THE ROLE OF ATOMIC HYDROGEN IN Q-DEGRADATION OF NIOBIUM SUPERCONDUCTING RF CAVITIES : ANALYTICAL POINT OF VIEW.

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ABSTRACT

This paper presents a study on the H contamination of Nb by various surface treatments, with emphasis on the analytical and chemical aspects. H was found to be concentrated near the surface. A discussion is presented about the mechanisms of hydrogen pollution and some indications about its prevention are given.

I) INTRODUCTION

Q degradations at low temperature ("100 K" effect) has been observed on RF niobium cavities in several laboratories [ref. 1,2,3]. These laboratories use different ways to prepare their cavities : hydroforming, stamping, spinning...but have in common a chemical polishing based on a mixture of HF, HNO_3, and H_3PO_4 in various proportions (a detailed review of different laboratories results shall be published by B. BONIN in the same proceeding).

As discussed in [ref. 1], the appearance of a weak superconducting phase near the

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surface of niobium is compatible with the experimental facts : a layer as thin as.20-30 nm, exhibiting poor Tc and Hc is enough to explain the observed important Q-degradations. Moreover, several phases of niobium hydrides are known at low temperature, which exhibit poor superconductivity or normal conduction depending on the H proportion [ref. 6]. (It should be noted that, although their phase transitions were not much studied at low temperature, several niobium suboxides also exhibit poor superconductivity [ref. 7], but they are less likely to be responsible from the Q-degradation as will be shown in the following.)

The main experimental facts from our laboratory are :

- Cavities that experience fast cooldown exhibit commonly quality factors Q_0 about 10^{10}(f = 1.5 GHz, T = 1.8 K).

- Cavities spending some hours between 100 and 200 K during cooldown show a degradation of Q_0 up to a factor 100. This effect reaches saturation when cooling exposure exceeds three hours.

- Annealing of degraded cavities at room temperature followed by fast cooldown restores high Q_0.

- Heat treatments can immunize cavities against this effect : two hours at 1500°C in UHV are enough to make "100 K" effect totally disappear [ref. 4]. At moderate temperature and vacuum (2 hours, 750°C, 10^{-7} torr) cavities showed slight surface degradation, probably due to partial diffusion of oxygen from the oxide layer toward the metal, but remained insensitive to cooldown speed.

- A moderate chemical polishing (1HF-1HNO_3-2H_3PO_4, ~ 2 µm) suppresses the surface degradation of a cavity treated at 750°C without restoring the "100 K" effect. In this case, the oxide layer is similar to the one before the heat treatment, a fact which rules out completely any direct effect of the oxygen distribution near the surface in the "100 K" effect .

- A long chemical polishing (1HF-1HNO_3-2H_3PO_4, ~ 1 h, 50-60 µm) restores the "100 K" effect to immunized cavities (but in a somewhat less effect). This proves the main role of chemical polishing as a source of the "100 K" effect.

Attempts [ref.3,4] have been made to use lactic acid instead of H_3PO_4 in the polishing bath. Although this technique was abandoned for safety reasons, cavities treated this way did not exhibit a "100 K" effect, thus giving indication of the noxious effect of H_3PO_4.

From all these facts, it seems evident that chemical polishing brings inside niobium a

contaminant which is likely to move out at moderate temperatures (650-750°C). At these temperatures, light interstitials like C, N, O should be mobile inside niobium (for instance O moves in a mean distance of about 0.3 mm in two hours at 750°C), but they would not be able to escape from the material as hydrogen [ref 5]. Indeed, except near the melting point of niobium, the diffusion coefficient of hydrogen is some 10^{15} to 10^{20} greater than the one for oxygen or nitrogen for instance (Fig. 1), and the activation energy necessary to cross out the oxide barrier is about 10 times lower than for the other light impurities [ref 6]. Moreover, the difference of behavior of cavities upon cooldown duration suggests a phase transition in the case of a temperature landing below 200 K (that will take ~ 3 hours), and quenching (tempering) of the "high" temperature phase in the case of rapid cooldown. This again, makes one suspect a noxious form of niobium hydride at low temperature.

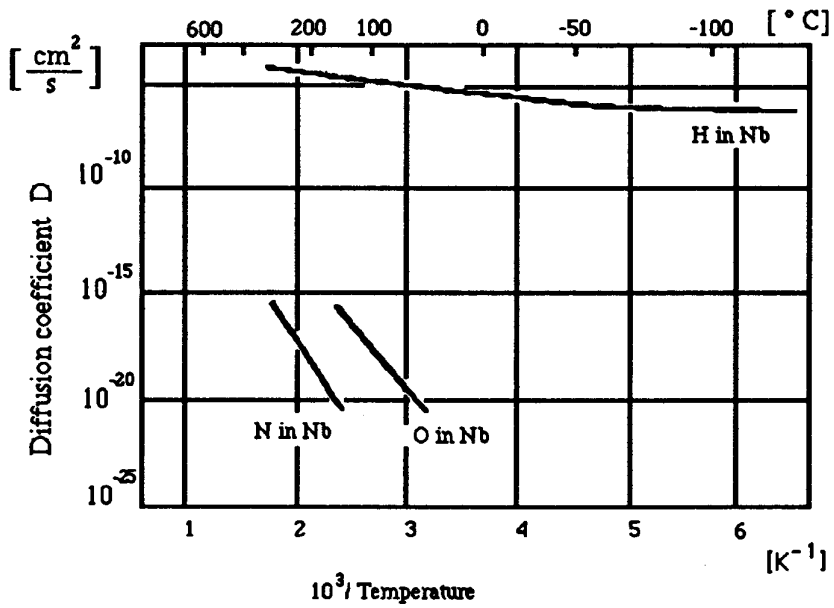

Figure 1 : Diffusion coefficients of H, N, and O in Nb

As suspected before [ref. 1,2,3], hydrogen, brought in by the chemical treatment, appears as the main responsible for the "100 K" effect. It is therefore important to determine the distribution and location of hydrogen in niobium after a chemical treatment.

