

Study of the chemical behavior of hydrofluoric, nitric and sulfuric acids mixtures applied to niobium polishing

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Abstract

This paper describes the experimental work that has been conducted to develop new chemical polishing baths for surface treatments of niobium RF cavities. The role of the different chemicals is detailed and a wide range of composition is explored. The relationship between the niobium etching rate and the concentration of each mineral acid is put in evidence. Optimization of the bath composition was done in order to get in the same time safe and easy handle conditions, brilliant surface and low grain boundaries etching.

Keywords: Chemical polishing; Niobium RF cavities; Etching rate; Surface state

1. Introduction

Using superconducting material allows building RF cavities with low thermal losses and high accelerating gradients for particle accelerators. Among all the possible material, bulk Niobium, a pure metal with $T_c = 9.2K$, exhibits the best superconducting behavior when submitted to high RF fields. In order to achieve high quality factors (Q_0) and high accelerating field (E_{acc}), smooth and defects free inner surfaces are necessary. Indeed, all dissipations occur in a 50-100 nm surface layer, which includes a native oxide layer (5-10 nm) and surface contaminants (adsorbed layers, dust particles).

Usually, electrochemical or chemical polishing procedures generate correct surfaces. Good performances for Nb cavities have already been reached from chemical polishing mixtures such as "FNP 1:1:2" (i.e. hydrofluoric acid, Nitric acid and orthoPhosphoric acid, 1:1:2 in parts by volume) developed by [1].

But with the improvement of general fabrication techniques (higher purity supply, improved welding techniques, ultra-cleanliness...), the surface state obtained with that surface treatment is now known to be the source of the limitation in the race toward accelerating gradient higher than 35-40 MV/m [2].

Such high accelerating gradient have been already obtained on mono-cell with the use of electropolishing

techniques [2,3], but this technique appears to be quite difficult to apply to large RF structures like multi-cells cavities.

The Nb used for RF application is very pure (> 99.98 %, residual resistivity ratio ~ 300). Surface segregation of the order of a few nm have been observed but don't appear to have an influence on the chemical etching [5, 18-21]. The usual FNP polishing is known to etch preferentially at grain boundaries, dislocation emergences and along crystallographic planes. After mechanical grinding, or long exposition to air, the etching rate is a little higher, probably due to surface pollution, but it becomes stable within 5 μm . This traduces a high sensitivity to defects and impurities.

We have tried to overcome this trouble with the use of sulfuric acid which is also used as a viscosing agent in the electropolishing solution.

Therefore, we have tried to develop new chemical etching mixtures with a special care for the following criteria:

- The Nb dissolution rates and generated surface states,
- The possibilities of polishing Nb close to room temperature (18-30°C) with low etching rates (0.2 to 1.5 $\mu m/min$), for attack duration from 0.5 to 6 hours in safe conditions,
- The lifetime of "FNS" solutions (chemical stability and number of cavities treated by the same polishing bath)

Uzel et al. have already studied a ternary mixture of hydrofluoric (F), Nitric (N) and Sulfuric (S) acids [4]. They developed in particular a bath which included HF

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(40%), HNO₃ (65%) and H₂SO₄ (96-98%) under a 1:1:2 volume ratio and was held at a 78°C temperature. Good results (reduced grain-boundary etching, high Q₀) were obtained, in comparison with the usual "FNP 1:1:2" mixture.

We have tested at Saclay "FNS x-y-z" baths at room temperature with diverse compositions in parts by volume such as "1:1:1", "1:1/2:9" and "1:1:8". High Q₀ (0.5 to ~2.10¹¹) and E_{acc} (30 to 35 MV/m) have been regularly obtained [5] on Nb RF cavities.

Now, systematic studies have been developed in order to better understand the influence of each mineral acid towards the Nb dissolution rates, the quality of surface states and to finally define a "FNS" polishing bath which can be used many times and applied to the surface treatments of RF resonators with improved performances.

Note: Preparation procedure of etching baths and protocol of samples polishing are respectively described in annex 1 and 2.

2. General behavior of the three mineral HF, HNO₃ and H₂SO₄ acids

As will be shown hereafter, water plays an important role in the chemical behavior of the solutions. Water originates not only from the concentrated acids, which still contain an appreciable amount of water, but is also a reaction product. Acids act as proton donors.

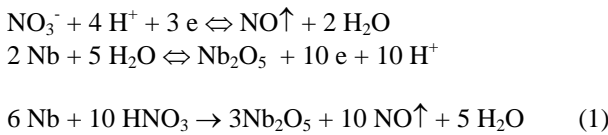
Furthermore, HNO₃ is an oxidant of Nb⁰ while HF is a complexing agent toward Nb⁵⁺.

Notes:

- *In the case of FNP, the role of HF and HNO₃ are similar. By changing H₃PO₄ to H₂SO₄, we intend to modify the viscosity and the etching rate, and thus the surface state.*
- *In the case of oxipolishing and electropolishing procedures, no oxidizing agent is present into the solution, but a positive bias (10 to 100 V) applied to niobium (anode) provides the oxidation of the metal*

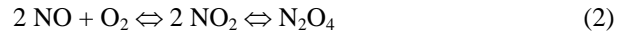
2.1. Reactions between Nitric Acid and Niobium

By its nitrate ions (NO₃⁻), nitric acid oxidizes Nb metal to its oxidation state +5 under the intermediate Nb₂O₅ compound (niobium pentoxide), according to the two semi-electronic equations resumed in (1):



The niobium pentoxide created in presence of water leads to diverse forms of niobic acids [7] such as diniobic, triniobic or pentaniobic acids with respective formula H₄Nb₄O₁₂ (2Nb₂O₅, 2H₂O), H₇Nb₃O₁₁ (3 Nb₂O₅, 7H₂O), H₇Nb₅O₁₆ (5Nb₂O₅, 7H₂O), which finally precipitate in the form of more or less hydrated gels (Nb₂O₅, nH₂O)

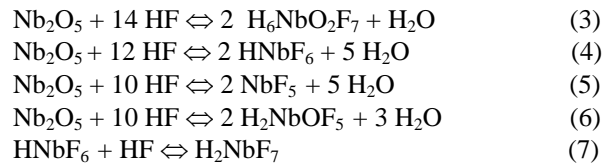
Note: In the presence of atmospheric O₂, the synthesis of NO (bubbles of colorless gas in the aqueous media) and its emanation leads to the formation of nitric dioxide NO₂ (brown gas) and its dimeric species N₂O₄ (red fumes generally noticed with etching baths containing nitric acid):



In the absence of nitric acid, the thin and superficial Nb₂O₅ layer, which is always present on Nb substrate, is readily dissolved by HF in a short while (≤ 2 min). Then the chemical reaction stops because HF and H₂SO₄ are not oxidizing agents.

