

# HYDROGEN SURFACE ANALYSIS OF NIOBIUM IN FUNCTION OF VARIOUS ELECTROCHEMICAL CONDITIONS

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## Abstract

Electropolishing is presently accepted like most efficient surface treatment obtaining high gradients in niobium RF cavities. This treatment seems to introduce more hydrogen in niobium than chemical etching [1]. We have investigated hydrogen contamination changes in various electrochemical conditions (like anodic protection) during chemical etching and electropolishing, and other conditions like hot water rinsing, hydrofluoric acid rinsing, etc... Hydrogen contamination near the surface is analyzed with HFS (hydrogen forward scattering). This technique allows exploring 200 to 300 nm of the surface (i.e. little bit more than the field penetration depth) and it is used to monitor the hydrogen up-take inside niobium in various electrochemical conditions.

## INTRODUCTION

H is known to provoke “Q-disease”. Former publications showed that [1-3]:

- Moderate heating makes it disappear (750°-800° C, 2h, UHV)
- Heavy chemical polishing (BCP) makes it reappear
- Electropolishing (EP) give rise to heavy Q-disease

But also that

- Hydrogen is segregated near the metal-oxide interface, i.e. about the penetration depth [4, 5]
- EP is not at the origin of H contamination, but contact with the EP solution without bias is [6, 7]

In most of the work done previously, H determination is done by bulk analysis. In complement to this work, have investigated hydrogen contamination in various electrochemical conditions (like anodic protection) during chemical etching and electropolishing, and other conditions like hot water rinsing, hydrofluoric acid rinsing, etc... Influence of the concentration of H<sub>2</sub>O and HF has also been explored.

## EXPERIMENTALS

### Experimental Issues

Several points have been tested. First we wanted to better characterize the hydrogen contamination brought by electropolishing. As already showed by Higuchi [7], EP itself is not the source of H contamination. We have confirmed these results by measuring with a better precision the surface contamination; in particular we have

checked the respective influence of atomis hydrogen vs molecular hydrogen.

Moreover we have been trying to explore some ways of protection against H uptake. Indeed, we have found in the literature some indications that contacting a metal sample with a more noble metal might be effective to prevent H embrittlement for Nb and Ta (anodic protection) [8]. We wanted to check if this effect is still effective in the case of anodic polarization during electropolishing.

We have also tested the influence of various rinsing procedure. Indeed, still in literature [9], the harmfulness of halides (F<sup>-</sup>, Cl<sup>-</sup>...). Moreover, we had already observed it for Cl<sup>-</sup> [4].

Effectiveness boiling water rinsing has also been observed on anodically oxidized Nb. In [10], it is claimed that chemical polishing leaves a film that keeps at the oxide-metal interface upon further oxidation, if not previously leaked in boiling water. As we have also detected anionic impurities from the etching solution imbedded inside the oxide [11, 12], it was also interesting to check the effect of hot water rinsing.

### HFS (Hydrogen Forward Scattering)

HFS is used to monitor the hydrogen up-take inside niobium in various electrochemical conditions. This technique allows exploring 200 to 300 nm of the surface (i.e. little bit more than the field penetration depth), with a depth resolution about 30 nm. It means that the first “layer” of the analysis includes surface contamination (adsorbed water, hydrocarbons...) and cannot be taken into consideration. Thus the layer of interest is the second one : ~30-60 nm, which corresponds more or less to the penetration depth. The limit of detection is ~ 0.3 At.%, and the relative error is ~10 % for comparison between the samples.

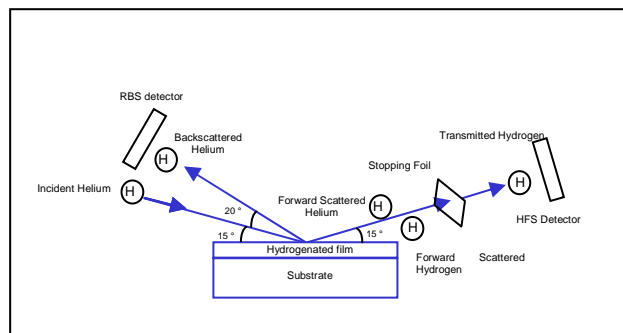


Figure 1: Schematic diagram of HFS technique.