II) CHARACTERIZATIONS

Nb samples were subjected to different treatments, trying to reproduce various processes used in different laboratories.

Low concentration of Hydrogen (≤ 100 At ppm) and its precise location (better than 50 nm) are quite difficult to determine through only one technique. Therefore four techniques

were used to check the hydrogen concentration of these samples, which give indications about either global or surface composition of the material, with increasing resolution. Specificities and experimental conditions of the different methods are shortly described in the following, before exposing results :

-1) A "thermal method"[3] which consist in heating the sample in a nitrogen atmosphere. The thermal conductivity of N_2 is measured as a function of H-desorbtion by the sample. For refractory metals like Nb,complete extraction of the gas impurity is hardly achieved, unless using small test samples (typically 1 g of Nb). Thus the sensitivity of the method is poor, and it is hardly possible to measure less than 100 At ppm (1 Wppm). This method is a global one and gives information about the H content of the whole volume of the sample. The results led to amounts of hydrogen near or below the sensitivity of this method, i.e. ≤ 100 At. ppm, for all the samples.

This concentration, if it is uniformly distributed inside the material, seems a little too feeble to account for important Q-degradations [ref. 8].

-2) SIMS (Secondary Ion Mass Spectroscopy) : sample surface is eroded with an Ar^+ beam and the resulting secondary ions are analyzed with a mass spectrometer. Sputtering rates must be quite higher than usual with this technique for avoiding lateral H diffusion. 60 to 80 microns deep of the surface were analyzed, with only a resolution ≥ 100 nm. The analyzed secondary ions were Nb_2H^+ and H^+.

	H	V	C	S	D	F
[H]	(15)	-	30	45	100	3
Δ[H]/[H]	10%	-	10%	30%	10%	10%

Table (I) : relative H concentration as determined by SIMS (At.ppm)[4]

- "H" = Nb sheets as received from Heraeus
- "V" = "H" subjected to one night in HCl 1% (in order to test if there are Fe inclusions). This treatment is commonly used on Nb sheets
- "C" = "V" subjected to 1 HF-1 HNO_3-1 H_3PO_4 chemical polishing (cf Cornell laboratory). (Note : rinsing has been done only with pure water instead of a H_2O_2 solution in some cases)
- "S" = "V" subjected to 1 HF-1 HNO_3-2 H_3PO_4 chemical polishing (cf Saclay laboratory)
- "D" = "V" subjected to 1 HF-1 HNO_3-4 H_3PO_4 chemical polishing (cf Desy laboratory)
- "F" = "V" after several hours at 1000°C and 5.10^{-7} Torr.

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[3] Experiments performed by the "Laboratoire d'Analyses Physico-Chimiques" at the CEA-Fontenay-aux-Roses.France

[4](Experiment performed at the CEREM-SRCA at the CEA-Grenoble.France)