2.2. Behavior of Hydrofluoric Acid towards Nb₂O₅

When H₂SO₄ or H₃PO₄ are not introduced into solution, the Nb₂O₅ layer synthesized from (1), is rapidly transformed by HF into fluoride and oxofluoride acidic species, depending on the HF concentrations [8]:



◆ The range ≈1 M < [HF] < ~ 7.9 M leads, for example, to the hydrolyzed compounds H₂NbOF₅, H₂O or H₂Nb(OH)₂F₅ (6) and H₆NbO₂F₇ or H₄NbOF₇, H₂O (3). These compounds belong to the family of chemical species with general formula [NbO_xF_y, H₂O]^{5-2x-y}.

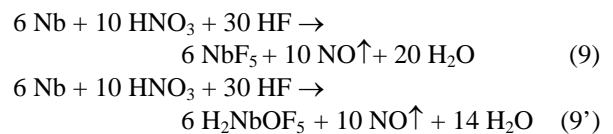
◆ Starting from [HF] ≈ 2 M to very high F⁻ anions concentrations, the synthesis of heptafluoronioic acid H₂NbF₇ or NbF₅, 2 HF is also favored (7)

◆ The range ~ 5.65 M < [HF] < 22.6 M provides the formation of hexafluoronioic acid HNbF₆ or NbF₅, HF (4) which is equilibrium with the solution in the ternary system H₂NbF₇/HF/H₂O under the two-way reaction (7)

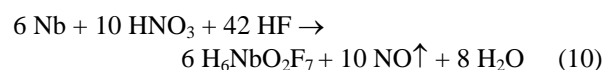
Furthermore, the NbF₅ salt created from (5) can readily reacts with nitric acid [9], considered as hydrated dinitrogen pentoxide (N₂O₅, H₂O), according to the following reaction that produces trinitratoniobium (Nb^V) and nitryl fluoride:



For example, in the "FNS 1:1:0" bath, where [HF] = 7.84 M, the effects of HF and HNO₃ can be resumed by the equations (9) and (9') given below (intermediary product Nb₂O₅ to be inferred). In this case, the molar ratio between the concentrations of total H⁺ ions and Nb is equal to 6.67 (6.48 ± 0.45 has been experimentally found):



On the other hand, in the case of "FNS 1:9:0" bath, where [HF] ≅ 2.26 M, the synthesis of heptafluoxynioic acid is favored, and the following equation has to be considered:



In the absence of HF, such as in the "FNS 0:1:1" mixture ($[\text{HNO}_3] = 7.55 \text{ M}$ - $[\text{H}_2\text{SO}_4] = 8.86 \text{ M}$) or with an aqueous solution of HNO_3 3.84 M, the existence of a passive layer of Nb_2O_5 prevents the dissolution of Nb.

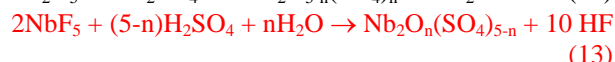
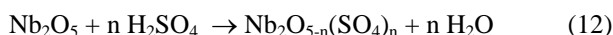
2.3. Reactions between Sulfuric Acid and Nb^{V} salts

In "FNS" mixtures, H_2SO_4 plays many roles:

◆ Protons donor, in presence of an appropriate amount of water, according to (11):



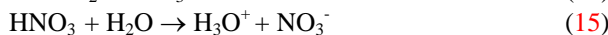
◆ Complexing agent towards Nb^{V} (Nb_2O_5 and/or NbF_5) to form oxysulfate compounds [7], cf. equations (12 and 13) where $n = 1$ to 4:



Note: The complexing reaction (13) is far less efficient than the one with NbF_5 . Intermediate fluorinated compounds favor the action of H_2SO_4 .

At high concentrations, the elevated viscosity of the sulfuric solution contributes to the synthesis of a passive layer, according to [10-15]. Moreover, as this acid is highly hygroscopic when concentrated, the hydrolysis of HF and HNO_3 by water is strongly reduced, and the quantity of complexing F^- and oxidizing NO_3^- anions free in solution is decreased.

The reverse reactions (to the left side) of the (14) and (15) equilibriums are consequently favored:



These phenomena induce the decreasing of the niobium dissolution rates (chapter 3.2)

Others reactions also exist [7,9] between NbF_5 and sulfuric acid, considered as hydrated sulfur trioxide (SO_3 , H_2O). The following equations lead to Nb^{V} fluorosulfate (16), or oxysulfate, plus pyrosulfuryl fluoride (17):



2.4. Conclusion

The reactions between Nb and the mineral acids generate intermediate oxonitrated, fluorinated or oxofluorinated and oxosulfated compounds. These compounds are then hydrolyzed into more or less hydrated pentaniobic acids, with general formula Nb_2O_5 , $n \text{H}_2\text{O}$, which form a gelatinous layer analogous to a kind of $(\text{HNbO}_3)_n$ polymer [16,17]. This kind of viscous layer should improve the polishing effect like in electropolishing, but hardly dissolves into water upon rinsing. Incorporation of anions and other impurities from the solution is frequently observed [8,12,13,18].

The most simple of them, HNbO_3 (metaniobic acid), is equivalent to monohydrated niobium pentoxide (Nb_2O_5 , H_2O)

3. Experimental part

3.1 Influence of HF on niobium etching rates and surface states

That study was done on Nb tests sheets with concentrations of HF varying into the range 0 to 14.20 M and under a quasi-constant molar ratio between the two others acids ($[\text{H}_2\text{SO}_4]/[\text{HNO}_3] = 1.155$ to 1.288).

