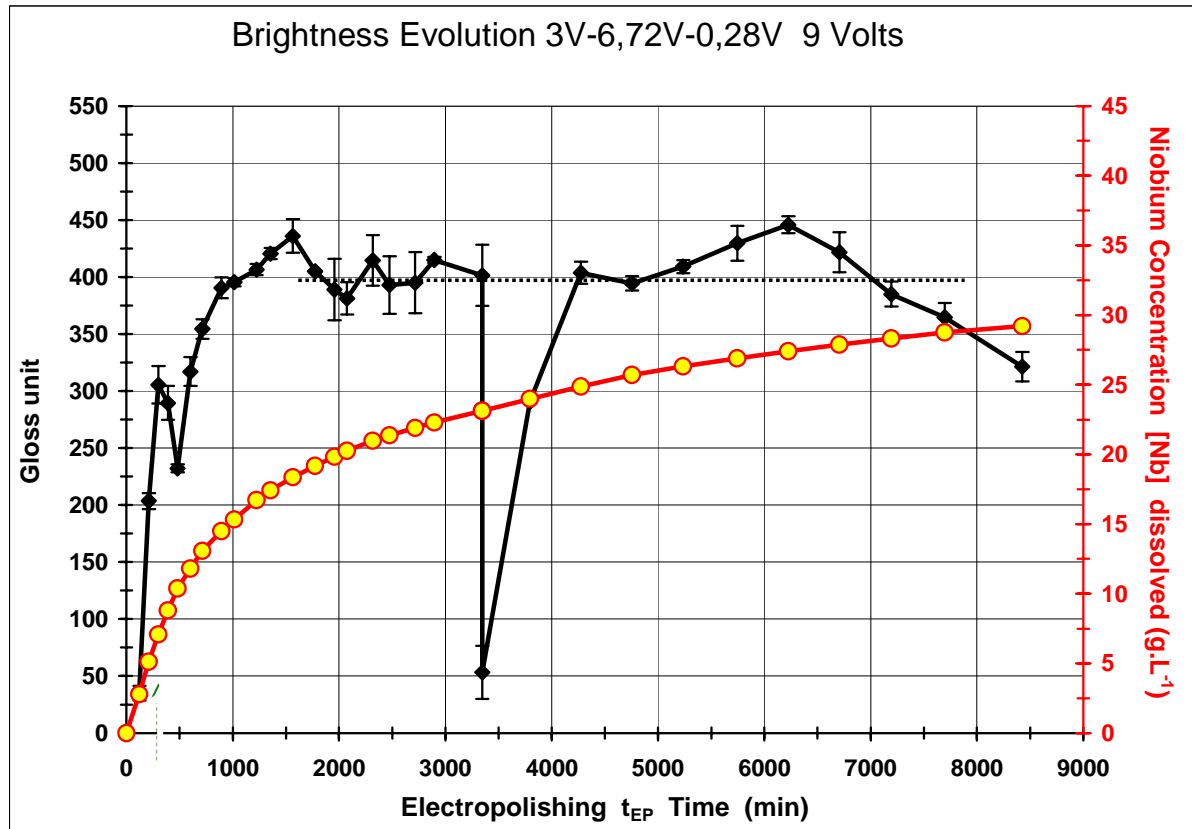


Figure 33: B60 and concentration of dissolved niobium evolution for EP with 3V-6.72V-0.28V mixture 9 Volts. The sample was changed after 3345 min EP. Nb concentration in the solution exceeds 29 g.L⁻¹ at the end of the experiment.

Sulfur extraction has been carried out with this bath. No sulfur was found.

b) Conclusion

Highly concentrated HF mixtures appear to provide precious advantages compared to a 1V-9V mixture:

- It generates no sulfur.
- Lifetime in term of dissolved niobium could be multiplied by four.
- Removal rate is very fast.

Nevertheless, high HF concentrations induce inevitable drawbacks:

- The plateau on I(V) curves is lost, thus we might not be able to get uniform etching inside cavities.

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- Hydrogen contamination must also be taken into account, as it was demonstrated that HF promotes H uptake inside Nb [40]. Tests on cavity will show if such a treatment affects Q_0 factor.
- Temperature must be controlled at lower values. Cooling system must be efficient
- It is more dangerous for safety and environment.

