H in Niobium: Origin And Method Of Detection

C.Z. Antoine, S. Berry

CEA,DSM/DAPNIA/Service des Accélérateurs, Cryogénie et Magnétisme, CE-SACLAY,
F-91 191 Gif-sur-Yvette Cedex

Abstract. Hydrogen is involved in the degradation of the quality factor of superconducting niobium cavities. Knowing better the origin of this contamination, as well as the behavior of hydrogen in the metal by proper means of detection can help in preventing this effect. The aim of this paper is to review some basis of the interaction of niobium with hydrogen sources, with emphasis on the most hazardous ones, and to detail some detection methods of interest for the SC RF community.

INTRODUCTION

Hydrogen has been recognized since long ago as being responsible for the degradation of the quality factor Q_0 observed in Nb RF cavities and called "Q–disease" [1-3]. Knowing better the physical and chemical properties of the Nb-H system can help us in preventing hydrogen penetration during cavity fabrication. Fortunately this system has been widely studied, on one hand to understand the particularly good corrosion resistance of Nb and on the other for hydrogen storage as niobium figures among metals able to accept and restitute a large volume of hydrogen even at room temperature. (For instance one can store five times more hydrogen in niobium than in the equivalent volume of liquid hydrogen). In both cases the prevalent role of the native oxide layer that always exists onto niobium has been put into evidence. Careful reviews of the literature help us to discover how hydrogen is brought inside niobium during the preparation stage of superconducting cavities. We will see in the following that it originates mainly from water and aqueous species and that contamination occurs principally during chemical and/or electrochemical polishing of niobium cavities. Then some indication of the way to prevent it, as well as the way to measure hydrogen inside niobium, will be given.

Chemical Polishing vs. Electropolishing

After their fabrication, the inner surface of RF cavities needs to be etched in order to remove damage layers and any surface contamination. The most common technique is BCP (buffered chemical polishing) with HF, HNO_3, H_3PO_4 1-1-1 to 1-1-4 in volume, developed for RF cavities at Stanford, Cornell or Wuppertal in the 80's. HF provides the F^- ions, which are able to complex Nb^{5+} ions and drive them into solution while NO_3^- ions act as an oxidant toward the $Nb°$ (metal) to transform it into Nb^{5+} ions

(oxidized). The role of H_3PO_4 (or any other buffer) is to change the viscosity and/or etching rate of the mixture. So chemical etching can be considered as a controlled corrosion situation, i.e. simultaneous oxidation of the metal and dissolution of the oxide. BCP has proven to re-establish Q–disease on heat-treated cavities [1].

Electropolishing was initially developed in Germany [4], and then extensively used at KEK (Japan) [5]. This technique has recently proved to improve achievable accelerating field of RF cavities [6,7], but is known to provoke heavy Q–disease. In this case, the etching takes place in a $HF-H_2SO_4$ solution, 15-85 in volume, and the oxidation of Nb° originates from an anodic polarization of the cavity (~8-10 Volts). F^- plays the same complexing role as in chemical etching. H_2SO_4 is a buffer with high viscosity, known to improve the surface state in many polishing "recipes".

Role Of The Oxide Layer

Bare metals easily absorb monatomic hydrogen, but niobium owes its corrosion resistance to the presence of a readily formed, adherent, passive oxide film. The oxide film is mainly composed of Nb_2O_{5-x}, plus some impurities incorporated from the external media. If it forms in pure water or in dilute aqueous solutions, the oxide is in the form of a thin compact film and the corrosion resistance is excellent [8,9]. This oxide layer is protective against H penetration as well as desorption as long as it keeps passive. Passivity is enhanced in oxidizing condition (either anodic polarization or presence of oxidizing species), while it is destroyed by cathodic polarization, or the presence of alkaline or halide species, especially F^- [10,11]. The Nb_2O_5 layer disappears above ~250°C, although some monolayers of oxygen always remains at the surface even under ultra high vacuum [12,13].