3.1.1. Influence on etching rate

Constant etching rate is first noticed for 12 "FNS" baths compositions. For further times of immersion, all the " $e_{\text{Nb}} = f(t)$ " curves tend asymptotically to a maximum quantity of removed metal. This slowing down is obviously linked to the consumption of the three involved acids, and sets the limit of use of the bath.

Fig. 1 exhibits $\text{Log}(V_{\text{Nb}}) = f([\text{HF}])$ and one can observe the following features:

◆ For $[\text{HF}] = 0$, Nb^{V} complexing and dissolution are not possible in the absence of F^- anions (e.g. "FNS 0:1:1" bath, cf. §2) and no etching is observed.

◆ Within the range $0 < [\text{HF}] \leq 1.13 \text{ M}$ ($6.65 \geq [\text{NO}_3^-]/[\text{F}^-] \geq \infty$), the Nb dissolution rates will dramatically enhance as Nb^{V} complexing by F^- anions starts.

◆ For $1.13 \text{ M} \leq [\text{HF}] \leq 14.20 \text{ M}$, a near exponential variation is put in evidence. This behavior expresses that in the presence of sufficient concentrations of HNO_3 ($0.22 \leq [\text{HNO}_3]/[\text{HF}] \leq 6.65$), the quantity of dissolved Nb is directly proportional to the HF concentration.

◆ Over $[\text{HF}] = 14.20 \text{ M}$ and $[\text{HNO}_3]$ approaching infinite dilution ($0 \leq [\text{NO}_3^-]/[\text{F}^-] \leq 6.65$), the V_{Nb} rates will, in a first step, still increase. Nevertheless, the reactions will rapidly stop according to the consumption of HNO_3 . No attack of Nb metal occurs in the absence of oxidizing NO_3^- anions such as with "FNS 1:0:1 and 1:0:10". No tests were done to verify this assertion, as the "FNS 2:1:1" and "3:1:1" mixtures had already given very high Nb rates (200-300 $\mu\text{m}/\text{min}$), accompanied by strong emanations of red nitrous fumes (violent bubbling), strong and rapid rises in temperature (25 to 45°C/min). Nb samples also exhibited strongly degraded surfaces.

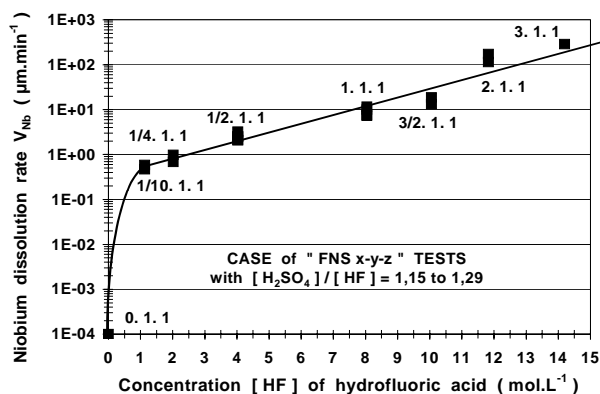


Fig. 1. Semi-logarithmic variation of Nb dissolution rate V_{Nb} versus [HF] concentration under the molar ratio $[H_2SO_4] / [HNO_3] = 1.155$ to 1.288 .

In that study, where [HF] was the increasing factor, the molar $R_1 = [HNO_3]/[HF]$ ratio was decreasing from 6.65 to 0.22. Nitric acid, being the oxidizing agent, is thus the limiting reactant.

The molar ratio $R_3 = [H_2O]/[H_2SO_4]$ varies within the range 1.4 to 7.6. Enough quantity of water is present to favor the dissociation of HF and HNO_3 according to (13) and (14) reactions.

Note: For relative short duration, the temperature increases with HF concentration and immersion time.

For further immersions times, the consumption of the three acids and the slowing down of the reactions lead to T_{Bath} decrease.

This phenomenon appears more quickly for solutions highly concentrated in HF.

3.1.2. Nb^V solubility, surface state

Within the experimental range $7.39 \cdot 10^{-2} M \leq [Nb]$ dissolved $\leq 6.73 \cdot 10^{-1} M$, different colorings were noticed for these mixtures after their uses:

- ♦ For [HF] = 0 to 8.04 M, the solutions were colorless to yellow-green and limpid (absence of solid precipitates).

- ♦ For $\sim 8.04 M \leq [HF] \leq 14.20 M$, the solutions were green to dark green and limpid (absence of precipitates). These colors indicate that, with regard to [HF], different fluorinated species are synthesized and remain soluble into such strong acidic media.

The surface states (photographs 1 to 3, annex 4) generated by these baths ($1.13 M \leq [HF] \leq 10.05 M$ and $0.59 \mu m/min \leq V_{Nb} \leq 18.71 \mu m/min$) were all good: Relatively low roughness, shiny surfaces (Table 1) and little grain-boundaries etching.

Within the range $10.05 M \leq [HF] \leq 14.20 M$, the treatments severely degraded the surfaces (photograph 4, annex 4): presence of deep craters (10-40 μm depth), grain-boundaries preferential etchings and small faceted Nb crystallites.

Another way to characterize the effectiveness of the polishing bath is to measure the duration of brightness. The reflecting distances give an estimation of the reflecting power of a brilliant surface, and consequently an indication of the micro roughness (Table 1).

After an appreciable consumption of reactants, it is no more possible to get brilliant surfaces.

Table 1
Evolution of brightness duration and reflecting distance in function of HF concentration.

Reference of FNS bath	Duration of attack (min)	Duration of brightness (min)	Reflecting Distance (cm)
0. 1. 1	2540	0	Unpolished
1/10. 1. 1	147	130	4.5 - 5
1/4. 1. 1	110	80	1.5 - 2.5
1/2. 1. 1	70	67	1.5 - 2.5
1. 1. 1	30	28	2.0 - 2.5
3/2. 1. 1	20	19	3.5 - 4.0
2. 1. 1	4.5	0	Degraded
3. 1. 1	6.5	0	Surfaces

3.1.3. Conclusion

From [HF] = 0 to [HF] $\sim 1.13M$, the etching rate evolves very quickly. Between [HF] = 1.13 M and [HF] = 14.20 M, the etching rate is then proportional to HF, and always gives brilliant surfaces. All the etching products remain soluble into solution.