6) Tests carried out with additional water

Long time experiments were carried out with a 1V-9V-1V mixture at 29°C for a potential of 14 Volts.

Brightness evolution is given in Figure 34:

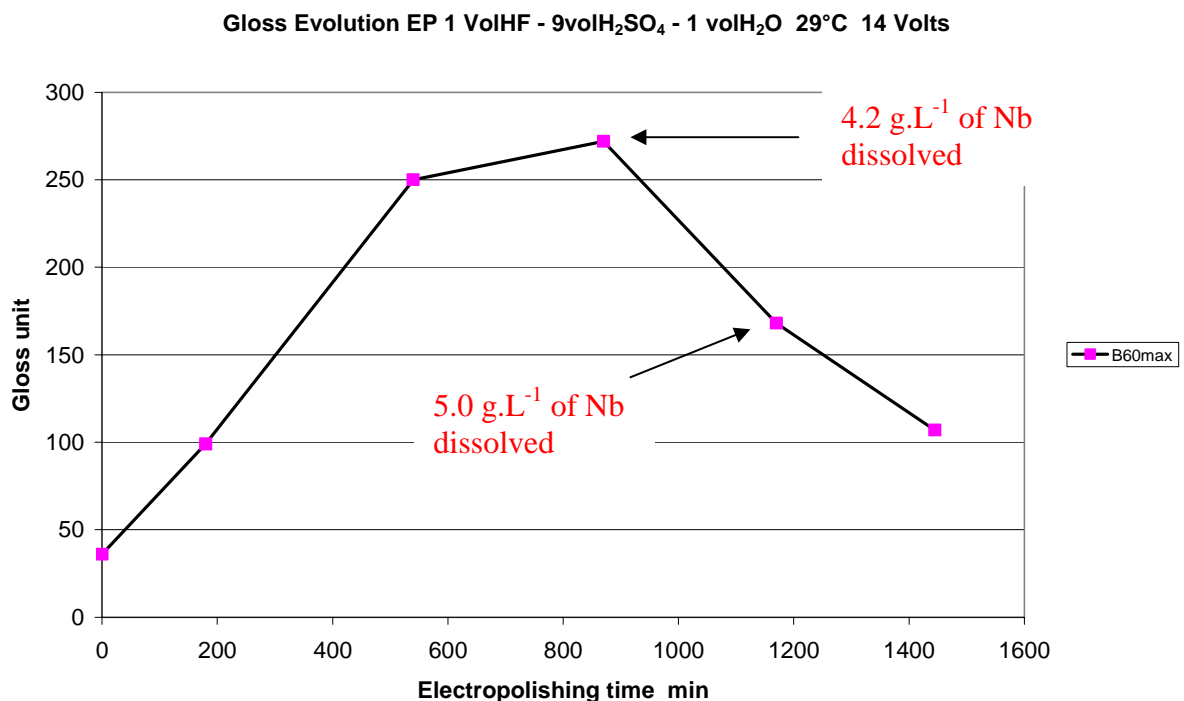


Figure 34: B60 evolution for EP with 1V-9V-1V mixture 14 Volts and mass of dissolved niobium during B60 decrease. Brightness first increases with time and then decreases after 870 min EP. Quantity of niobium that might be dissolved before the decrease is very low compared with other mixtures.

Obviously, this bath does not seem appropriate to achieve efficient electropolishing:

- Removal rate is low.
- Brightness is worse compared to other mixtures.
- Surface deteriorates quickly. Moreover brightness decreases for low amounts of dissolved niobium: lower than 5.0 g.

7) Is it possible to improve further brightness?

In this paragraph, we will check if brightness might be improved by a bath renewal after a previous long time EP experiment. This experience has been carried out with a 0.5V-9V mixture. Results are displayed in Figure 35.

