

# Analysis of Hydrogen Contamination of Superconducting Cavities

Xiaoping Cao\*

Deutsches Elektronen-Synchrotron DESY  
Notkestraße 85, 2000 Hamburg 52, Germany

## Abstract

According to the thermodynamic behaviors hydrogen can be dissolved in the niobium even niobium hydride can be formed below 1000K. A model of hydrogen diffusion in niobium is proposed. The internal stress caused by dissolved hydrogen can establish the steady state of hydrogen distribution. The hydrogen contamination during chemical polishing is inverse proportional to the doping rate of the chemical polishing acid and its thickness is  $\sim 10 - 30\mu$ . During annealing at lower temperature an area of saturation solid solution can be formed and its boundary can become the nucleation sites, then the precipitation on the cavity surface can be reduced when the cavity is cooldown.

## 1 Introduction

Hydrogen atoms occupy interstitial sites in metals and diffuse much faster than any other atoms. Hydrogen absorbed in niobium during chemical polishing and precipitated as niobium hydrides on the surface of the superconducting cavity will reduce severely the Q value of the cavity[1].

In this paper the thermodynamic behaviors of hydrogen in niobium are discussed. A model of hydrogen diffusion in niobium is proposed to discuss the hydrogen contamination during chemical polishing and niobium hydride precipitation on the surface. By using this model the experiments on hydrogen contamination of superconducting cavities [1] can be explained. Therefore, investigation on hydrogen behaviors in superconducting cavities will be advantageous to further improve the performance of the cavity.

## 2 Thermodynamic behaviors

The chemical potential of hydrogen dissolved in niobium can be represented as[2]

$$\mu_H = \mu_H^{NbH} + RT \ln(\gamma_H C_H) \quad (2.1)$$

\*on leave of absence from Department of Chemistry, Tsinghua University, P.R. China

where  $\mu_H^{NbH}$  is the chemical potential of hydrogen in niobium hydride;  $C_H$  is the concentration and  $\gamma_H$  is the activity coefficient of hydrogen which represents the interaction between solute and matrix.  $RT \ln \gamma_H$  can be regarded as the excess chemical potential

$$\Delta\mu_H \equiv RT \ln \gamma_H \equiv \Delta h_H - T \Delta s_H \quad (2.2)$$

where  $\Delta h_H$  and  $\Delta s_H$  are the excess enthalpy and entropy, respectively. If  $\mu_H^{NbH}$  is assumed to be zero, then the excess chemical potential  $\Delta\mu_H$  is equal to the hydrogen chemical potential in a unit concentration solid solution.

The chemical potential  $\mu_H$  decreases with decreasing hydrogen concentration  $C_H$ . Niobium hydride will be precipitated when  $\mu_N \geq \mu_H^{NbH}$ , so the maximum solubility of hydrogen in niobium  $C_H^{max}$  can be written as

$$C_H^{max} = \frac{1}{\gamma_H} = \exp\left(-\frac{\Delta\mu_H}{RT}\right) \quad (2.3)$$

The chemical potential of hydrogen gas can be written as

$$\frac{1}{2}\mu_{H_2} = \mu_H^{NbH} + \frac{1}{2}RT \ln P_{H_2} + \frac{1}{2}\Delta\mu_{H_2} \quad (2.4)$$

According to Nb-H phase diagram[4],  $\beta-NbH$  exists below 360K, so the niobium hydride will be precipitated when  $\frac{1}{2}\mu_{H_2} \geq \mu_H^{NbH}$  and  $T \leq 360K$ . The maximum partial pressure of hydrogen can be written as

$$P_{H_2}^{max} = \exp\left(-\frac{\Delta\mu_{H_2}}{RT}\right); \quad T < 360K \quad (2.5)$$