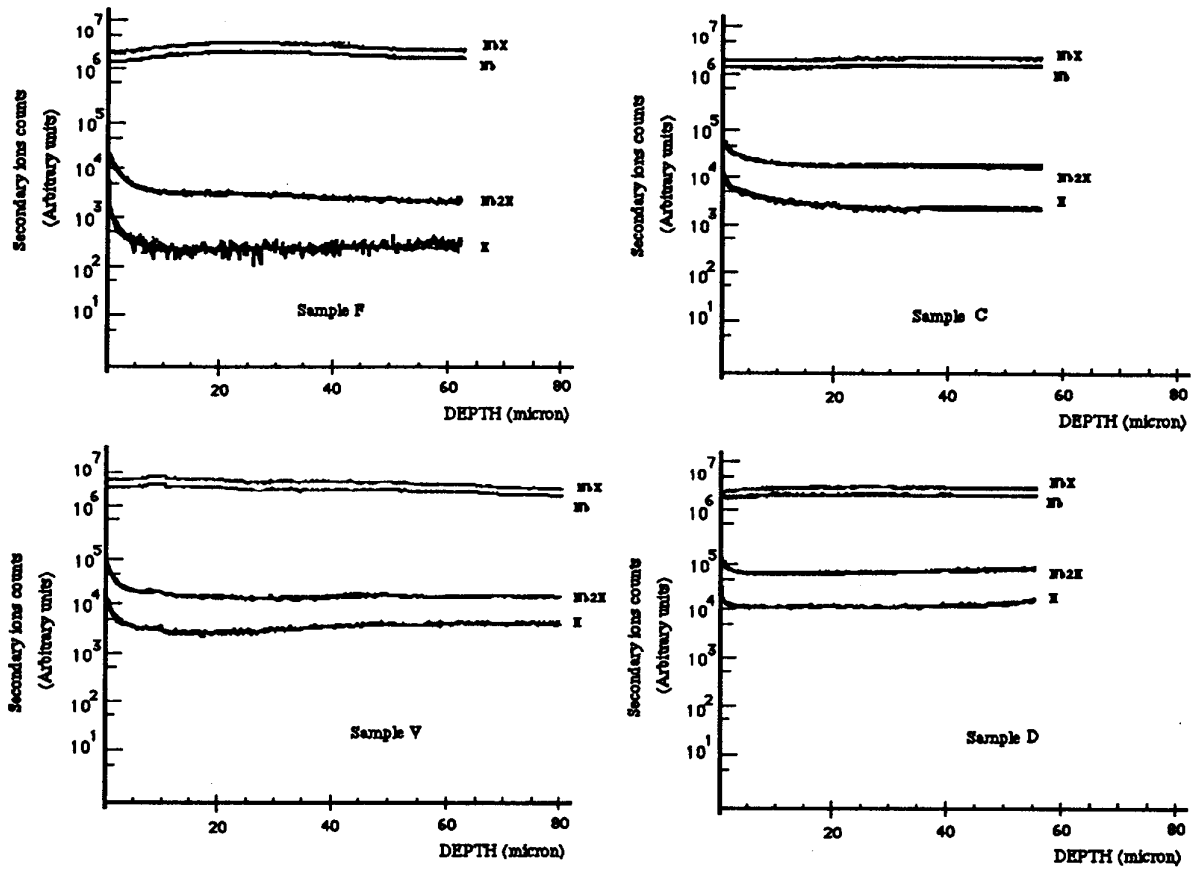

Fig.2- Examples of SIMS spectra.

Spectra exhibit an enrichment near the surface of the samples ; because of the poor depth resolution, this was attributed to surface contamination. The end of the spectra exhibit relatively flat features, which indicates that the composition of the bulk of the material (some 10 micron deep) does not vary any more (Fig. 2). One can note that there are little difference between samples (a factor 3 at maximum), except for the "F" one where the relative concentration of H is very low.

-3) GDL (emission spectroscopy in a Glow Discharge Lamp). This method is quite similar to the previous one : a plasma of Ar^+ is created in the lamp and leads to the erosion of the material of the sample too. The wavelength of the light emitted by the ejected neutral atoms is characteristic of each species, and one can observe several types of atoms simultaneously. Nevertheless it is difficult to get a well defined standard, especially for low concentration, as erosion speed depends strongly of the general characteristics of the material (conductivity, roughness, etc...). Thus the results obtained by this technique are once more qualitative and not

quantitative[5].

In our case, H, Nb, O, C, N and P were observed in the first micron depth (1μm) of the surface. The averaged erosion speed is about 70 nm/s. Attention must be drawn to the fact that the erosion speed at the very beginning of the spectra is not well defined since the discharge is still not well established, and moreover the oxide layer at the surface of niobium is not as conducting as the pure metal (Fig. 3).

Surprisingly again, few differences could be observed from one sample to another in spite of the different treatments applied to them, except in the case of a sample type "F" : heat treatment reduces a lot the whole surface contamination to a layer of ~ 10 nm.

All spectra (except "F") present a very perturbed superficial layer about 35 nm (first 500 milliseconds of erosion), but after 70 nm (1 sec.) the composition varies only very slowly toward the bulk one. Superficial layers are characterized by the presence of an oxygen signal, that probably arise mainly from the natural oxide layer (~ 6 nm) which always exists on niobium. Nevertheless it cannot be excluded that a first part of the signal might be attributed to superficial contamination, as well as to the first parts of H, C and P signals at the beginning of the discharge (see Fig.3 bis). By the way, these signals can be attributed to adsorbed contamination layers : hydrocarbons, CO, H_2O ...

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[5] Experiment performed at the "Laboratoire d'Analyses Physico-Chimiques at the CEA-Fontenay-aux-Roses. France.