(A well-known way to get rid of this protective layer is to recover Nb with a thin layer of Ni [14], Pt [15] or Pd after a heat treatment under vacuum. This layer acts as a protection against oxidation and a catalyst towards H_2 dissociation [16], and allows reversible storage/desorption (hydrogen storage). Unfortunately, a metallic over-layer is not recommended for superconducting cavities!)

Origin Of The Hydrogen Contamination

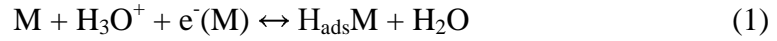One has to keep in mind that the hydrogen contamination inside the Nb is in the form of interstitial individual atoms. Thus, the molecule H_2 (gas) is not the only possible contamination source, and the species present inside aqueous solutions: H_2O, H^+, OH^-… are certainly better candidates.

Indeed, air contains less than $5.0 \ 10^{-5}$ % of H_2 and molecular hydrogen does not dissociate on oxide, although it does readily on bare metals (catalyzed process). Moreover, even if it is produced in larger amounts during electropolishing, this phenomenon occurs at the cathode, i.e. not directly in contact with the niobium surface.
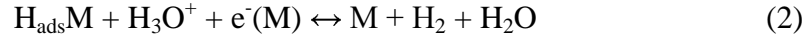
On the other hand the niobium oxide can be considered as amphoteric [8] and polar molecules like H_2O or H_3O^+ readily dissociates at its contact. During chemical polishing and electropolishing, which occur in concentrated acid mixtures, the presence of high concentration of H^+ directly affects hydrogen contamination.

The mechanisms of apparition of hydrogen during acidic processes are reviewed in details in [10]. Four types of reactions are involved and/or competing, and the effective pollution results from the balance between these different reactions:
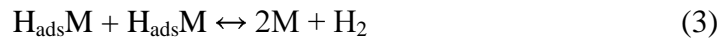
(1) Volmer process (fast):
$$M + H_3O^+ + e^-(M) \leftrightarrow H_{ads}M + H_2O \tag{1}$$

(2) Heyrovsky-Horiuti process (slow):
$$H_{ads}M + H_3O^+ + e^-(M) \leftrightarrow M + H_2 + H_2O \tag{2}$$

(3) Tafel process (slow):
$$H_{ads}M + H_{ads}M \leftrightarrow 2M + H_2 \tag{3}$$

(4) Absorption process, (slow) competing with (2) and (3):
$$H_{ads}M \leftrightarrow H_sM \tag{4}$$

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.

Process (4) is probably the main source of H interstitials. Molecular H_2 has to dissociate first before diffusing inside the metal and this process requires more energy.

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 the reaction (4):

- Halogen ions like F^- or Cl^- and/or cathodic polarization of the Nb surface are known to depassivate the oxide layer and favor absorption of H and precipitation of hydrides [10]. The presence of HF without a strong oxidant can explain why electropolished cavities are heavily charged with hydrogen. This phenomenon occurs when the cavity is in contact with the EP solution without bias (i.e. anodic polarization) [17].

- Oxidizing conditions or anodic polarization results in dissociation of the hydrides and formation of a new oxide layer. The presence of a strong oxidant (NO3-) explains why chemically polished cavities present less hydrogen up–take than electropolished ones. Anodized cavities also seem to be less sensitive to Q–disease [18].

- In presence of very oxidizing species like NO_3^-, 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 during chemical polishing, where the oxidizing species is brought by HNO_3.
  For instance, the reaction (2) could rewrite (5):
  $$H_{ads}M + 3H_3O^+ + e^-(M) + 2NO_3^- \leftrightarrow M + 5H_2O + 2NO_2 \tag{5}$$
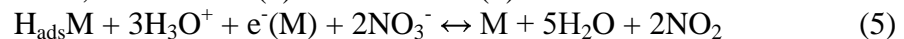
- H^+ is not able to diffuse directly through the oxide layer. Indeed, when the polar molecule H_2O is adsorbed on the niobium surface the dipole induces a field as high as $\sim 10^6$V/m [11]. This field promotes the diffusion of Nb^{5+} from the metal to the solution, and eases the diffusion of all the negative species inside the oxide layer until the oxide itself screens the electrical field. (i.e. when the oxide reaches 5-6 nm). This phenomena plays an important role during chemical polishing: unfortunately ionic species