After 2580 min of Electro Polishing, the maximum brightness is 372 and the surface began to deteriorate. We then decided to change the bath with a fresh solution. We improved B60 brightness by 27.4% (new maximum: 474) after 2490 min of Electro Polishing with the new bath. As the two durations are similar, we may conclude that the experiment is reproducible. Furthermore, the corresponding dissolved quantities of niobium are: 7.7 g and 7.2 g. During the last sequence, temperature was lowered down at 10°C. It did improve neither gloss nor surface state. Moreover, this experiment rules out any aging effect due to a transformation of the Nb surface with time (e.g. formation of insoluble “grey oxide⁵”)

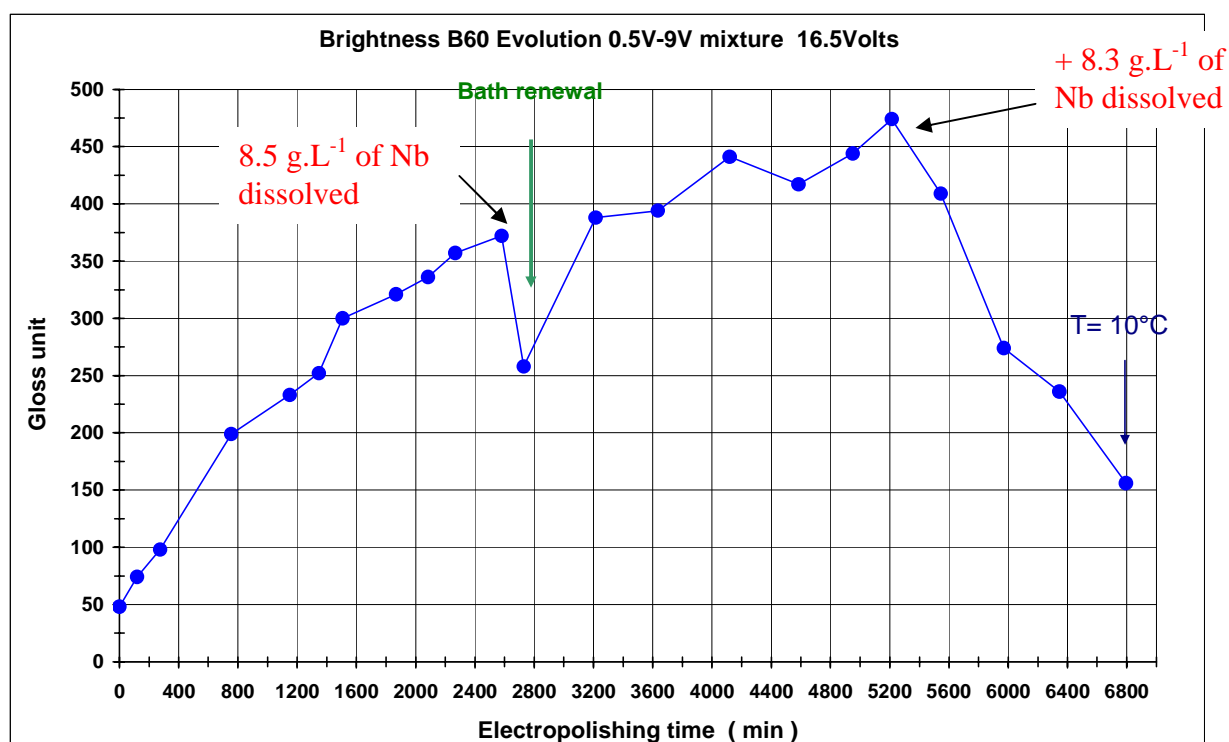


Figure 35: B60 evolution for a 0.5V-9V mixture 16.5Volts and information concerning dissolved niobium. B60 improved after bath renewal. A decrease in bath temperature did not improved brightness at the end of the experiment.

0.5V-9V bath and sulfur synthesis

Sulfur was found in that bath after this experiment. It confirms that high sulfuric acid concentrations favor sulfur and H₂S generation (H₂S was also smelled at the sample's surface after each sequence).

8) Composition evolution

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.

⁵ NB : the formation of an insoluble, grey oxide is sometimes observed after several oxypolishing sequences, which prevents from further etching. It is attributed to the formation of anhydrous pentoxide at high voltage.

*Chapter IV Aging of the Bath**a) Ionic chromatography: HSO₃F makes the diagnostic difficult*

The analytical method used is ionic chromatography: the mixture is diluted and then put in a separating column with an eluent. A column separates either anions or cations. Furthermore, a calibration is required for each expected ions. In our context, anions will be investigated. We expect to find 2 anions in different HF-H₂SO₄ tested mixtures: F⁻ and SO₄²⁻ ions. Nevertheless, chromatographs point out the presence of 3 anionic species. This effect is attributed to the equilibrium between hydrofluoric, sulfuric and fluorosulfonic acids given by:



It was previously pointed by Saito and al. [5], who used fluorosulfonic acid for refreshing the bath. Complementary experiment showed that the retention time of the unknown specie corresponds to FSO₃⁻.