Meanwhile, etching rate is very high, except when [HF] < 2M. It seems very difficult to find out proper etching conditions with such $[H_2SO_4] / [HNO_3]$ ratios.

3.2. Influence of HNO_3 on niobium rates of attack and surface states

That variable was studied from two sets of experiments:

- ♦ A constant molar ratio $[HF]/[H_2SO_4] = 1.303$ with the HNO_3 concentrations varying within the range 0 to 10.35 M, i.e. $R_2 = [F^-]/[NO_3^-]$ decreasing from 15.05 to 0.28.

- ♦ A constant molar ratio $[HF]/[H_2SO_4] = 0.13$ with the HNO_3 concentrations varying from 0 to 2.22 M and $0.85 \leq R_2 \leq 16.78$. That second series had the aim to both obtain lower dissolution rates for Nb and lower rise of the temperatures in the reactive media (safety reasons) This option allowed to better control the chemical kinetics thanks to the inhibition effect of high concentrations of H_2SO_4 .

The observed behavior is similar as in § 3-1: in absence of HNO_3 , no reaction occurred and the etching rates increase very quickly with HNO_3 concentration.

3.2.1. Low concentration of H_2SO_4 $[HF]/[H_2SO_4] = 1.303$

Fig. 2 shows some examples of quasi-linear variations between the thickness of dissolved Nb (e_{Nb} in μm) and the times of immersion (t in min)

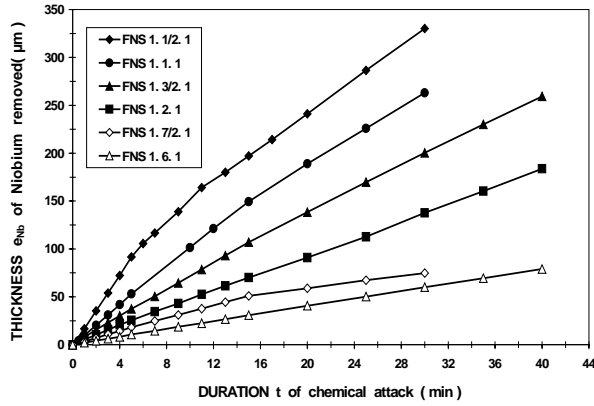


Fig. 2. Variation of the thickness e_{Nb} of Nb dissolved versus the time of immersion when $[HF]/[H_2SO_4] = 1.303$

Note: In this first series, the temperature range (25 to 58 °C) varied inversely to the HNO_3 concentrations.

The resulting curve $V_{Nb} (\mu m/min) = f([HNO_3])$ put in evidence a maximum peak corresponding to the "FNS 1:1/2:1" test (Fig. 3)

◆ Within the range $0 \leq [HNO_3] \leq 2.4$ M, the V_{Nb} etching rates increased simultaneously with the nitric acid concentration, in the presence of enough complexing F⁻ anions ($\infty \leq R_2 \leq 3.35$)

◆ Within the range $2.4 \text{ M} \leq [HNO_3] \leq 10.41$ M, the Fig. 3 shows that the increase in the HNO_3 concentration leads to the diminution of the dissolution rate. The relative proportions of HF versus HNO_3 (R_2 ratio) controls this phenomenon. Nitric acid favors the formation of the inhibiting Nb_2O_5 layer according to the reaction (1) while HF dissolves it through the (3) to (7) equations.

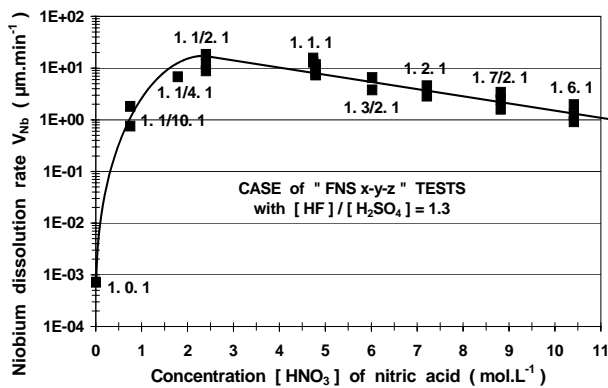


Fig. 3. Semi-logarithmic variation of Nb dissolution rate V_{Nb} versus $[HNO_3]$ concentration with $[HF]/[H_2SO_4] = 1.303$.

In that range, the polishing power of "FNS" baths is slowed as $[HF]$ decreases while $[HNO_3]$ raises.

3.2.2. High concentration of H_2SO_4 $[HF]/[H_2SO_4] = 0.13$

The case of $[HF]/[H_2SO_4] = 0.13$ ratio is shown in Fig. 4. The behavior is similar to the one registered with weaker H_2SO_4 concentrations, but lower Nb dissolution rates ($V_{Nb} < 1 \mu m/min$) are obtained.

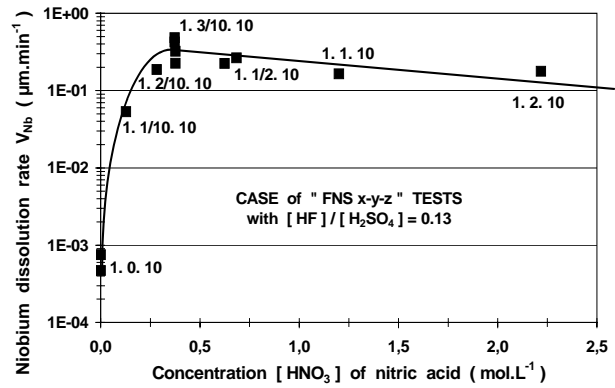


Fig.4. Variation of Nb dissolution rate V_{Nb} versus $[HNO_3]$ with $[HF]/[H_2SO_4] = 0.13$

Indeed, the R_2 ratio had evolved from 16.78 to 5.65 for FNS 1:0:10 to 1:3/10:10 while it decreased toward $R_2 \leq 5.65$ from FNS 1:1/2:10 to 1:2:10. ($0.85 \leq R_2 \leq 3.36$)

As in the previous case, the etching rates V_{Nb} increase when $R_2 \geq 3.36$. This R_2 ratio controls the niobium dissolution and is comparable to the theoretic molar ratios given by the equations (9) and (9'). However, the presence of higher concentrations of H_2SO_4 inhibits partially the effects of the two others acids, probably by reducing their respective hydrolysis. This explains the lower dissolution rates obtained.