(mainly Nb^{5+}) diffuse far more quickly than neutral ones through a thin oxide-like layer, and the "cleaning" is not that effective, although several 10µm of metal are etched [19].
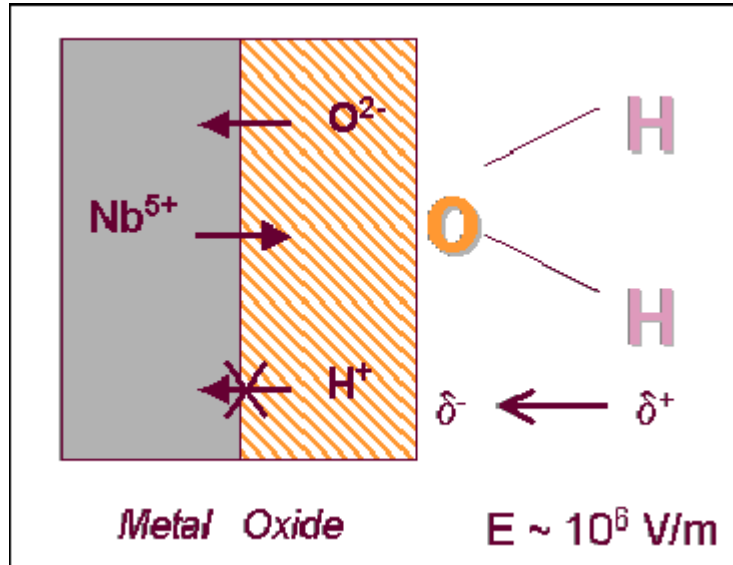
FIGURE 1. Field driven dissolution: in case of electropolishing (external applied field) as well as during chemical polishing, the diffusion of ionic species is about 10^6 faster than neutral atoms, because of the local electric field due to absorption of dipolar species.

SEGREGATION OF HYDROGEN AT SURFACE

Hydrogen contamination after a chemical polishing has been measured and is rather low: a few Wppm maximum in the bulk [1,20]. This concentration is clearly insufficient to generate hydride precipitates. Actually, the dramatic effect of this hydrogen contamination arises from the fact that hydrogen segregates near the niobium surface, i.e. precisely in the penetration depth region. In this region, concentration can reach several % [20,21].

A well known phenomenon about H in metals is its tendency to interact with crystal defects like impurity atoms, dislocations, grain boundaries, etc...forming a "Cottrell cloud", where H concentrates and can even reach hydride precipitation limit [10,22,23].

This effect is even more sensitive among very pure metals since fewer defects exist inside the lattice, and the surface remains the principal defect left. The interaction between the metal and interstitials is transferred via the elastic stresses applied to the lattice by the defects, and adds a potential term to the usual Fick diffusion law:

$$j = -D \cdot grad(C) + C \cdot grad(\Delta W)/kT \qquad (6)$$

(j = Hydrogen current, D = diffusion constant, C = hydrogen concentration, ΔW = energy of interaction between H and a defect [24])

In the case of H which has a very high mobility inside niobium, it 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, although they are sensitive to earth attraction. 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: $\Delta W_{interface} > \Delta W_{dislocation} > \Delta W_{isolated\ atoms}$ [25]. Of course, the surface of the metal, with its natural oxide layer, acts as a peculiar case of bi-dimensional defect (Nb-Nb_2O_5 interface). Note that similar phenomenon should also occur at grain boundaries, which constitute another bi-dimensional type of defects. 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. One can estimate that the local concentration is high enough so that H might be in the form of niobium hydride even at room temperature.

Then, an explanation of the Q–disease could be the existence of a phase transition (between 100 and 200 K), between two phases of hydrides [20].