Furthermore, for a 1V-9V mixture the calculated concentration gives 2.2 mol.L⁻¹ for [F⁻] and 16 mol/L for [SO₄²⁻]. The measured effective concentrations are smaller, but keep consistent if we consider the equilibrium reaction with FSO₃⁻. More precisely, the [F⁻] value for a new mixture is 1 mol.L⁻¹ and there is also roughly 1 mole missing for H₂SO₄. Thus we can attribute the third retention peak to 1 mol.L⁻¹ of HSO₃F (it was not possible to standardize this measure).

b) Fluorine evolution with time

F⁻ and FSO₃⁻ concentration were monitored for the 1V-9V mixture during an experiment with an 8 Volts voltage. We plotted the evolution of the concentration for these two anionic species (see Figure 36). It was not possible to calibrate the chromatograph for FSO₃⁻. As a consequence, the unit for that ion is arbitrary.

During the 2300 first minutes of Electro Polishing, F⁻ concentration remains stable and then decreases steadily. On the contrary, FSO₃⁻ concentration falls dramatically in the 2300 first minutes of Electro Polishing. It seems that HSO₃F constitutes a reservoir for fluorine ions: when F⁻ is consumed, equilibrium is displaced toward right in equation (20). So as long as there keeps some FSO₃⁻ inside the EP solution, F⁻ content will keep around 1 mol.L⁻¹. Once it is totally consumed, F⁻ will also decrease, and one can imagine that the polishing efficiency decreases too. These results are indicative because error on measures is appreciable. 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.

Meanwhile, we have recently improved the monitoring of F⁻ with the use of NMR. (The main difficulty lies in finding out material compatible with the concentrated HF-H₂SO₄ mixtures). The first results look promising; furthermore as no dilution is required prior measure, we hope to improve its precision.