### Measured Contamination

Typical spectrum and the results are showed in figure 2 and table 1 for a sample after chemical etching.

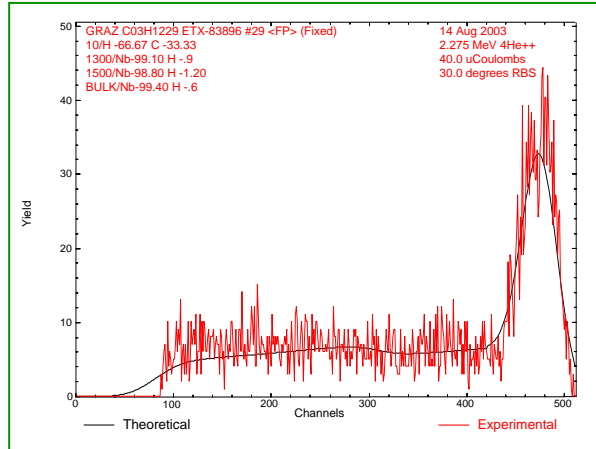


Figure 2: HFS spectrum of a chemically etched niobium sample (usual BCP).

Table 1: Atomic concentration of hydrogen, carbon and niobium determined by HFS.

Depth (Å)	Atomic Concentration		
	H	C	Nb
0-11	67**	33**	-
11-311	0.8*	--	99.2
<b>311-611</b>	<b>0.8</b>	<b>--</b>	<b>99.2</b>
611-911	1.0	--	99.0
911-1211	0.9	--	99.1
1211-1511	1.0	--	99.0
1511-1811	1.2	--	98.8
1811-2111	1.3	--	98.7
>2111	1.5	--	98.5

\* There is a large uncertainty in the estimation of the inner contamination due to superficial hydrocarbon, water, etc.  
 \*\* a layer of "pure" hydrocarbon is systematically assumed on the surface.

Comments:

- The surface concentration is about 100 times higher than the concentration determined by global methods, due to surface segregation.
- There is a hydrocarbon layer on the surface of each sample.
- There is a large uncertainty in the H concentration in the upper ~300Å of the samples due to this hydrocarbon layer.
- The second layers gives more accurate results, moreover it concerns the penetration depth of the superconductor.

For these reasons, we have summarized in table 2 only the 2 first layers (after hydrocarbon layer) for various treatments.

Note: Although Pt is a noble metal, embrittlement was observed after long term utilization of the cathode. We have discovered traces of Pt on the surface of Nb, in a concentration inversely proportional of the distance to the

cathode. We suppose that it arises from dust particles deposited on the surface. The electropolished sample wasn't polluted. We need to check if similar behavior appears on Aluminum cathode.

Table 2: Summary of the surface contamination of the first layers of niobium after various surface treatments.

SURFACE TREATMENT \ HYDROGEN CONTENT (At%)	1 <sup>st</sup> layer (300nm)	2 <sup>nd</sup> layer (300nm)
Référence : (750°C, 2h, UHV), stored under vacuum	1.4	1.4
<b>Rinsing, "dipping" without bias :</b>		
Ref + boiling H <sub>2</sub> O rinsing, 1mn	2.6	2.6
boiling H <sub>2</sub> O, 1 h	9.0	9.1
[HF] 2.5 M, 1h	3.0	2.4
1h in EP-bath, no bias, no holder	1.5	1.5
1h in EP-bath, no bias, Pt holder	3.0	2.2
1000 mn in EP-bath, Nb holder, no bias *	3.5	2.3
1000 mn in EP soln, Teflon holder	2.5	2.5
1000 mn in EP-bath, no bias, Nb holder, near/upside H <sub>2</sub> bubbles*	9.0	6.5
in contact with cathode during EP, 1000 mn*	8.0	6.0
near/upside H <sub>2</sub> bubbles, Pt holder	6.8	6.5
<b>Polishing :</b>		
FNP, 1h, ~ 360 µm	0.8	0.8
EP~150 µm, Pt holder	1.0	0.5
EP 280µm (1000 mn), Pt holder	1.0	0.4
EP ~ 150µm, Pt holder, + 1h without bias	2.5	0.8
intermittent EP, ~150 µm	2.0	1.2
EP100 µm + hot H <sub>2</sub> O rinsing, 1mn	1.9	1.9
EP ~ 150 µm, PTFE filter, Pt holder	1.0	0.6
EP ~ 150 µm, PTFE filter, Pt holder, + 1h without bias	2.0	1.0

\* presence of Pt on the very surface.