Note: In that second series, the temperature range varied also inversely to the HNO_3 concentrations, but for the reasons already mentioned, lower temperatures were effectively achieved.

3.2.3. Nb^V solubility and surface state

After their uses, these mixtures presented diverse colorings:

◆ With the first series of baths, the solutions were colorless, yellow-green to orange-maroon with regard to the increasing of $[HNO_3]$ ("FNS 1:0:1 to 1:6:1"). They were all limpid (absence of solid precipitates) and the different salts synthesized remained soluble as long as $0.192 \text{ M} \leq [Nb] \text{ dissolved} \leq 0.535 \text{ M}$.

◆ In the second series, all the solutions were colorless and limpid for $7.9 \cdot 10^{-3} \text{ M} \leq [Nb] \text{ dissolved} \leq 1.76 \cdot 10^{-1} \text{ M}$. With that 2nd series of tests, no bubbles and noticeable emanations of nitrous vapors were observed. The presence of high $[H_2SO_4]$ seems to trap the NO synthesized (1) and to prevent the formation of NO_2 and N_2O_4 (2). This point is still under study.

The surface states (photographs 5 to 8, annex 4) generated by these baths all looked better than the ones given by the "FNP 1:1:2". Those obtained with the 1st series of tests were more or less comparable to the ones presented by the study done under $[HF]$ variable, while those realized under high $[H_2SO_4]$ were less brilliant but always smooth and with no grain-boundaries etchings (Table 2)

Table 2
Evolution of brightness durations and reflecting distances in function of HNO_3 concentrations

Reference of FNS Bath	Duration of attack (min)	Duration of brightness (min)	Reflecting Distance (cm)
1. 0. 1	70	No attack	No attack
1. 1/4. 1	65	Degraded surfaces	
1. 1/2. 1	30	29	1.5 - 2.0
1. 1. 1	30	28	2.0 - 2.5
1. 3/2. 1	80	77	3.0 - 4.0
1. 2. 1	90	85	2.5 - 3.0
1. 7/2. 1	85	81	3.0 - 3.5
1. 6. 1	160	156	2.0 - 2.5
1. 0. 10	45	No attack	No attack
1. 1/10. 10	110	Unpolished surfaces	
1. 2/10. 10	3050	Degraded surfaces	
1. 3/10. 10	150	55	1.5 - 2.0
1. 1/2. 10	220	190	1.0 - 1.5
1. 1. 10	135	30	1.0 - 1.5
1. 2. 10	170	105	1.5 - 2.0

3.2.4. Conclusion

In summing up these two series of tests, the involved HF concentration counterbalances the influence of increasing concentrations of nitric acid. Over a value of the ratio $R_2 = [F^-]/[NO_3^-] = 3.35$, passivation occurs and the oxidizing power of HNO_3 is not further expressed.

3.3. Influence of H_2SO_4 and H_2O on Nb etching rates and surface states

In the literature about electrochemistry of Nb, a lot of authors [10-15] have shown the importance of water and anionic species in the chemical equilibriums. These equilibriums exist between the passive layer on the metal surface, the interfacial film (between that layer and the solution) and the solution itself.

The precipitation of hydrated oxides or salts on the surface, under the dehydration of the interfacial film, can partially or totally inhibits the Nb dissolution.

In the case of all chemical "FNS" treatments done, very thin interfacial films (yellow to green films with depths < 0.5 mm) were observed through the colored and limpid solutions. They covered the surface samples, moved on it with the stirring and reduced when bubbling of NO_x and the temperatures became strong.

As sulfuric acid, when highly concentrated, is a **viscous** and dehydrating **compound** together, a modification of chemical compositions of the interfacial films and passive layers probably occurs.

We will see in the following experimental that these two properties of H_2SO_4 are effective as soon as $[H_2SO_4] > 11$ M.

The influence of H_2SO_4 was studied from "FNS" mixtures in which the sulfuric acid concentrations varied within the range 0 to 15.63 M under a constant molar ratio $R_2 = [HF]/[HNO_3] = 1.587$.

3.3.1. Influence on etching rate

For relative short attack durations, linear variations were also registered. For further times of immersion, all the " $e_{Nb} = f(t)$ " curves tended asymptotically to

maximum values which are expected due to the consumption of the reactants.

The variation of Nb dissolution rate V_{Nb} versus the molar $R_3 = [H_2SO_4]/[H_2O]$ ratio is shown on Fig. 5. The water concentration has been calculated from the hereafter formulas:

$$V_{H_2O} = (0.6 \cdot V_F \cdot d_F + 0.3 \cdot V_N \cdot d_N + 0.05 \cdot V_S \cdot d_S)$$

$$[H_2O] = (10^3 \cdot V_{H_2O} \cdot \rho_{H_2O}) / (V_{Bath} \cdot M_{H_2O})$$

V_{H_2O} = Volume (ml) of water in the prepared bath

V_F, V_N, V_S = Volumes (ml) of commercial acids

$[H_2O]$ = Water concentration (mol/L) in the final bath

d_F = Density of commercial HF

d_N = Density of commercial HNO_3

d_S = Density of commercial H_2SO_4

ρ_{H_2O} = Specific gravity of water (1 kg/L)

M_{H_2O} = Molecular weight (18 g/mol) of water

1) $R_3 < 1$

Water is the predominant reactant. In the "FNS 1:1:0 to 1:1:3" mixtures, $[H_2SO_4]$ increases from 0 M to 11.17 M, while $[H_2O]$ decreases from 39.7 M to 13.4 M, and V_{Nb} increases from 3.4 to 93.6 $\mu\text{m}/\text{min}$.

In this area, all the niobium dissolved remains soluble under pentavalent species ($0.192 \text{ M} \leq [Nb] \leq 0.634 \text{ M}$), except for the "FNS 1:1:5/2 and 1:1:3" tests which gave colorless and gelatinous precipitates. The inhibiting role of sulfuric acid is counterbalanced by the hydrolyzing effect of water towards the two others acids (reactions (11) and (12) to the right sides) and the synthesized compounds.