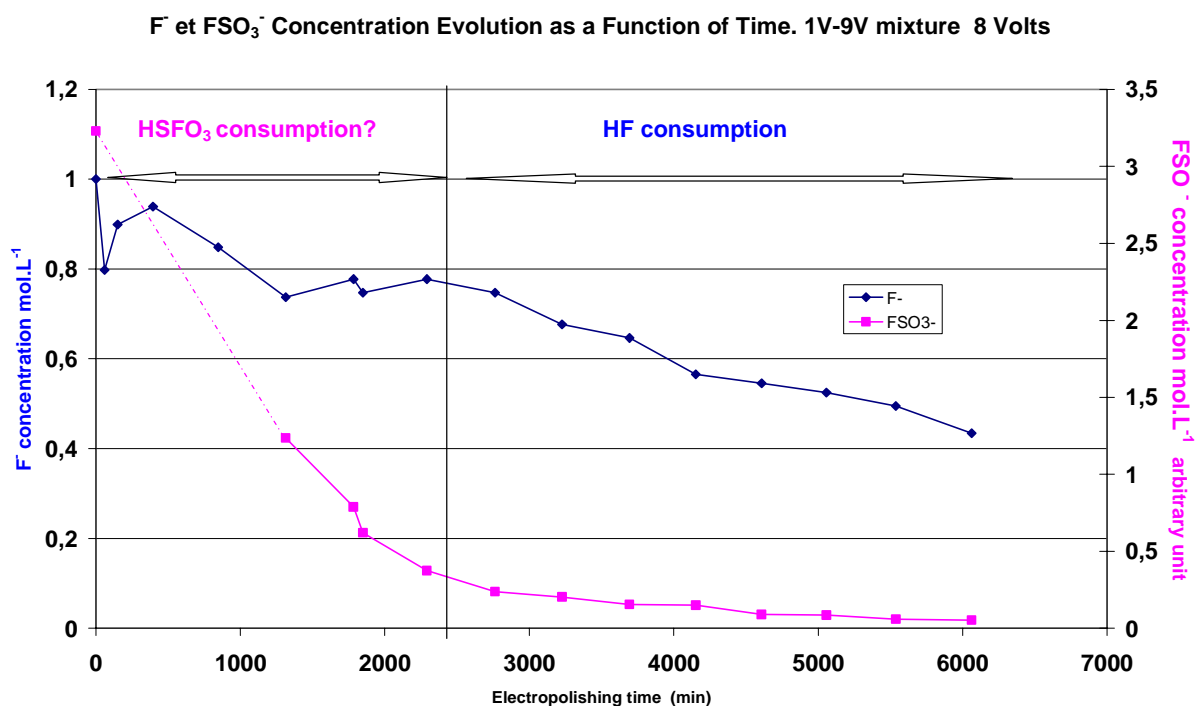


Figure 36: F⁻ and FSO₃⁻ evolution with time. 1V-9V mixture. 8 Volts. During the first 2300 min, HSFO₃ concentration decreases whereas HF remains stable. These results are indicative because water dilution necessary for ionic chromatography analysis modifies the equilibrium between HF, HSO₃F and H₂SO₄ species.

c) Fluorine evolution and brightness

We also compared F⁻ and B60 evolution as a function of time for this experiment. Results are displayed in the following graph in Figure 37: During the first 2000 minutes, brightness is improving. Afterwards decrease of F⁻ accentuates, while gloss is also decreasing. From this behavior, we can infer that HFSO₃ acts like a 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.

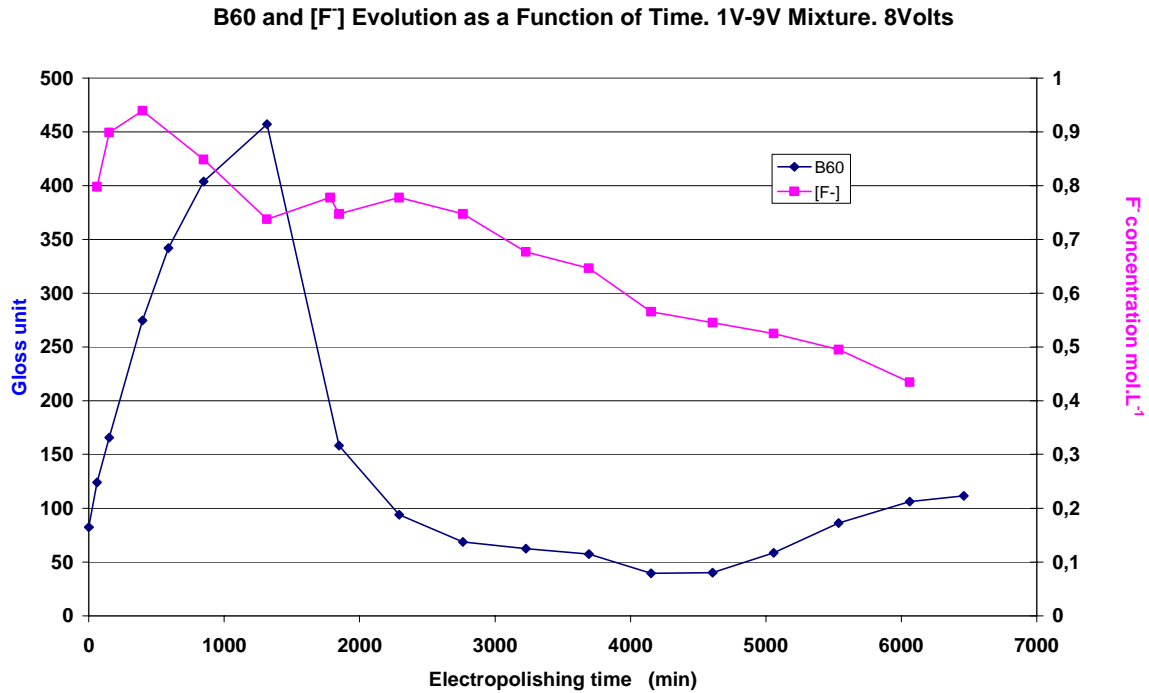


Figure 37: B60 and F⁻ evolution. 1V-9V mixture. 8 Volts.