HOW TO GET RID OF HYDROGEN

Once cavities are contaminated with hydrogen it should be very easy to make it disappear with a mild heat treatment. Nb hydrides dissociates over 100-150°C as long as [H]/[Nb] stays under 60%. But a baking is not sufficient to eliminate Q–disease [1,17] because the protective oxide layer remains until 250-300°C [16]. Moreover during any heat treatment, the degassing of the oven itself is generally predominant. Thus, the most efficient treatment seems to be an annealing of 2 hours about 750-800°C. It has several advantages: the degassing of the oven is fairly fast, and as the niobium re- crystallize at this temperature, the lattice present less defects afterwards. This improvement of the lattice quality has several advantages: the lattice is less sensitive to further H contamination, and the thermal conductivity at 2K is enhanced due to a better transmission of phonons. Nevertheless, this treatment is provisional: after several months exposed to air, the hydrogen amount near the surface is reconstituted, probably originating from humidity in the air (see figure 4 and [26]). As most of the time cavities are held under vacuum once installed inside an accelerator, this point is not very critical, provided that simple procedures (dry atmosphere, etc.) are held.

Cathodic protection has probably become the most widely used method for preventing the corrosion deterioration of metallic structures in contact with any forms of electrolytically conducting environments, i.e. environments containing enough ions to conduct electricity such as soils, seawater and basically all natural waters. Cathodic protection of the niobium by coating with Pd is also applied to increase the hydrogen uptake rate, with the coating providing the primary form of corrosion protection (avoiding the oxide film formation) [14,15]. If annealing is not possible, a very simple procedure of cathodic protection could be used during etching or electropolishing, i.e. contacting the metal to be protected from corrosion with a very small portion of a

more noble metal. This practical technique is very well known on tantalum, and there is some hints that it is also efficient with niobium with contacts made of Pt, or Pd [27].

AVAILABLE METHODS OF DETECTION

Too many methods of detection of hydrogen or its influence exist to be listed here. Not all of them are well adapted to RF cavities issues: i.e. to detect small concentration of H near metal oxide interface. Some of these techniques are very common (let's say "commercially available") while some need to be developed in contacts with specialized experts. Moreover, the ultimate efficiency of these methods might depend strongly on the samples state: for instance the depth resolution in profiling methods might be degraded by surface roughness, lateral diffusion of hydrogen, crystallographic orientation, etc… Some of the methods described hereafter are only applicable to thin foils or threads; some are relevant for very pure samples (RRR >5000) while other are effective only for heavily H charged samples. Some results might be partial, and more than one technique is general needed to be able to draw accurate conclusions.

Some experimental methods to investigate hydrogen-metal systems are reviewed in [28,29]. Many of the methods used to determine property changes must be first calibrated with an exactly known hydrogen concentration.

The usual concentration determination procedure is to start with a pure reference sample. This must be produced by proper high-temperature ultrahigh vacuum (UHV) degassing treatment [30]. An unknown amount of other impurities (C, O, N…) may cause serious errors. For instance, the characteristic volume change Δv is about twice as big for oxygen and nitrogen as for hydrogen. Thus, if the concentration is determined from the mass change of the sample, an impurity concentration of oxygen or nitrogen may appear as a hydrogen concentration more than ten times greater.

Table 1 summarizes the characteristics of the principal usable techniques for "normal" samples. More details can be found in the comments afterwards.

**TABLE 1. Analytical technique.**

Analytical technique	Signal detected	Detection limit	Depth resolution	Lateral resolution	Ref
Heat desorption /N_2	$\Delta\sigma_{therm}(N_2)$	100 at. ppm	global	-	
Electrical resistivity	id	>1 at%	global	-	[31]
Mass change	Mass	2.10^{-3} at%	global	-	[28]
SIMS	Secondary ions	10^{12}-10^{16} at/cm^2	5-30 nm (few at layers)	$1\mu m$	
TOF-SIMS	Secondary ions	10^8 at/cm^2	5 nm (1 at layer)	$0.15\mu m$	(a)
GDL	Emitted photons from ejected neutral atoms	qualitative		-	
ERDA or HFS	Elastically ejected H^+	0.1 at%	30-40nm	-	