In that same range, the respective $[HF]$ and $[HNO_3]$ decrease under the constant ratio $R_2 = 1.587$, according to the preparation procedure. The rise in H_2SO_4 titer:

♦ Progressively diminishes the water concentration

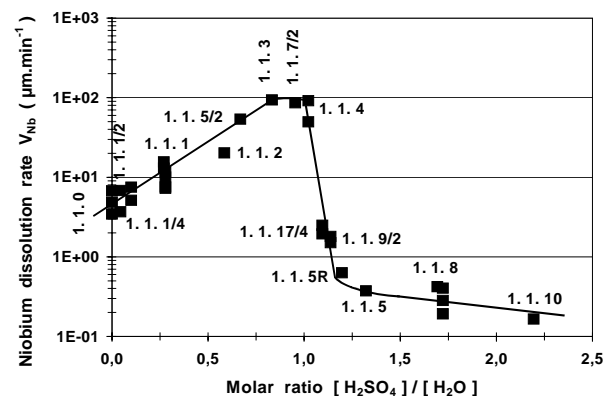


Fig. 5. Semi-logarithmic variation of Nb dissolution rate V_{Nb} versus the molar $R_3 = [H_2SO_4]/[H_2O]$ ratio and with $[HF]/[HNO_3] = 1.587$

(from 39.7 M to 13.4 M) and consequently the dissociations of HF and HNO_3 . The V_{Nb} nevertheless increase and suggest the three acids provide enough protons to the diverse chemical reactions.

♦ Allows the dissolving of the niobium pentavalent complexes ($0.192 \text{ M} \leq [Nb] \leq 0.634 \text{ M}$) such as the oxysulfates and/or fluorosulfates compounds from equations (11), (12), (15) and (16).

2) $R_3 \approx 1$

For $0.83 \leq R_3 \leq 1.02$, one can notice a maximum value on Fig. 5. This correspond to $[\text{H}_2\text{O}] = [\text{H}_2\text{SO}_4] \cong 12.2 \text{ M}$. ("FNS 1:1:3, 1:1:7/2 and 1:1:4"). On that plateau, two phenomena counterbalance the increase of Nb dissolution rate:

- ◆ Violent bubbling of NO_x into the baths and very high temperatures (62 to 77 °C).
- ◆ Formation of colorless gelatinous precipitates, which appear in the reacting vessel. They can be considered as hydrated compounds similar to those entering the structure of the passive layer [12], i.e. the numerous Nb^V complexes cited in §2 . They appear when the quantity of water present into these three baths begins to be insufficient (decrease of solubility).

2) $R_3 > 1$

In that case, the effect of sulfuric acid is predominant. In the "FNS 1:1:4 to 1:1:10" mixtures, $[\text{H}_2\text{SO}_4]$ increase from 12.29M to 15.63 M while $[\text{H}_2\text{O}]$ decreases from 12.03 M to 7.12 M. Weak HF and HNO_3 concentrations, respectively 4.00 M to 2.04 M and 2.66 M to 1.20 M, are also effective.

In this range, decreasing etching rates were measured: $V_{\text{Nb}} = 91.35$ to $0.165 \mu\text{m}/\text{min}$. One of the reactants becomes obviously a limiting species for the reaction.

In fact, the concentrations of water control this phenomenon.

The inhibiting effect of H_2SO_4 is put again in evidence (already noticed with the "FNS 1:X: 10" tests) and can be explained by two simultaneous phenomena:

- ◆ The presence of colorless gelatinous precipitates synthesized in all these attempts. These gels correspond to niobic acids with general $\text{Nb}_2\text{O}_5, n \text{ H}_2\text{O}$ or $[\text{NbO}_x\text{F}_y, 3 \text{ H}_2\text{O}]^{5-2x-y}$ or $\text{Nb}_2\text{O}_{5-n}(\text{SO}_4)_n, n \text{ H}_2\text{O}$. A part of these gelatinous compounds can be adsorbed on the metal surface while another part remains soluble into the attack solutions. The Nb metal concentration dissolved just before the appearing of these precipitates was weaker than those registered with the "FNS 1:1:0 to 1:1:3".

These gels thus inhibit the niobium attack, in the same way as the hydrated oxides or salts that precipitate at the interface metal-solution during electropolishing treatments.

- ◆ The decreasing of H_2O titers by the increasing $[\text{H}_2\text{SO}_4]$ leads to the diminishing of HF and HNO_3 hydrolysis and consequently to the decrease of V_{Nb} rates.

3.3.2. Colors of solutions, surface states, temperatures of baths

Diverse colorings were also observed for the remaining mixtures after their uses:

- ◆ For the "FNS 1:1:0 to 1:1:2" tests ($R_3 < 1$), the solutions evolved from blue, then green to yellow colors and were all limpid (absence of gelatinous precipitates). In that area and by comparison to the previous studies with varying [HF] and $[\text{HNO}_3]$, the appearance of blue

tints specifies the creation of ionized oxysulfate and/or fluorosulfate compounds.

- ◆ For the "FNS 1:1:5/2 to 1:1:4" tests (R_3 increased from 0.88 to 1.31), all the solutions were yellow colored and presented colorless gelatinous precipitates

- ◆ For the "FNS 1:1:17/4 to 1:1:10" tests ($R_3 > 1$), all the resulting solutions were colorless and presented colorless gelatinous precipitates.

- ◆ Very high bath temperatures (63 to 77 °C) were reached with the "FNS 1:1:3, 1:1:7/2 and 1:1:4". The surfaces were severely degraded (FNS 1:1:3 on photograph 9, annex 4)

- ◆ Intermediate bath temperatures (22 to 45 °C) were measured for the others "FNS" tests, in which four of them gave very shiny surfaces (Table 3), with weak

roughness within the Nb grains and light grain-boundaries etchings (photographs 9 to 12, annex 4). The sample remained brilliant during quasi all the immersion time. These attempts correspond to the "FNS 1:1:17/4 to 1:1:8" mixtures, where $12.59 \text{ M} \leq [\text{H}_2\text{SO}_4] \leq 15.63 \text{ M}$ and $R_3 > 1$.