9) Other considerations

a) *Brightness and roughness can be similar for several mixtures*

Some roughness measurements are displayed in the following table. We must precise that these measurements were carried after the first sequences corresponding to the surface deterioration. Thus, these results do not correspond to the best achievable leveling. Furthermore, a range of values is given because 3 measurements are carried out for each sample (respectively at the top, middle and bottom of the surface). Values in Table 3 correspond to minimum and maximum values.

Table 3: Roughness (minimum-maximum values) measured for different experiments. 3 measurements are carried out for each sample.

Bath (vol HF – vol H ₂ SO ₄)	Voltage V	Roughness Ra μm
0.5 – 9	16.5	2.05 - 6.14
1 – 9	19	2.04 - 2.94
2 – 9	6	0.85 - 1.59

Nevertheless, we can observe various surfaces states with similar roughness figures as it can be noticed in Figure 38. The best desired surface state would be chosen is the b) one (3V-6.72V-0.28V). We must also precise that plots may differ at different places of the same sample. We may conclude that hydrodynamics is a relevant parameter for surface state.

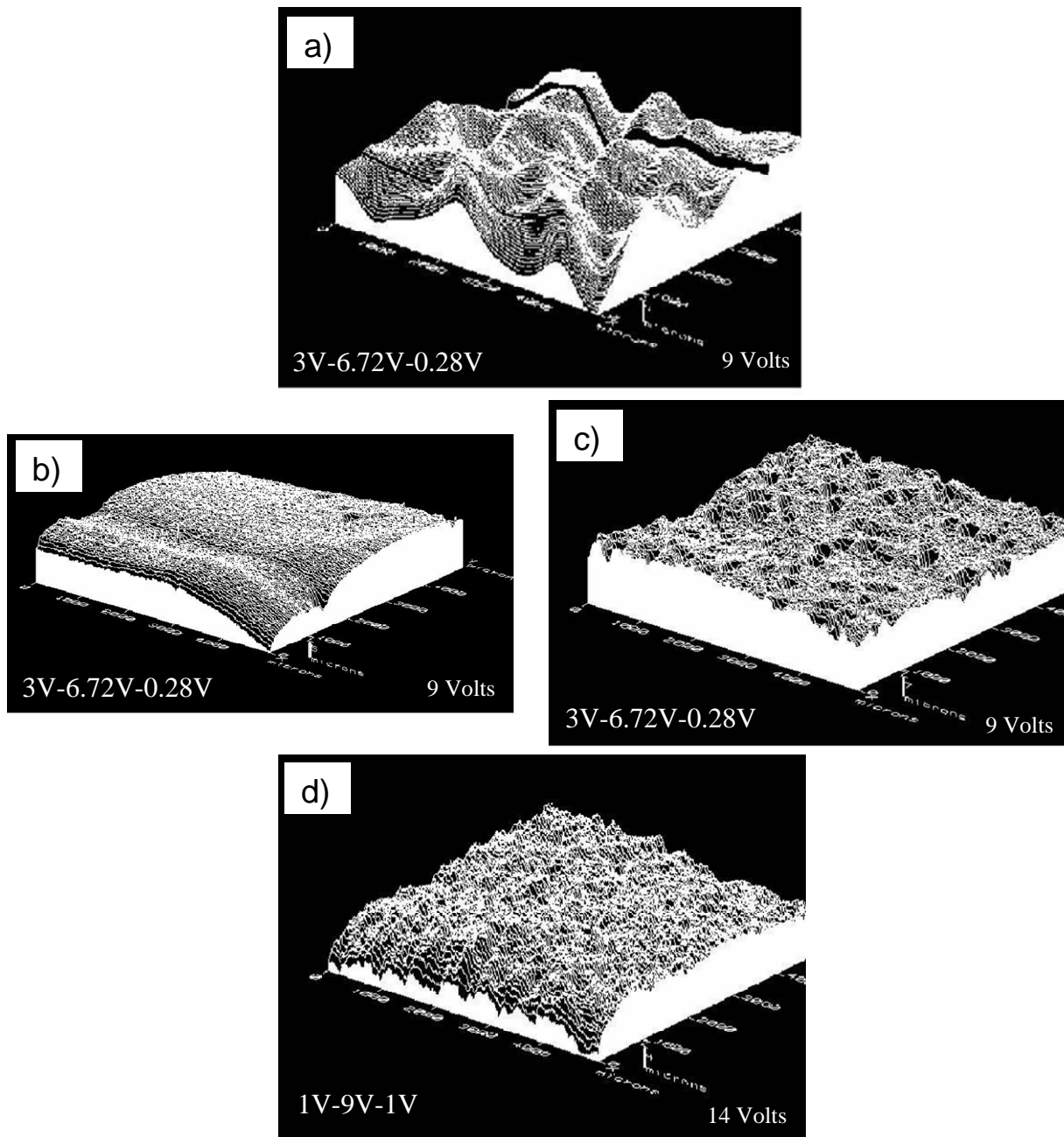







Figure 38: 3D surfaces for different samples after EP in 3V-6.72V-0.28V at 9V a),3345min b) 8425 min, “smooth area”; c) 8425 min, “area with pits”, d) 1V-9V-1V, 14Volts (19Volts at the end) 1445 min EP.

b) Removal rate depends on [HF] concentration

As it is shown in Table 4, high voltages induce faster reactions. Nevertheless, HF concentration is the key figure to gain in niobium removal rate. From a 1V-9V mixture to 2V-9V mixture with a lower voltage, removal rate doubles.

Table 4: Recapitulative results for the different studied mixtures

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Mixture VolHF- VolH2SO4 -VolH2O	Voltage Volts	Temp. °C	B60max	Dissolved Nb before B60 decrease g.L-1	Initial Removal rate µm.min-1	Ra**** µm	Sulfur Gener ⁿ	Surface at B60max x50
0.5-9	16.5	27-30	372*	<7.9	0.90	2.05- 6.14	X	
1-9	8	27-30	457	<8.6	0.94	?	X	
1-9	14	27-30	442	< 6.3	1.46	?	X	
3-6.72- 0.28	9	≈20	446**	<28.33	2.70	1.85- 3.78	No	
1-9-1	14	27-30	272	<4.5	0.74	1.33	?	

* Bath has been changed during the experiment

** Sample has been changed during experiment

*** 3 Measurements are carried out when surface has started to deteriorate

c) Unit management strongly depends on stocked chemicals and particularly on HF concentration

As it was explained in § III 1) b) HF is difficult to handle because of its effect on human health (severe burns, decalcification, and necroses) and its insidious aspects (painless at first contact). It is classified very dangerous (T⁺) for concentration over 7 w%.