(a) unpublished results

Surface methods

## *Secondary Ion Mass Spectroscopy (SIMS)*

Sample surface is eroded with an Ar^+ beam and the resulting secondary ions are analyzed with a mass spectrometer. Within dedicated facilities, with special care about ultrahigh vacuum, a very good depth resolution can be reached (some monolayers), with a sensitivity going below At ppm depending on which element. Lateral imaging is also possible with 1µm resolution. The sensitivity and the depth resolution can be further enhanced with TOF SIMS (Time-Of-Flight SIMS).
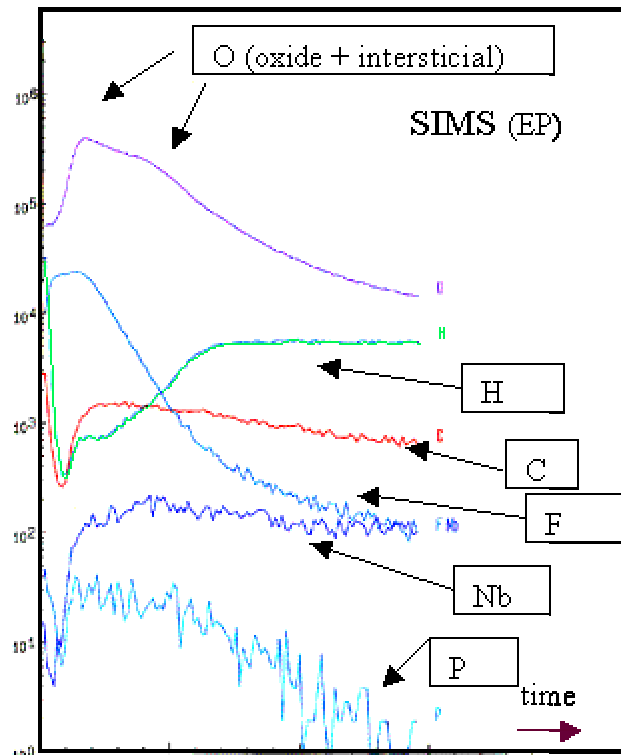
FIGURE 2. SIMS profiling of an electropolished Nb sample. On this spectra, one can clearly see that the oxygen peak is composite (oxide + intersticials), and that there is a depletion of hydrogen inside the "oxide". From other sources, it can be demonstrated that hydrogen is concentrated near the metal oxide interface

Emission Spectroscopy In A Glow Discharge Lamp (GDL)

This method is quite similar to the previous one: 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 rate and discharge voltage depend strongly on the general characteristics of the material (conductivity, roughness, etc.). Thus the results obtained by this technique are more qualitative than quantitative.
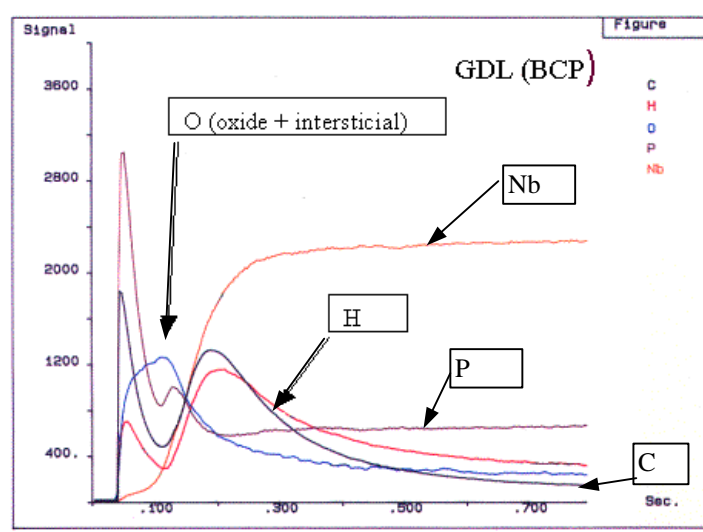
FIGURE 3. Glow discharge spectra of a chemically polished Nb sample. On this spectra one can distinguish superficial contamination (hydrocarbon, chemical residues) from a more internal one just behind the oxygen peak, i.e. at the oxide-metal interface.