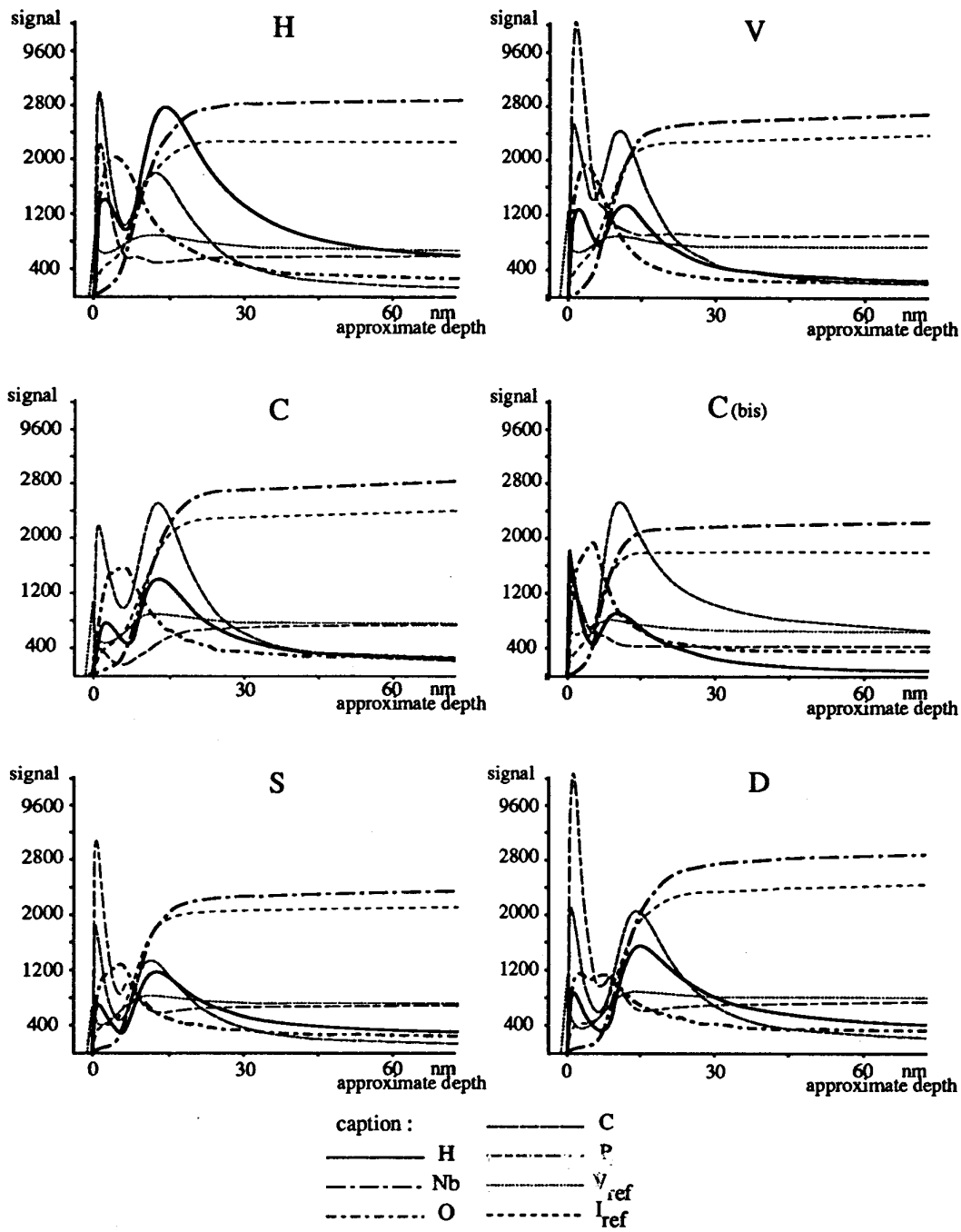

Figure 3 : GDL'spectra of various samples. V represents the bias of the discharge and Iref represents the average luminosity. They both evolve a lot at the beginning of the discharge, making any intensity comparison hazardous. These spectra only allow to determine the "range" of the different contamination layers from the surface toward the bulk.

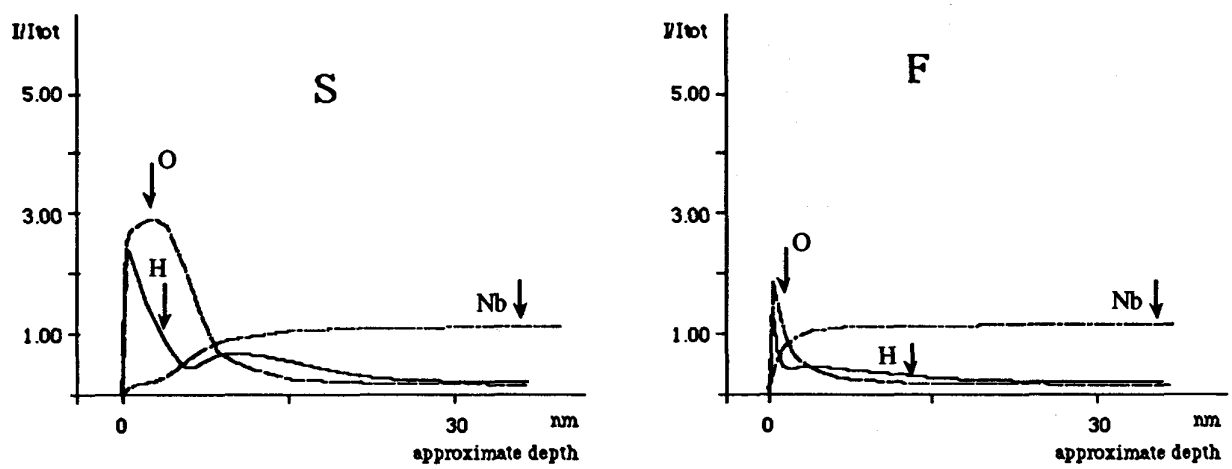

Figure 3 bis : Partial GDL'spectra showing O,H, and Nb signals. Here, intensity of each element is reported to total intensity, giving indication of the relative concentration in the both sample. (Note : one can make comparison of the same element only. The relative luminosity yield between two different elements is not known with precision).

Some more interesting points are the presence of phosphorus inside the oxide layer, just below the oxide-metal interface (this can be explained by the oxide growth mechanism : it begins in the acids bath, in presence of orthophosphoric acid, but reaches its equilibrium thickness during rinsing [ref 7 and ref. herein]). The presence of C and H (probably correlated) has also been detected, also near this interface, but neatly inside the metal, thus in a few tens of nm deep inside the niobium. This indicates that this contamination occurred probably before the oxide layer apparition, thus during the chemical treatment.

-4) ERDA[6] (Elastic Recoil Detection Analysis). An $^4He^+$ beam of a few MeV reach the sample with grazing angle and ejects elastically H^+ ions of the niobium. A few 100 nm are explored by this way and the resolution is presently limited to 30-40 nm due to detection method.