3.3.3. Conclusion

Under weak [HF], $[\text{HNO}_3]$ and $[\text{H}_2\text{O}]$ but very high $[\text{H}_2\text{SO}_4]$, the sulfuric acid favors the suppression of macroscopic and microscopic defects.

H_2SO_4 is alike electropolishing treatments where polymerized species (polyoxo and/or hydroxo anions) are created in the interface metal-solution and favor the Nb polishing. Meanwhile, the incorporation of sulfate ions inside the oxide layer is to be inferred although we do not know yet if this phenomenon has an influence on RF properties of Nb cavities.

Table 2
Evolution of brightness duration and reflecting distances in function of H_2SO_4 concentrations

Reference of FNS Bath	Duration of attack (min)	Duration of brightness (min)	Reflecting distance (cm)
1. 1. 0	100	60	0.5 – 1.0
1. 1. 1/4	90	87	2.5 – 3.0
1. 1. 1/2	60	58	3.0 – 3.5
1. 1. 1	30	28	2.0 – 2.5
1. 1. 2	23	8	1.0 – 1.5
1. 1. 5/2	17.5	No brilliant phase	
1. 1. 3	19	7	1.5 – 2.0
1. 1. 7/2	58	0.5	1.5 – 2.0
1. 1. 4	12	1	4.5 – 5.0
. 1. 17/4	16	13	. 10
. 1. 9/2	60	58	. 10
. 1. 5	75	63	.5 – 6.0
. 1. 8	45	45	.5 – 6.5
1. 1. 10	135	30	1.0 – 1.5

4. General conclusion on the influences of the three mineral acids

Through that study of the chemical behavior of ternary "FNS" mixtures, it has been put in evidence some linear relationships between the niobium dissolution rate and the concentration of each mineral acid.

These relationships have been obtained for particular molar ratios (R_1 , R_2 and R_3) between the concentrations of the two others acids.

In the case of mixtures including high H_2SO_4 concentrations, the essential influence of water on the etching rates V_{Nb} and the surface states of Nb tests sheets has been confirmed.

The etching solutions give colorless gelatinous precipitates when the molar ratio $R_3 = [H_2O]/[H_2SO_4]$ is < 1 . These precipitates inhibit the niobium attack but produce very shiny surfaces, in an analogous way of passive layers in electrochemical procedures.

More specific experiments about the physico-chemical mechanisms of niobium polishing still need to be developed.

Further work is also under progress on the possibility to readjust the composition of the chemical polishing bath after an appreciable consumption of the reactants, to obtain similar performances for a long period.

The classification of the surface states with the help of "Müdge grid" (annex 3) shows that the "FNS 1. 1. 1" bath gives the best surface state, although the etching rate is a little bit high.

Acknowledgements

The authors acknowledge Y. Gasser and J.P Poupeau for their assistance in the numerous experiments done.

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Annex 1

Preparation procedure of "FNS x-y-z" baths

These strongly acidic baths were obtained by mixing well-defined volumes of commercial acids at high purity such as HF 40-41% ($d = 1.13$), HNO_3 63-69% ($d = 1.38-1.405$) and H_2SO_4 95% ($d = 1.83-1.84$). These mixings were always done under the following procedure:

- ◆ Introduction of the required volume of concentrated HF (23.15 M) into a closed Teflon vessel slightly stirred (250-400 trs.mn⁻¹) by a magnetic stirrer and cooled back to 8-12°C. This acid is always introduced firstly into the container as it incorporates a 59-60% of pure water.

- ◆ Slow additions of the necessary volume of concentrated H_2SO_4 (17.73-17.82 M). As the dissolution of sulfuric acid into water is strongly exothermic (the temperature can easily reach 80°C), the resulting mixture must be cooled to 8-12°C in order to reduce the partial distillation of HF.

Note: At high H_2SO_4 concentration, it is also imperative to operate into a closed vessel since that acid is strongly hygroscopic when highly concentrated. The fixation of water vapor from the ambient atmosphere leads, by simple dilution, to lower concentrations for each mineral acid.

- ◆ Final introduction of the required volume of concentrated HNO_3 (13.80-15.39 M) into the preceding mixture still stirred and cooled back to 8-12°C.

This preparation procedure gives solutions which are always colorless, limpid and without bubbles (before use). They are kept in tight-fitting polypropylene bottles.

They still exhibit a good chemical stability, after many months of storage.

Annex 2

Experimental protocol of "FNS" tests

Test sheets of pure niobium (RRR ~200), analogous to those employed for the fabrication of RF cavities, were used in these studies. They were first ultrasonically degreased by immersion into a strong basic TFD4 (10% volume - pH = 13.8) solution, held at 60 °C. They were then rinsed with ultra-pure water (18 MOhms.cm) and finally etched into "FNS x-y-z" baths. All the tests related in that paper were conducted according to the following protocol:

- ◆ Introduction of the required volume of "FNS x-y-z" bath into a closed and stirred (250-400 trs.mn⁻¹) Teflon vessel. This volume is determined by the ratio V/S, where V = bath volume (cm³) and S = niobium sample area (cm²). It was kept constant and equal to ~10 cm. Thus, this ratio keeps comparable to the V/S ratio available for cavities treatments.
- ◆ Sequential immersions (contact times = 15 sec, 1, 2... 30 min) of the Nb test sheet held by a "stainless steel 316 L" hanger (that material is first weakly attacked then becomes passive in all the "FNS" mixtures)
- ◆ The changes in the temperatures of reactive media were continuously registered versus the immersion durations (etching started at room temperature 15-22 °C)
- ◆ After one etching sequence, the sample of Nb went through the following operations:
 - Rinsing by ultra pure water,
 - Careful drying by filtered and compressed air,
 - Weighing on an analytical balance (Mettler 600),
 - Visual inspections of the surface states with an optical microscope (Leica DMRM).
- ◆ Further etching.

Annex 3

Photographs and Surface state evaluation by "Müdge grid"

The quantification of qualitative data like photographs can be done with the help of Müdge grid by comparison and quotation of data, two by two.