Elastic Recoil Detection Analysis (ERDA) or H Forward Scattering (HFS)

A $^4He^+$ beam of a few MeV reaches the sample with grazing angle and ejects elastically H^+ ions of the niobium. A few *100* nm are explored by this way and the current resolution is *30-40* nm. It can be further reduced with special care to the detection method [32]. The sensitivity is ~0.1 At%. An analogous technique is applied to thin foils and the hydrogen is forward scattered through the foil.
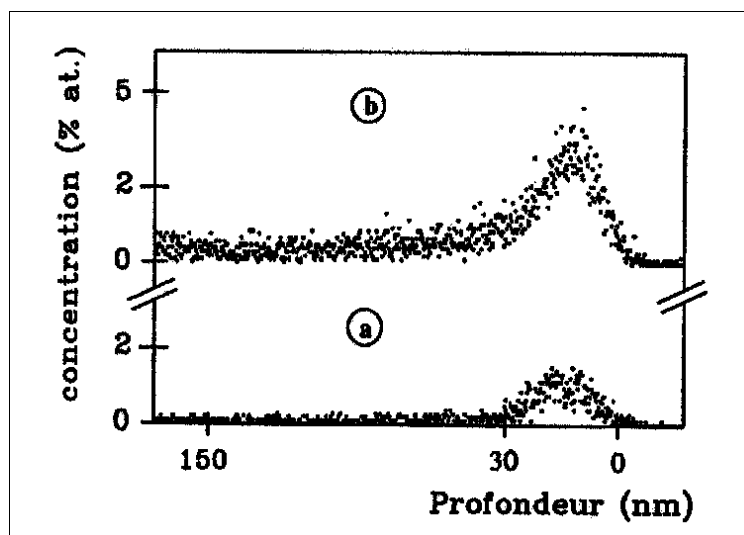
FIGURE 4. Hydrogen up–take with time: a = annealed sample, b = same sample after 18 month in air.

Resonant nuclear reactions also allow hydrogen profiling in solids, but with lesser sensitivity and depth resolution in the case of polycrystalline samples [33]. Better

depth and/or lateral resolution can be obtained with for instance monocrystalline films with small roughness [34].

Global methods

For large single-crystal samples the surface layer may be neglected, whereas for powder samples one may easily investigate only surface layers and thus have a large rather unknown error source.

Thermal Desorption / Gas Chromatography With Melting

The pressure increase during a high-temperature vacuum extraction of hydrogen is often used to determine the hydrogen content. Other gases are detected with the same sensitivity as hydrogen. As the influence of impurities is mainly within a surface layer (thickness of few microns), the accuracy of this method increases with decreasing surface to volume ratio of the sample. The emitted gas can be analyzed using a gas chromatography. In this method it is impossible to separate chemically bonded hydrogen from absorbed hydrogen.

A variant of this technique is a thermal desorption inside a gaseous carrier (nitrogen); the variation of the thermal conductivity of the carrier is influenced by the hydrogen amount desorbed by the sample. The sensitivity of the method is poor, and it is hardly possible to measure less than 100 At ppm (~1 W ppm), and usually high RRR niobium exhibit values of a few W ppm [1,17,20]. The value is an average of the hydrogen concentration in a bulk sample and includes hydrogen from the hydrocarbon contamination layer on the surface.

Mass Change Of The Sample

Measuring the mass change of the sample is indeed a widely used, fast and simple method to determine the concentration of dissolved hydrogen. As the influence of impurities is mainly within a surface layer (thickness of few microns), once again the accuracy of this method increases with decreasing surface to volume ratio of the sample.

Resistivity Relaxation

The high sensitivity and accuracy of the resistance measurement make this technique potentially useful for low concentrations of hydrogen. It must be recognized however, that the constancy of hydrogen-induced resistivity has been established only in a limited range of concentration and temperature (≥ 1 at. % above the room temperature in Nb). In fact, numerous experiments on substitutional impurities have established the influence of impurities on hydrogen-induced resistivity. The use of resistivity for the determination of the hydrogen concentration should, therefore, be made with some caution [23,31,35].