The spectra are very similar to the the GDL's ones, although the resolution does not allow to tell the very superficial contamination from the more internal one. Nevertheless this technique is quantitative and allows to determine with good precision the concentration and the location of H within the resolution (Fig. 4). Table (II) shows the atomic percentages as determined with fitting a model spectra to the experimental data. $[H]_1$ represents the H content

[6]Experiment performed in collaboration with B. ROUX, M.N. and A. CHEVARIER at the IPN-Lyon France (nuclear probe) and with J. GOSSET -Laboratoire Pierre Süe-CEA Saclay.France (microprobe)

in atomic percent of the first 40 nm of the niobium, including surface contamination, and $[H]_2$ represents the H content of the next layer : ~ 40 to ~ 200 nm.

	H	V	C	S	D	F
$[H]_1$	-	> 9	8	4	4	4
$[H]_2$	-	~4	0,9	0,7	0,7	0,4

Table (II) : H concentration in At.% as determined by ERDA

- "H" = Nb sheets as received from Heraeus
- "V" = "H" subjected to one night in HCl 1% (in order to test if there are Fe inclusions). This treatment is commonly used on Nb sheets
- "C" = "V" subjected to 1 HF-1 HNO_3-1 H_3PO_4 chemical polishing (cf Cornell laboratory). (Note : rinsing has been done only with pure water instead of a H_2O_2 solution in some cases)
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- "F" = "V" after several hours at 1000°C and 5.10^{-7} Torr.

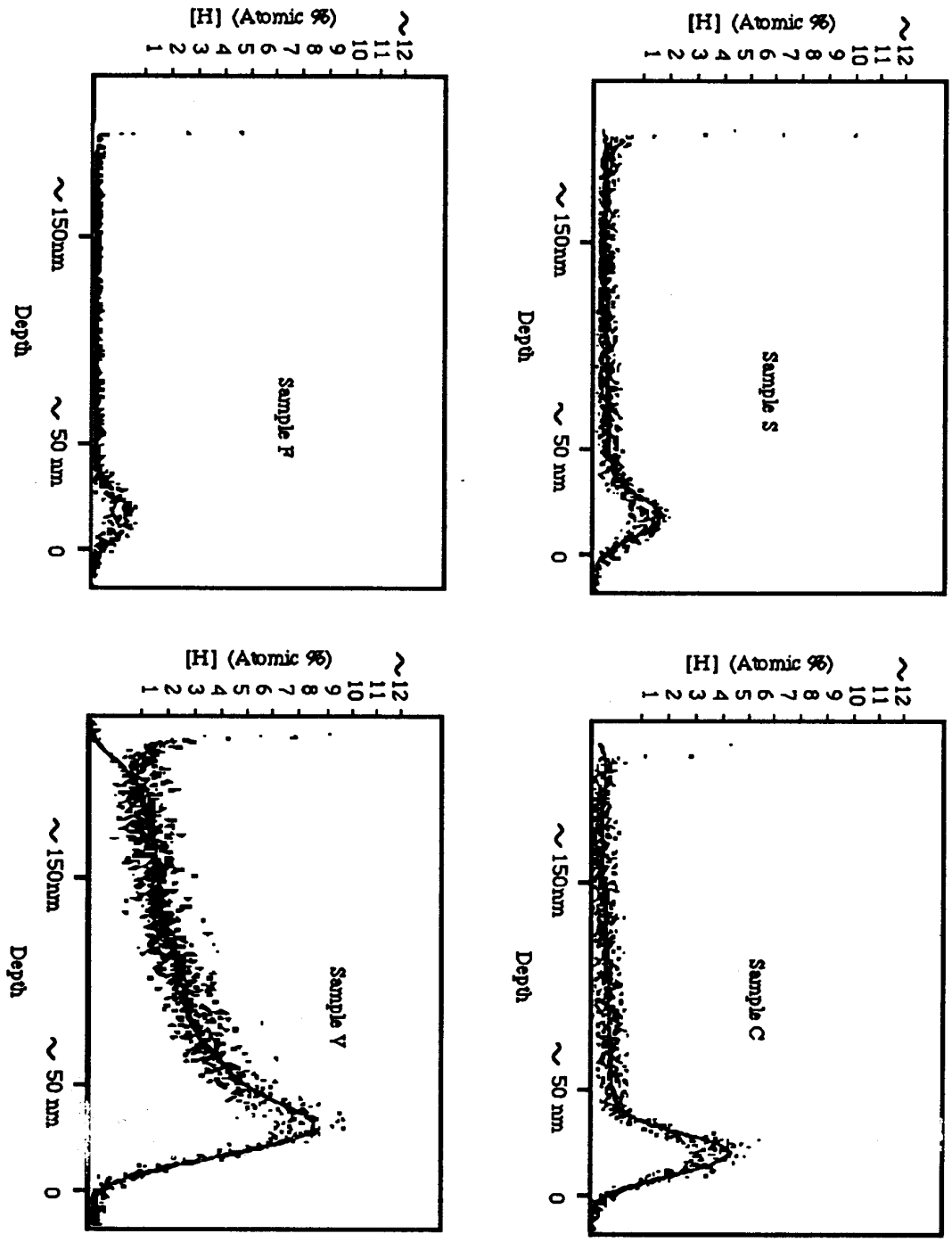


Fig.4- Examples of ERDA spectra.

One can note again that there is little difference between samples, except for sample "V". The increase of H interstitials inside niobium with HCl treatments has already been observed (see discussion + [ref. 9]), and can be explained with simple electrochemical

arguments.