Comments:

Reference :

- After furnace treatment there is still an appreciable amount of H near the surface. Possible explanation: without protective oxide, Nb gets polluted by residual vacuum and (the short) exposition to air.

Rinsing :

- HF brings in moderate contamination. This observation is somehow in contradiction with literature and former results: Halides (F, Cl...) should bring in a lot of contamination. This might arise from the fact that in the present study we have got very pure and very well recrystallized Nb (RRR > 400)
- Unexpected result: H<sub>2</sub>O, although an oxidant to Nb doesn't protect it. Prolonged contact with hot water

provokes a huge contamination. Shorter duration (1 mn) already brings in appreciable contamination.

Dipping without bias :

- These results confirm that EP bath (without bias) brings in some contamination, although a little less than pure HF. Contacting the sample with Pt doesn't appear to improve the situation.
- Cathodic polarisation and contact with H<sub>2</sub> bubbles bring in heavy contamination. This last point is rather surprising, because it is not very favourable from the thermodynamic point of view. Possible explanation: because of the presence of HF in the EP bath, the oxide layer is not passive/protective anymore, and direct contact with Nb<sup>o</sup> promotes H<sub>2</sub> dissociation.

Polishing

- Chemical polishing seems to reduce H contamination compared to the reference sample. This is in contradiction with former observed results [4]. Possible explanation: the samples used in this study are post purified, with a RRR ~x3 times higher than for the other publications. Highly purified material, with few defects seems to be less sensitive to recontamination.
- Those results confirm that continuous EP reduces efficiently surface contamination. The longer the treatment the most efficient it is.
- Intermittent treatment, were the metal surface is in contact with solution without being anodically polarized (and thus without protective oxide layer) brings in moderate contamination. As well as further staying in the solution without bias.
- The use of a Teflon membrane doesn't change significantly the results in our configuration, where the sample and the cathode are immersed vertically in the EP bath. But as we have showed that the niobium without protective oxide is very sensitive to H<sub>2</sub>, it is recommended to further use it as a protection.

*EP Optimization*

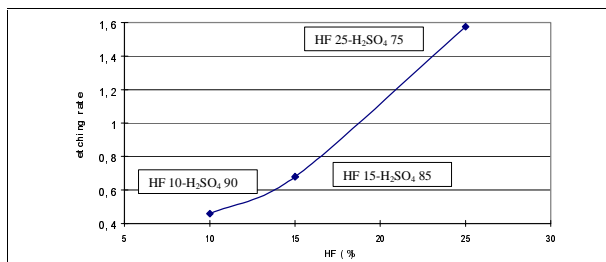


Figure 3: Influence of HF on etching rate.

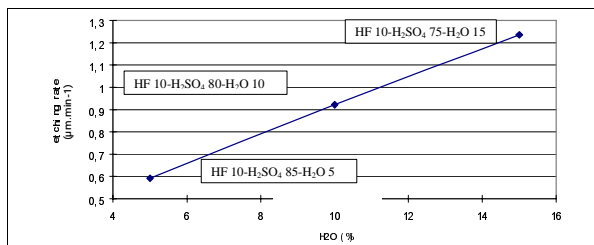


Figure 4: Influence of H<sub>2</sub>O on etching rate.

EP gives promising results, but the etching rate is rather slow. Few experiments show that the composition of the EP bath has a large influence and the etching rate can be improved by changing the proportion of the components.

**CONCLUSION**

- All samples show an important surface contamination.
- As already shown by [7], EP is not contaminating as long as bias is maintained.
- Compared to medium RRR material (~200), very pure niobium (RRR~ 400) seems to be less sensitive to hydrogen contamination arising from electrochemical condition (H<sup>o</sup>).
- It is still very sensitive to contamination from the gas bubbles (H<sub>2</sub>).
- Cathodic protection was not demonstrated.
- There are many clues for EP optimizing.
- Of course further experiments are still needed in order to master this new surface treatment.

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