X rays and neutrons

Measuring The Relative Lattice Parameter Change By X-Ray Or Neutron Diffraction

Once a reliable calibration exists, measuring the relative lattice parameter change by x-ray or neutron diffraction or the relative length change indicates the hydrogen concentration. The penetration depth of the x-rays or neutrons in most cases easily exceeds the thickness of the perturbed surface layer. But this technique applies mainly to monocrystals with well-defined orientation.

Combining Relative Lattice Parameter Change And Huang Diffuse Scattering Intensity

A method has been applied by Metzger et al. [36] to cross check the hydrogen concentration of their samples. Combining relative lattice parameter change and Huang diffuse scattering intensity gives the interstitial concentration independent of any other information. The results agreed very well with the results from two other methods ($\Delta a/a$ and mass change).

Channeling Method [31]

The ion channeling technique makes use of the channeling motion of ions in a metal lattice and their reaction with hydrogen nuclei. In relatively simple structures, the location of the hydrogen nuclei can be determined by measuring the yields for several different directions of the incident ion beam.

Channeling experiments can be done only on single crystals, and those of very high quality (without mosaic angular spreading of >0.01° or any appreciable stress to avoid dechanneling of the incident ion beams).

The sensitivity of the channeling technique is rather high. In site-location experiments, practical limits on the hydrogen concentration, usually set by machine time considerations, are [D]/[M]~10^{-2} [H]/[M]~10^{-1}.

X-Rays Emission And Absorption

X-ray emission (and also UV photoemission) or absorption measures electronic properties (spectral measurement of Density Of States)

X-ray absorption near-edge structure (XANES) measurements were used to probe the H-charging-induced electronic structure changes of a 2400 Angstrom Nb film capped with Pd [37].

Neutron Scattering

Neutrons are scattered by nuclei, rather strongly by hydrogen isotopes among others. The diffraction of coherently scattered neutrons allows one to determine the

lattice location of hydrogen even in complex structures and, furthermore, to delineate the density distribution (i.e. the wave function) of hydrogen nuclei in the metal lattice.

Neutron spectroscopy is an appropriate method for the investigation of vibrations in the range of the acoustic and optic spectrum of the host lattice [31].

Diverse

Mechanical Relaxation

Mechanical relaxation methods are used to study the dynamics of bulk hydrogen [28,38,39].

If the defects are highly mobile like H in metals, they cause a diffusional relaxation in a strain gradient. The mechanical relaxation due to hydrogen atoms can be classified into:

- the dilatational relaxation caused by the long-range motion of hydrogen atoms (Gorsky effect)
- the shear relaxation caused by the short-range re-orientational motion (Snoek effect, internal friction)

One can measure the effect of hydrogen on the vibration modes of a torsion pendulum or bended samples. Usually they are made of Nb threads of high purity (RRR ~ 6000), covered by palladium, and then electrolytically charged with hydrogen by cathodic polarization.

NMR

Interaction of hydrogen with other impurities (O, N) inside niobium can be followed by NMR. This method is limited to thin foils (RF penetration depth ~some µm), and rather high concentration of H ($>10^{15}$ atoms in 1 µm thick). [40],[41].

CONCLUSION

Upon buffered chemical polishing, as well as for electropolishing, the hydrogen contamination originates mainly from adsorbed hydrogen on Nb generated from aqueous species. In case of electropolishing, anodic polarization protects the metal from H up take, and the contamination occurs when the niobium is in contact with the solution without bias, because HF tends to dissolve the passive oxide layer. During BCP, the presence of a strong oxidant (NO_3^-) reduces hydrogen up take.

The contamination could be further decreased by the use of cathodic protection, e.g. by contacting a small portion of the cavities with a piece of palladium.

Nb RF cavities can be cured from the H contamination by a simple heat treatment of a few hours at 750-800°C. Moreover this heat treatment is recommended because it improves several properties of interest: decrease of [H], reduction of crystalline defects (dislocations, grain boundaries…), improvement of the 2K thermal conductivity.

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