The very important fact from these studies is that the concentration of H near the surface is far higher than the bulk one (as determined by the thermic method). It can even reach the limit of precipitation of the hydride phase β at ambient temperature which is ~ 5 at % at 25°C. (Nevertheless these concentrations may be slightly overestimated because of the contribution of the adsorbed layers).

We conclude from this series of investigation that after a chemical treatment, i.e. polishing or even HCl treatment :

- main contamination is restricted to the first 100 nm of the surface of the material.

- it can be decomposed in two layers : a very superficial one (adsorption layers) and a more internal one which is located near the oxide-metal interface.

- the presence of H might be correlated with other chemical impurities.

- samples that were subjected to different concentrations of H_3PO_4 do not exhibit big quantitative differences in H concentrations, although these different treatments applied to cavities led to very dispersed results in Q-degradation. This indicates that maybe contamination occurred also during other steps of the preparation of the cavities ; the structural history of the niobium sheets might also play a key role in the keeping of hydrogen.

III) DISCUSSION

1) Origin of hydrogen ?

The mechanisms of apparition of hydrogen during acidic processes are reviewed in details in a recent paper [ref 9]. Four types of reactions are involved and/or competing, and the effective pollution results from the balance between these different reactions :

(1) Volmer process (fast) :

$$H_3O^+ + e^-(M) \leftrightarrow H_{ads}M + H_2O$$

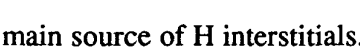
(2) Heyrovsky-Horiuti process (slow) :

$$H_{ads}M + H_3O^+ + e^-(M) \leftrightarrow 2M + H_2$$

(3) Tafel process (slow) :

$$H_{ads}M + H_{ads}M \leftrightarrow 2M + H_2$$

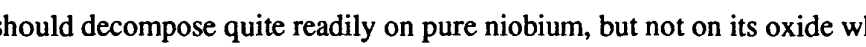
(4) absorption process, competing with (2) and (3) :



$$H_{ads}M \leftrightarrow H_sM$$

where H_{ads} represents hydrogen, in the atomic form, adsorbed on the surface of the metal, and H_s dissolved (= absorbed) under the surface of the metal.

In presence of very oxidizing species like NO_3^-, it is well known that the product of the reaction (2) is H_2O instead of H_2, a fact which explains why molecular hydrogen (H_2) release is not observed in presence of HNO_3. For instance, the global reaction (1) + (2) could write (5) :



$$H_{ads}M + 2H_3O^+ + e^-(M) + 2NO_3^- \leftrightarrow 2M + 3H_2O + 2NO_2$$

Process (4) is probably the main source of H interstitials. Molecular H_2 is less likely to be a source of dissolved hydrogen since it has to dissociate first, before diffusing inside the metal. H_2 should decompose quite readily on pure niobium, but not on its oxide which plays a protective role against H_2. On the other hand, oxide is not a barrier against atomic H. Of course, the composition and structure of the oxide layer, as well as the presence of other adsorbed species on it will have a great influence on the kinetics of this last reaction ; for instance halogen ions like F- or Cl- are known to depassivate the oxide layer and favours hydrogen dissolution [ref 9].

The external media (polishing solution) also plays an important role in the balance between the different reactions involved, because of its electrochemical properties. As shown in reference 9, cathodic polarization of the Nb surface can favor the absorption of H and precipitation of hydrides, while anodic polarization results in dissociation of the hydrides and formation of a new oxide layer. This can explain why electropolishing carried out in non oxidizing conditions (like in [ref 10]) leads to hydrogen evolution (H_2) and contamination (H), while anodized cavities seems to be less sensitive to 100K effect [ref 11].

Of course these reactions are quite idealistic. As shown by the GDL spectra, more complex reactions involving other chemical reactants can not be excluded, and it could explain the incorporation of phosphorus or carbon inside the material for instance. Moreover,

adsorption or absorption of these other reactants of the solution can influence the competition between the different processes involved, thus favouring or preventing the penetration of hydrogen.

2) Why is H concentrated near the surface of niobium ?

The next question that arise from these results is how and why the hydrogen keeps concentrated near the surface, even when samples are kept at room temperature for several weeks or months. Indeed, diffusion coefficients found in literature are very high [ref. 12, 13, 14, 15].:

$$D \sim 5.10^{-10}\ m^2.s^{-1} \quad \text{at } 300\ K$$

Using the approximation : $\sigma \sim 2\,(D \times t)^{1/2}$ one can estimate an average distance (σ) of a few millimeters travelled by an H in one hour. It should be obvious then, that any sample kept at room temperature more than a few hours should have a uniform hydrogen content.

Nevertheless attention must be drawn to the fact that these diffusion coefficients are often measured on polycrystalline high purity samples, with RRR ranging from 4000 to 6000. Evidence has been found of interaction of H with interstitials like O or N, following a trapping - detrapping mechanism which can lower D by a factor up to 100 [ref 12, 14, 15, 16]. (One surprising effect of this mechanism is that it seems to prevent hydride precipitation at low temperature [ref 14, 16], by stabilizing the α-phase structure at low temperature). The lowering of diffusion coefficient is anyway not important enough to explain the stay of hydrogen near the niobium surface.