The excess chemical potentials depend on the units of concentration and pressure of hydrogen. In this paper the units of concentration  $C_H$  and pressure  $P_{H_2}$  are *wppm*( $\mu gH/gNb$ ) and *mbar*, respectively. The excess chemical potentials measured by experiments[2] are:

$$-\Delta\mu_H = 11240 - 89.05T(J/mol) \quad (2.6)$$

$$-\frac{1}{2}\Delta\mu_{H_2} = 49530 - 65.69T(J/mol) \quad (2.7)$$

Here  $-\Delta\mu_H$  can be regarded as the chemical potential of NbH from dissolved hydrogen(1wppm) and niobium;  $-\frac{1}{2}\Delta\mu_{H_2}$  the chemical potential of NbH from hydrogen gas(1 mbar) and niobium. The maximum solubilities and

Table 1: The maximum hydrogen solubilities and pressures

T(K)	350	300	250	200	150
$C_H^{max}$	941	494	201	52	5.5
$P_{H_2}^{max}$	$1 \cdot 10^{-8}$	$4 \cdot 10^{-11}$	$1 \cdot 10^{-15}$		

Units:  $C_H^{max}$  (wppm);  $P_{H_2}^{max}$  (mbar)

pressures of hydrogen are presented in Table 1. The partial hydrogen pressure in atmosphere is about  $10^{-4}$  mbar and it can reach  $10^{-10}$  mbar in an ultra-high-vacuum chamber in which  $H_2$  is the mainly residual gas. When the vacuum pumps are shut off,  $H_2$  pressure increase for a transient period to  $10^{-6} - 10^{-7}$  mbar[3]. The niobium hydride will be stable thermodynamically below room temperature even in ultra-high-vacuum chamber. From experiments[1] the hydrogen contamination only concentrates on the niobium surface so that the dynamic behavior of hydrogen in niobium must be considered.

The hydrogen contamination in niobium can be removed by vacuum heat treating. From equations (2.1) and (2.4), i.e.,  $\Delta\mu_H = \frac{1}{2}\Delta\mu_{H_2}$ , we can get

$$\frac{P_{H_2}}{C_H^2} = \exp\left(-\frac{9211}{T} - 5.62\right) \quad (2.8)$$

To remove hydrogen in niobium the temperature should be higher than 1000K, e.g.,  $P_{H_2}/C_H^2 = 3.6 \cdot 10^{-7}$ ,  $T = 1000K$  and  $P_{H_2}/C_H^2 = 1.7 \cdot 10^{-6}$ ,  $T = 1200K$ , so the hydrogen concentration can be less than 1wppm under vacuum heat treatment.

In order to study hydrogen contamination during chemical polishing and hydride precipitated successively on the niobium surface we must further investigate the diffusion behaviors of hydrogen in niobium.

### 3 Diffusion model

Dissolved hydrogen can cause the niobium lattice to expand[4]:

$$\Delta a/a = 4.72 \cdot 10^{-4} / \%H/Nb$$

Thus, the internal stress caused by the dissolved hydrogen can act as diffusion barriers, which can establish the steady state of hydrogen distribution. These induced excessive elastic stresses may lead to plastic deformation and cracks especially at dislocations and grain boundaries.

The driving force for diffusion is a chemical potential gradient. From (2.1)

$$\frac{\partial\mu_H}{\partial x} = \frac{RT}{C_H} \left(1 + \frac{C_H}{\gamma_H} \frac{\partial\gamma_H}{\partial C_H}\right) \frac{\partial C_H}{\partial x} \quad (3.1)$$

The current density  $j_H$  can be written as

$$j_H = -M_H \frac{\partial\mu_H}{\partial x} = -D_H^* \frac{\partial C_H}{\partial x} \quad (3.2)$$

with  $M_H$  the mobility and  $D_H^*$  the chemical diffusion coefficient. Substituting (3.2) into (3.1), we get

$$D_H^* = D_H \left(1 + \frac{C_H}{\gamma_H} \frac{\partial\gamma_H}{\partial C_H}\right) \quad (3.3)$$

where

$$D_H = \frac{RT}{C_H} M_H$$

is the trace diffusion coefficient ( $C_H \sim 0$ ), which can be measured by experiment.