If A and B are two "objects" to be compared, then we assume :

If A >> B, then A = 3 and B = 0

If A > B, then A = 2 and B = 0

If A ~ B, then A = 1 and B = 1 (case of good data)

If A ~ B, then A = 0 and B = 0 (case of bad data)

In the case of photographs showed in annex 4, the following figures (Table 4) can be drawn out:

Table 4
Comparison and quotation of photographs

	P ₁	P ₂	P ₃	P ₄	P ₅	P ₆	P ₇	P ₈	P ₉	P ₁₀	P ₁₁
P ₁₂	1\1	1\1	0\2	3\0	2\0	1\1	1\1	3\0	3\0	2\0	1\1
P ₁₁	1\1	1\1	0\2	3\0	2\0	1\1	1\1	3\0	3\0	2\0	
P ₁₀	0\2	0\2	0\2	3\0	1\1	1\1	1\1	2\0	3\0		
P ₉	0\3	0\3	0\3	0\0	0\3	0\3	0\3	0\0			
P ₈	0\3	0\3	0\3	1\1	0\2	0\3	0\3				
P ₇	0\2	1\1	0\2	3\0	1\1	1\1					
P ₆	0\2	2\0	0\2	3\0	1\1						
P ₅	0\2	1\1	0\2	3\0							
P ₄	0\3	0\3	0\3								
P ₃	2\0	2\0									
P ₂	1\1										

The sum of these numerical values leads for example to:

$$P_3 = 2+2+2+3+3+2+2+2+3+2+2 = 25$$

$$P_9 = 0+0+0+0+0+0+0+0+0+0+0 = 0$$

One can finally classify the surface states according to Table 5.

Table 5
Quotation of each photograph

Photograph	Bath composition	Quote
P3	FNS 1-1-1	25
P1	FNS 1/10-1-1	20
P11	FNS 1-1-9/2	18
P12	FNS 1-1-8	18
P2	FNS 1/2-1-1	16
P6	FNS 1-3/2-1	16
P7	FNS 1-7/2-1	15
P5	FNS 1-1/2-1	12
P10	FNS 1-1-1/4	11
P4	FNS 3-1-1	1
P8	FNS 1-3/10-10	1
P9	FNS 1-1-3	0

In this way, the best surface state generated by all the FNS baths described in this paper is the one obtained from FNS 1:1:1 mixture.

Annex 4 – Photographs



Photo 1 : FNS 1/10. 1. 1

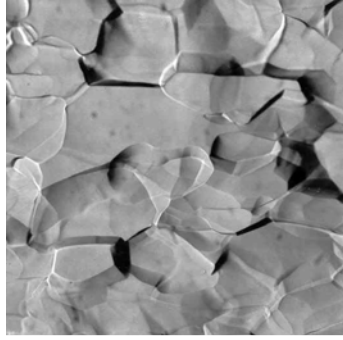


Photo 2 : FNS 1/2. 1. 1



Photo 3 : FNS 1. 1. 1

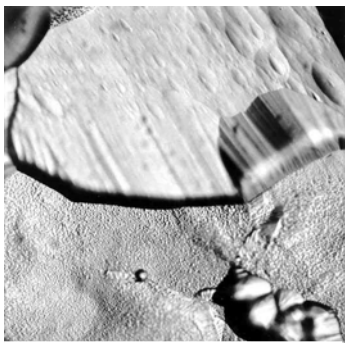


Photo 4 : FNS 3. 1. 1

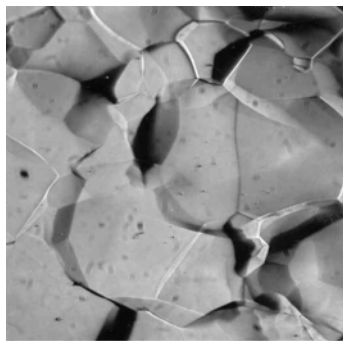


Photo 5 : FNS 1. 1/2. 1

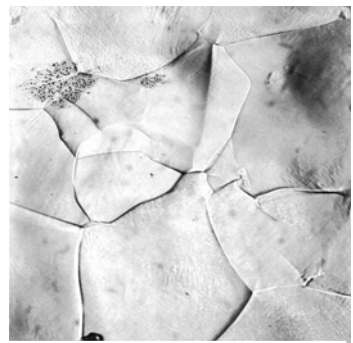


Photo 6 : FNS 1. 3/2. 1



Photo 7 : FNS 1. 7/2. 1

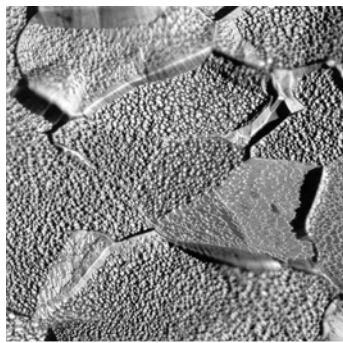


Photo 8 : FNS 1. 3/10. 10

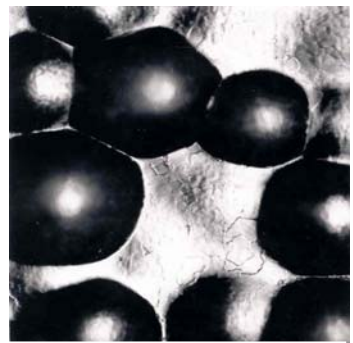


Photo 9 : FNS 1. 1. 3



Photo 10 : FNS 1. 1. 1/4

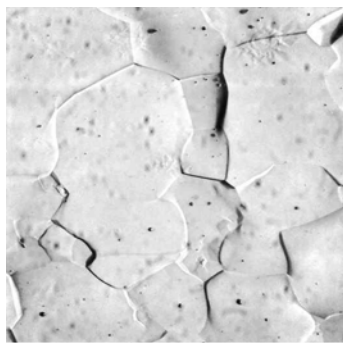


Photo 11 : FNS 1. 1. 9/2

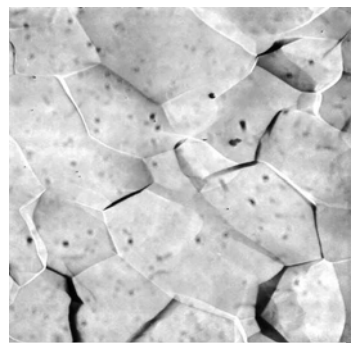


Photo 12 : FNS 1. 1. 8