One other well known phenomenon about H in metals is its tendency to interact with crystal defects like impurity atoms, grain boundaries, dislocations, etc...forming a "Cottrell cloud", where H concentrates and can even reach hydride precipitation limit [ref 9, 18, 19]. This kind of interaction is due to elastic stresses applied to the lattice, and adds a potential term to the Fick diffusion law :

$$j = -\,D.\mathrm{grad}(C) + C.\mathrm{grad}(\Delta W)/kT$$

(j = Hydrogen current, D = diffusion constant, C = hydrogen concentration,

ΔW = energy of interaction between H and a defect [ref 19])

This means that H is not really trapped, but it keeps concentrated near the defect in the same way the atmosphere is more dense near the surface of the earth than in high altitude : the air molecules are still free to move. Moreover ΔW, the energy of interaction between H and a trap defect is generally higher for an interface between two phases than with other defects like

isolated impurities or dislocations [ref 21] : $\Delta W_{interface} > \Delta W_{dislocation} > \Delta W_{isolated\ atoms}$. Of course, the surface of the metal, with its natural oxide layer acts as a peculiar case of this defect (Nb-Nb_2O_5 interface) ; moreover the thermodynamic surface parameters might also differ from the bulk ones : it is known that ΔH_s, the heat of solubilisation of H in Nb is more negative near the surface than in the bulk [ref 20]. These kinds of interaction are good candidates to explain the surface concentration of H in niobium at room temperature. Moreover, the local concentration of H could be much more than what is measured with most characterization techniques which integrate an appreciable portion of the surface and depth of the sample[7]. One can estimate that the local concentration, probably due to interaction with various defects, is high enough so that H might be in the form of niobium hydride even at room temperature.

Then, an explanation of the "100 K" effect could be the existence of a phase transition (between 100 and 200 K), between two phases of hydrides and not the precipitation (i.e. apparition) of an hydride : for instance the transitions $\alpha + \varepsilon \rightarrow \alpha + \eta$ at ~ 210 K, or $\alpha + \eta \rightarrow \alpha + \upsilon$ at ~ 140 K in the phase diagram presented in (fig. 5). The phase ε suspected in [ref 3] is a poorer candidate since under ~200 K it exists only for H/Nb ≥ 0.45, i.e. for very elevated concentration, and moreover it does not present any direct transition between 0 and 225 K (only the matrix undergoes a change : $\alpha + \varepsilon \rightarrow \eta + \varepsilon$ at ~ 210 K, $\eta + \varepsilon \rightarrow \upsilon + \varepsilon$ at ~180 K, and not the hydride precipitates of ε). In this case, the argument about the fast diffusion of hydrogen in niobium even at low temperature does not hold any more : H would be stabilized into the ε hydride form and should not diffuse any more in the range 0-225 K. Moreover, the "100 K" effect seems to disappear with an annealing between 165 K and 200-220 K, varying with experiments. This indicates that the local concentration in the hydride precipitates might correspond with a region of the phase diagram where transition temperature vary with H concentration, i.e. between 10% and 60% (fig. 5).

One another phase transition, for instance between two phases of niobium sub-oxide, could not be totally excluded as very few studies have been made at low temperature for Nb compounds except hydrides. But, due to its very small radius, ($r_{H^+} \sim 10^{-15}$ m), movements of hydrogen in the niobium matrix, even if it is about a few atomic radii (as it is generally the case in crystallographic phase transitions), would still be easier than for any other contaminants. Thus H is still the best candidate for being responsible of the "100K" effect.

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[7](An expérience performed at the CEA, in collaboration with the Laboratoire Pierre Süe, with a 30 µm side nuclear microprobe clearly showed up inhomogeneities in the distribution of hydrogen when displacing the microprobe along a path crossing several grain boundaries.