The maximum solubility of hydrogen in niobium is very small below room temperature (Table 1), so we can expect that the interaction between hydrogens during saturation is very strong. From (2.3),  $\gamma_H = (C_H^{max})^{-1}$ , thus

$$\frac{\partial\gamma_H}{\partial C_H} = -(C_H^{max})^{-2}; \quad C_H \sim C_H^{max} \quad (3.4)$$

then the chemical diffusion coefficient

$$D_H^* = D_H \left(1 - \frac{C_H}{C_H^{max}}\right) \quad (3.5)$$

Hydride and solid solution can coexist during saturation ( $C_H = C_H^{max}$ ). The hydrogen concentration on phase boundaries is discontinuous, so the chemical diffusion coefficient must be zero.

$C_H^{max}$  is very small when temperature is below room temperature, so we can expect that the interaction between hydrogen ( $\partial\gamma_H/\partial C_H$ ) may be constant when  $C_H < C_H^{max}$ .

If  $C_H > C_H^{max}$ , then  $D_H^* < 0$ . It means that the hydrogen will diffuse from low concentration to high concentration in the super-saturated solution. This chemical diffusion coefficient (3.5) can be used to describe the segregation process (pre-precipitation). The segregation process can be accelerated since not only the concentration gradient but also the chemical diffusion coefficient can increase with time.

The trace diffusion coefficient  $D_H$  and  $C_H^{max}$  decrease exponentially with temperature, thus  $D_H^*$  during supersaturation is nearly independent of temperature. Therefore, the segregation from super-saturated solution will develop very rapid even at very low temperature. This is agreement with the experiments[6].

According to Nb-H phase diagram[4],  $\epsilon - Nb_4H_{3-x}$  will be precipitated from super-saturated solution when  $T < -70C$ . The hydrogen concentration in  $\epsilon - Nb_4H_{3-x}$  is about 7795 wppm. When hydrogen concentration is near to this value, the chemical diffusion coefficient must re-approach to zero and the equation (3.5) is invalid.

The density of niobium is  $8.55g/m^3$  and that of  $\epsilon$  is  $\sim 8.72g/m^3$ , so the volume will be reduced during precipitation. This will cause to form dense dislocations with prismatic loop around hydride particles.

The internal stress may increase during segregation, but will be relaxed during precipitation, so the amount of niobium hydride precipitated on the niobium surface may mainly depend on the segregation process. The nucleation can be formed during segregation.

Therefore, we can use the chemical diffusion coefficient (3.5) to discuss the hydrogen contamination during chemical polishing and hydrogen segregation.

## 4 Hydrogen contamination

Under the influence of internal stress caused by the dissolved hydrogen, the steady state can be established in which the hydrogen current density in niobium  $j_H$  is equal to the doping rate of the chemical polishing acid  $v_H$ :

$$j_H = -D_H \left(1 - \frac{C_H}{C_H^{max}}\right) \frac{\partial C_H}{\partial x} = v_H \quad (4.1)$$

The boundary condition  $C_H(x=0) = C_H^{max}$ , then

$$C_H(x) = C_H^{max} - \sqrt{\frac{C_H^{max} v_H x}{D_H}} \quad (4.2)$$

and the maximum diffusion depth

$$x_{max} = \frac{C_H^{max} D_H}{v_H} \quad (4.3)$$

The amount of hydrogen content

$$AH = \int_0^{x_{max}} C_H(x) dx = \frac{1}{3} x_{max} C_H^{max} \quad (4.4)$$

The chemical polishing is highly exothermic. The temperature gradient can affect the temperature distribution. From (2.1)

$$-\frac{\partial \mu_H}{\partial T} = \Delta s_H - R \ln C_H \quad (4.5)$$

If  $\partial \mu_H / \partial T = 0$ ,

$$C_H^{cr} = \exp\left(\frac{\Delta s_H}{R}\right) \sim 4.5 \cdot 10^4 \text{ wppm}$$

Thus, when the hydrogen concentration is smaller than  $C_H^{cr}$ , the hydrogen will move to high temperature under the temperature gradient. Therefore, under the effect of temperature gradient the hydrogen depth penetrated into niobium  $x_{max}$  can be further reduced.