c.i User safety

Damages on human health are weakened if HF is diluted in water or sulfuric acid. For safety reasons, it is then preferable to work with low concentrated HF mixtures.

c.ii T or T+

Legislation takes into account dangers inherent to HF use, in order to protect humans and environment. This point must also be considered in the choice of an appropriate bath, likely to be used in large scale cavity production.

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Depending on the local regulations, the status of the laboratory and the allowed stored of T+ products may vary a lot.

Our laboratory is classified as an « ICPE (Installation Classée pour la Protection de l'Environnement) soumise à déclaration ». With such a status, maximum storage capacity of T⁺ chemicals is 250 kg. To be allowed to exceed this limit, the laboratory needs be classified “ICPE soumise à autorisation”, which would change the whole CEA Saclay status (into “SEVESO classification”). In this case the security regulation would become so heavy, that we are recommended not to go into this direction. As a consequence, concentrations lower than 7 w% will be favored in a first experimental approach.

Although this level might change with local country rules, one has to keep in mind such criteria is an important argument in the choice of the effective EP mixture

Chapter V Monocell Electropolishing Device

We got some information concerning niobium electropolishing on samples. We need now to study the EP in the case of the cavity treatment. Such a device is being implemented in our laboratory in Saclay.

1) General layout

The general layout of the monocell set-up follows similar already existing facilities. We have studied the feasibility of some improvement like an HF vapor condenser. Unfortunately, this study failed as the problem revealed to be far more complex than expected: it is not possible to model HF behavior in such mixtures as their behavior is far from an “ideal” mixture (in the thermodynamic sense). We have also tried to address the sulfur generation, with the addition of proper filtering. The main issue is the filter colmatation, but we shall use strainers which can easily be dismantled and rinsed with chloroform.

2) Establishing of procedures for operators

It is crucial to establish the procedures for the operators for different reasons:

- To evaluate dangers of the unit.
- To meet security obligations (see next §).
- To be able to run the unit in short terms.