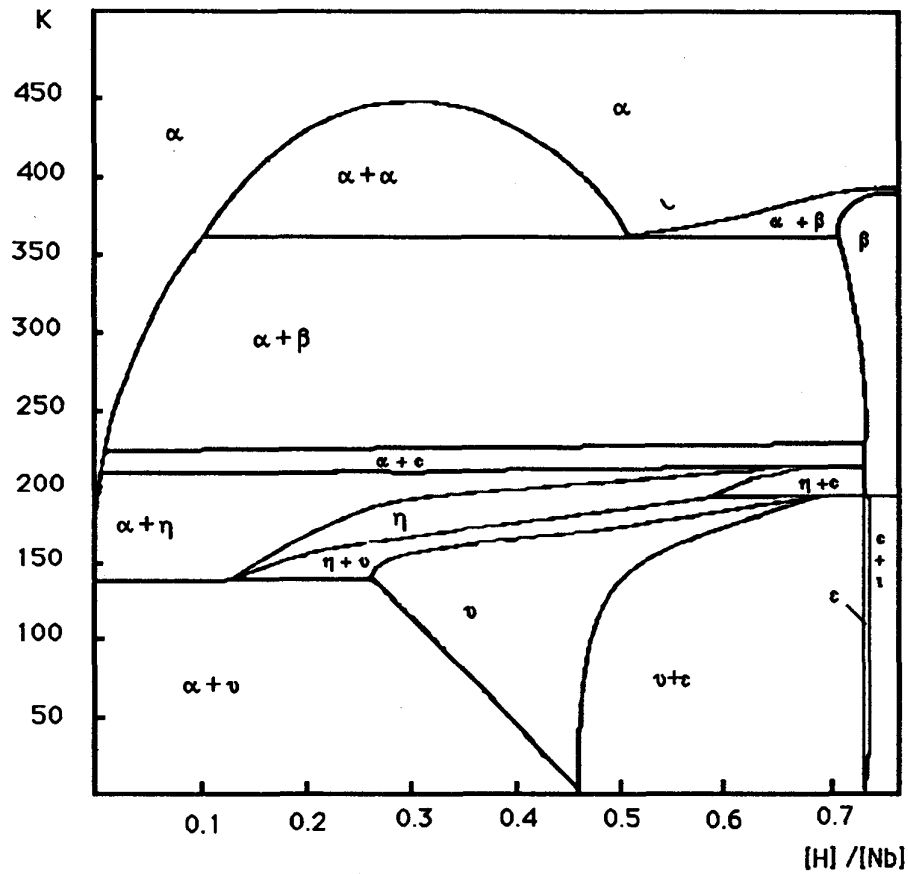

Fig.5- Phase diagram of the Nb-H system determined from static suceptibility measurements.
Ref : Kobler and Welter J. Less Comm. Met., 84, pp 225-235, (1982).

3) Differences between different treatments

All characterization techniques showed little difference between the samples which were subjected to various chemical treatments. In fact, the only difference was in the chemical composition of the mixture : HCl versus chemical polishing, and H_3PO_4 concentration of the polishing baths. On the other hand, the same type of niobium was used for all the samples, with the same conditions of temperature, agitation, rinsing, etc...This of course cannot pretend to mimic completely the various chemical treatments done in other laboratories.

Nevertheless, attention must be drawn to the existence of other contaminant of the surface than hydrogen. If the quantity of H is about the same in each sample, its way of chemical linking could be different. Studies based on electrochemical considerations are now on progress to determine what is the role of the various chemical reactants from the polishing baths : the contamination they bring, if they favour H penetration in the metal, and in which form.

Other studies, based on deformation of Nb samples are also on progress to determine if this can play a role in the distribution of hydrogen : indeed laboratories use different ways to prepare their cavities : hydroforming, stamping, spinning, and this could also explain the wide differences in results obtained at various places [ref 22].

IV) CURES

Literature gives indication about some treatments, either thermic or electrochemistry methods (including simple chemical polishing). Some of these are presently under experiment on cavities in different laboratories and will be noticed if results are available.

The most simple method consist to heat cavities a few hours above 1300°C in ultrahigh vacuum, or wrapped in yttrium, to prevent oxygen recontamination of the niobium. This treatment clears the metal from most of his interstitials and leads to recrystallization., thus a large increase of RRR is observed. These treatments have been tested and are fully effective [ref 23], but too expensive to be applied on large scale.

As seen at the beginning of this paper, moderate heating (≥ 600°C) is enough to get rid of hydrogen, but provokes a slight surface contamination (probably oxygen). Tests are now on progress to determine if heating at 300°C would be enough to get rid of hydrogen and to avoid modification of the oxide layer [ref 24]

The other way to produce hydrogen free cavities is to control it chemically, either with a polishing process which hinders hydrogen penetration, or with a treatment which suppresses the contamination layer. Two factors seem to influence this : the polarization of the niobium surface, and the existence of other contaminants which can promote hydrogen solubilization [ref 9].

As seen before, cathodic polarization of the surface (i.e. low electrochemical potential) favors hydrides formation, thus a good polishing process should take place at the highest potential as possible. This can be realized in theory by imposing a high potential with an electrode (i.e. electropolishing), or with the choice of highly oxidant species like NO_3^- in the solution. In both cases, potential conditions should stay compatible with good polishing conditions, i.e. high current or dissolution rate, which is the delicate practical point.

Most of the polishing and electropolishing baths for niobium use therefore a mixture of HF for its strong dissolution properties of niobium oxide and HNO_3 for its oxidant qualities (its role is also to regenerate the soluble form of niobium oxide). Other reactives : H_3PO_4, H_2O, H_2SO_4, glycerin, alcohol, etc...have mainly a role of buffer and/or complexant, and will

modify polishing rate [ref 25].

A mixture of one volume of HF and one volume of HNO_3 polishes cavities without inducing "100 K effect" [ref 26], but the niobium removal rate is very high even at low temperature (10-15 µm/mn at 0-5°C). A more promising mixture seems to be one volume of HF to nine volumes of HNO_3, given in [ref 22], the rate of which is approximately 1 µm/mn at 25°C (presently under experiment).

The same reference studies a method which consists in contacting niobium with another metallic element that has a low hydrogen overvoltage and is electrochemically cathodic to niobium in the same environment : platinum, palladium, gold, etc...Relatively small areas of contact, made by riveting or welding, are effective against hydrogen embrittlement in corrosive media like concentrated HCl [ref 25].

The same principle is used to keep very pure niobium : after an UHV treatment, a 1 µm thick layer of palladium is deposited on the oxide free niobium. This prevents hydrogen reabsorption from the residual vacuum, and moreover, catalyses hydrogen release through the palladium layer, with moderate heating (150°C) at atmospheric pressure. Samples with hydrogen content as low as 1 Atppm and RRR 4000-6000 have been prepared this way [ref 17 and ref herein].

This method has not been yet applied in polishing of cavities, but could be worthwhile if no other polishing mixture can easily be handled.

Of course, references 25 and 27 collect a large choice of polishing and/or electropolishing procedures, but a few of them take account of hydrogen contamination. If simple electrochemical arguments reveal themselves inadequate, testing all these processes on superconducting cavities might be rather fastidious !

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