If  $x_{max} = 20 \mu$ ,  $D_H \sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $C_H^{max} = 500$  wppm, then

$$v_H = \frac{D_H \cdot C_H^{max}}{x_{max}} \sim 2.5 \text{ cm} \cdot \text{wppm} \cdot \text{s}^{-1}$$

If the thickness of the sample is 2mm, then the average hydrogen content is  $\sim 3$  wppm.

In chemical polishing the hydrogen contamination (4.4) is proportional to  $(C_H^{max})^2$ ,  $D_H$  and inverse proportional to  $v_H$ .  $C_H^{max}$ ,  $D_H$  and  $v_H$  usually increase with temperature and can be respectively represented as

$$C_H^0 \exp\left(-\frac{E_C}{RT}\right), D_H^0 \exp\left(-\frac{E_D}{RT}\right), D_T^0 \exp\left(-\frac{E_T}{RT}\right)$$

Their mainly changes may happen at different temperature ranges because of their different activation energies.

The binding energy between oxygen and niobium is very large. The enthalpy of NbO from oxygen gas and niobium is  $\sim -416070 \text{ J mol}^{-1}$  [2], and the enthalpy of NbH is only  $\sim -49530 \text{ J mol}^{-1}$  (2.7), so the oxide layer will exist on the niobium surface below 1000K and its thickness is  $\sim 2 - 6 \text{ nm}$  [5]. This oxide layer can act as the barriers for hydrogen diffusion, but it can not completely prevent the hydrogen diffusion. The experiments [5] show that the oxide layer grows faster when  $OH^-$  ion exists in solution. We can expect that the  $OH^-$  ion will be beneficial to form (OH) in niobium, so it will accelerate the growth of oxide layer and cause the layer positive charging [5].

The etching process can be expected as the hydrogen must first diffuse into the oxide layer, then  $F^-$  can also diffuse into and cause the niobium dissolved in acid. Because the enthalpy of niobium fluoride is very large, this chemical reaction is exothermic.

In water chemical polishing [1] (WCP:  $HF : HNO_3 : H_2O = 1 : 1 : 5$ ) from  $10 - 40^\circ \text{C}$  the removal rate increases and the hydrogen contamination decreases. Above  $40^\circ \text{C}$  the removal rate and hydrogen contamination increase acceleratively.

At low temperature ( $10^\circ \text{C}$ ), the oxide layer is more stable because of  $OH^-$ , so the etching rate and doping rate of hydrogen are lower, then the hydrogen contamination is higher. When temperature increases, the concentration of  $OH^-$  will decrease and hydrogen activity increase, then etching rate increases and hydrogen contamination decreases. When temperature is larger than  $40^\circ \text{C}$  the diffusion current will increase so rapidly that the internal stress can not be accumulated sufficiently especially on the dislocations or grain boundaries. Thus at high temperature, the grain boundary etching and dislocation pitting may happen.

In buffered chemical polishing (BCP;  $HF : HNO_3 : H_3PO_4 = 1 : 1 : 4$ ) [1] the oxide layer will still exist on the niobium surface because of the concentrated nitride acid. The doping rate is lower because of high viscosity of the  $H_3PO_4$ , then the hydrogen contamination may be larger. There is no  $OH^-$  in BCP, so (OH) does not exist in the oxide layer, thus there is no decrease of hydrogen contamination with in some temperature range.

It is very interesting to note that the prevention of hydrogen contamination mainly depends on hydrogen themselves. In some condition the hydrogen contamination may become severe if the hydrogen doping rate is very small.

## 5 Segregation and precipitation

After the chemical polishing at room temperature a 2-6 nm oxide layer and 10-30  $\mu$  depth of hydrogen contamination may be exist on the niobium surface.