3) Security report

The installation of 2 new set-ups (single cell EP unit and « Integrated Chemistry ») gave us the obligation to revue all the safety program of the installation. This report was submitted to the CLS (Commission Locale de Sécurité) on October the 13th 2005.

Construction and running of a new unit must be first approved by the “Commission Locale de Security”. In that way, a report must be presented. It includes the following headlines:

- Context.
- Description of the administrative structure.
- Process description.
- Risk evaluation.
- Means of prevention.
- Measures taken in case of emergency.

The analysis deals with two units that are being implemented in the laboratory:

- The monocell electropolishing unit that was briefly previously put forward.
- The “Integrated Chemistry”: A unit for polishing cavities with a FNP mixture in closed circuit .

The report has been published internally: “CLS n° 241 du 13/09/2005 : Projet de mise en service des installations de chimie intégrée et d’électropolissage au bâtiment 719”, Ref 5-2-E-026-LaboChimieRF-004-A. The risk analysis part built from the “MES” method is included.

4) Commissioning

This set-up is now under commissioning, and will be soon used to run comparative experiments with cavities, where we shall apply and verify the general trends observed on samples.

Acknowledgements

We acknowledge the people who helped us within the context of the EP-monocell project: Stephane Berry, Michel Luong, Yves Gasser, Yves Boudigou, Jean-Pierre Poupeau and Jorge Novo. I especially thank Jean-François Denis who designed a special data monitoring system for us.

We wish also show our gratitude for people from different laboratories in Saclay: Yves Charles, Florence Goutelard, Patrick Berthault, Vincent Derycke, who gave us the opportunity to analyse several samples. This contribution is of paramount importance in this study.

We have also benefited from valuable discussions and exchanges with A. Matheisen and N. Steinhau-Küehl from DESY.

*Conclusion***Conclusion**

Niobium electropolishing has been investigated thanks to experiments on samples. Precise mechanisms have not been yet clearly demonstrated. In particular, the role of the oscillations has not been elucidated. Such conclusions would require implemented investigation techniques. Nevertheless, some tendencies have been put forward:

- The more the HF, the more niobium might be dissolved in solution. Moreover is this dissolution very fast. Nevertheless, HF does not favor the formation of a viscous layer, and could lead to a faster polishing of the iris of the niobium resonators.
- Water is not desirable for niobium electropolishing: it slows down the niobium removal rate and does not favor brightening, probably because of the growth of organized niobium structures at low hydrofluoric acid concentrations. Observation with microscopy exhibits deteriorated surface state characteristic of high water concentrations. Furthermore, aging of the bath could thus be explained as the decrease of the $[\text{HF}]/[\text{H}_2\text{O}]$ ratio.

A way to enhance fluorine content is to add it in the form of a salt. In this way, dissolution of fluorinated salts in aged mixtures could be a way to refresh them. Experiments are now being carried out in that way.

One must not forget that niobium electropolishing generates impurities. Sulfur is generated at the cathode, especially in presence of highly sulfuric concentrated electrolytes. Unfortunately, hydrofluoric acid favors aluminum cathode corrosion. A balance must be determined. Moreover, impurities impact on cavity and efficiency of rinsing procedures towards sulfur must be established. Ethanol rinsing on TESLA cavities is now under testing at TTF following CEA-Saclay recommendations.

Electropolishing in itself can be further optimized now, and the impact of surface state on cavity performance has to be clearly established. The next step of the study lies in the reproducibility on cavities of surface states obtained with samples and in the determining of resulting RF performances. If brightening is found to be linked with surface state, this work proves that specifications (9 g.L^{-1} of dissolved niobium in solution) are not suitable for cavity treatment. If not, optimization should proceed with following issues:

- Obtaining a uniform polishing.
- Getting an enhanced lifetime for EP solutions.
- Polishing with a high removal rate.
- Using mixtures with a concentration compatible with safety recommendations.

Concerning the understanding of polishing mechanisms, complementary experiments are still needed; and techniques such as SIE are contemplated in short terms. These studies could be carried out in collaboration with external laboratories. Moreover, modeling reveals to be of paramount importance. It has been first tested on simple configuration to evaluate the impact of main parameters. It could also be a powerful tool to simulate hydrodynamics in the case of a cavity treatment, but will require significant development.

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