The hydrogen distribution (4.2) can be rewritten as

$$C_H^T(x) = a^T - \sqrt{b^T x} \quad (5.1)$$

In the above-mentioned example:  $T=300\text{K}$ ,  $x_{max} = 20 \mu$ ,

$a^T = 500 \text{ wppm}$ ,  $b^T = 12500(\text{wppm})^2 \cdot \mu^{-1}$  and total hydrogen content  $AH=3333.3 \text{ wppm} \cdot \mu$ .

The solubility limit decreases rapidly with the temperature (Table 1), so under the operation of the cavity at 4.2K the depth of  $\epsilon - Nb_4H_3$  can reach  $0.4\mu$  if all hydrogen were precipitated on the surface. The  $R_s$  of  $\epsilon - Nb_4H_3$  is  $\sim 15m\Omega$ [7] and the effective skin depth is  $\sim 0.6\mu$ , thus the Q value of the cavity can be reduced sharply. The field penetration at superconducting state is  $\sim 40nm$ , so only the NbH precipitated on the surface can affect the performance of the cavity.

If we keep the cavity at lower temperature, e.g. 250K, then hydrogen will be re-distributed. At 250K,  $C_H^{max} \sim 200 \text{ wppm}$  (table 1). From (5.1) we get

$$C_H^{300K}(x = 7.2\mu) = a^{250K} = 200 \text{ wppm}$$

When  $x < 7.2\mu$ ,  $C_H > C_H^{max}$ , then  $D_H^* < 0$  and segregation can happen i.e. the hydrogen content above 200 wppm ( $720 \text{ wppm} \cdot \mu$ ) will be precipitated on the surface, thus a saturation area ( $x < 7.2\mu$ ) can be formed.

When  $x > 7.2\mu$  and near  $7.2\mu$ ,  $C_H \sim C_H^{max}$ , then  $D_H^* \sim 0$  i.e.  $j_H \sim 0$ , thus under the internal stress the hydrogen concentration near  $7.2\mu$  will be reduced

If the total hydrogen content ( $x > 7.2\mu$ ) maintain constant, then steady state of hydrogen distribution at 250K can be represented as

$$C_H^{250K}(x) = \begin{cases} 200 & x < 7.2 \\ 200 - \sqrt{2272.7(x - 7.2)} & 7.2 < x < 24.8 \end{cases} \quad (5.2)$$

This hydrogen distribution (5.2) have two large gradients at  $x=0$  and  $x=7.2\mu$ , respectively. These gradients can approach infinity if steady state is reached. It may take very long time to reach steady state because the chemical diffusion coefficient is very small.

When the cavity is finally cooldown to 4.2K, the segregation at  $x=0$  and  $x=7.2\mu$  can happen and these location can become the nucleation sites of the precipitations. In this case only  $1440 \text{ wppm} \cdot \mu$  hydrogen are precipitated on the surface and other  $1893.3 \text{ wppm} \cdot \mu$  are precipitated at the layer  $x = 7.2\mu$ .

From this example, if we keep the cavity at higher temperature then cooldown, the precipitation on the surface will be further reduced.

Rinsing at temperature  $20^\circ C$  for several hours may reduce the precipitation on the surface, thus this can explain why the Q value is large at the first cooldown.

From the experiment[4], the precipitation were sub-micron size particles with dense prismatic loop dislocations. When the specimen was warmed again, these particles were redissolved but some dislocation skeletons remained. Cooling again below the solvus, these dislocation skeletons often provided nucleation sites for the precipitating hydrogen. This is also a reason to explain that the Q value degrades after successive cooldown.

In this paper the analysis of the hydrogen behaviors is mainly concentrated on the steady states. In order to find

the optimum condition for the cavity it is necessary to do transient analysis. To establish the transient model depends on further investigations and experiments.

## 6 Acknowledgments

This work is based on the papers[1,7], so many thanks are due to these authors. The author also thanks Dr. K.Asano for providing a lot of references and their works in KEK.

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