Improved oxygen diffusion model to explain the effect of low-temperature baking on high field losses in niobium superconducting cavities

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Radio-frequency (rf) superconducting cavities made of high purity niobium are widely used to accelerate charged particle beams in particle accelerators. The major limitation to achieve rf field values approaching the theoretical limit for niobium is represented by “anomalous” losses which degrade the quality factor of the cavities starting at peak surface magnetic fields of about 100 mT, in the absence of field emission. These high field losses are often referred to as Q drop. It has been observed that the Q drop is drastically reduced by baking the cavities at 120 °C for about 48 h under ultrahigh vacuum. An improved oxygen diffusion model for the niobium-oxide system is proposed to explain the benefit of the low-temperature baking on the Q drop in niobium superconducting rf cavities. The model shows that baking at 120 °C for 48 h allows oxygen to diffuse away from the surface, and therefore increasing the lower critical field towards the value for pure niobium. © 2006 American Institute of Physics. [DOI: 10.1063/1.2220059]

Over the last few years, particle accelerators rely more and more often on superconducting cavities to efficiently accelerate charged particle beams. Superconducting cavities are commonly operated in the TM_{010} mode and their performance is characterized by the dependence of the quality factor Q_0 on the accelerating field E_{acc} (excitation curve) or on the peak surface fields (electric or magnetic). The quality factor $Q_0 = \omega U/P$ is defined as the ratio between the cavity stored energy (U) and the power dissipated in the cavity walls in one rf radian (P/ω). The surface resistance of the cavity material is inversely proportional to the quality factor, the proportionality factor G given by the cavity geometry and the excited mode.

The accelerating field is defined as the ratio of the accelerating voltage V_{acc} (ratio of energy gained by a particle going through the cavity to the particle's charge) and the cavity length. The peak surface electric (E_p) and magnetic (B_p) fields are proportional to the accelerating field by a coefficient which depends on the cavity geometry and the excited mode.

The excitation curve of a superconducting cavity, made of bulk niobium, in the gigahertz range shows a rapid decrease of Q_0 starting at B_p of approximately 100 mT, in the absence of field emission, as schematically shown in Fig. 1. These enhanced losses, referred to as Q drop, limit the maximum accelerating field of the cavities to about 25 MV/m. Several years ago it was found that *in situ* low-temperature (100–150 °C) baking of the cavity can contribute a strong reduction of the Q drop and an improvement of the maximum accelerating field of about 10%–20%.^{1,2}

Surface analysis studies^{3–5} on niobium samples and measurements on niobium cavities⁶ show that during bakeout a decomposition of the natural oxide (Nb_2O_5) layer into metallic suboxides (NbO and NbO_2) and oxygen diffusion towards the bulk are initiated. The other most common impurities in niobium have diffusion constants, between 100 and 150 °C, which are many order of magnitudes too small⁷

(carbon and nitrogen) or too high⁸ (hydrogen) to explain the observed modifications in the niobium surface up to a depth of about 100 nm (the penetration depth of the rf fields in Nb is ~ 40 nm).

An estimate of the concentration profile of interstitial oxygen in niobium after baking had been done by solving the diffusion equation in one dimension. In one approach,⁹ the oxide layer is considered an infinite source of oxygen, so that the concentration at the niobium-oxide interface is always equal to the solubility limit. In another approach,¹⁰ the oxygen contribution from the oxide layer is neglected and the concentration at the niobium-oxide interface decreases for longer baking time and higher temperatures.

We propose in the following an improved model where we take into account both contributions from the interstitial oxygen initially present at the niobium-oxide interface and from the decomposition of the natural niobium pentoxide layer. The diffusion equation for the oxygen concentration in niobium $c(x,t)$ is given by

FIG. 1. Typical excitation curve of a superconducting cavity made of bulk niobium before and after baking.

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$$\frac{\partial c(x,t)}{\partial t} = D(T) \frac{\partial^2 c(x,t)}{\partial x^2}. \quad (1)$$

Due to the linearity of the equation, it is possible to consider the contribution of the two sources (oxide layer and interstitial oxygen) independently and then add the two solutions to obtain $c(x,t)$.

By heating niobium in ultrahigh vacuum between 100 and 400 °C, the niobium pentoxide decomposes according to the following reduction sequence;^{3–5}

and the dissolution process is independent of the initial oxide thickness. The overall reduction rate k_{ox} is given by

$$k_{\text{ox}}(T) = A e^{-E_d/RT}. \quad (2)$$

Measurements with x-ray photoelectron spectroscopy (XPS) at 170 and 210 °C yield the following values for the frequency factor¹¹ A and the activation energy¹² E_a : $A \approx 3 \times 10^9$ 1/s and $E_a \approx 135$ kJ/mol. It was also determined that the reaction is of first order,⁴ so that the amount of oxygen produced during the baking C_0 is given by

$$C_0(t, T) \propto 1 - e^{-k_{\text{ox}}(T)t}. \quad (3)$$

We think that Eq. (2) with the indicated values of the parameters is sufficiently accurate to describe the source term, since the residual gas analysis of the XPS chamber showed no oxygen present, which could otherwise cause additional oxide growth. Furthermore, physisorbed gases will desorb upon heating, which makes the chances of additional oxide growth even smaller.¹¹ The partial pressure for oxygen during a study on baking of superconducting cavities between 90 and 180 °C reported by the author in a previous article⁶ is about 10^{-9} mbar. This corresponds to a sticking coefficient for oxygen on oxidized niobium of less than 10^{-15} ; therefore the oxygen pickup during baking can be neglected.¹³

The diffusion coefficient of oxygen in niobium in the range of 100–150 °C is given by⁹

$$D(T) = 0.0138 e^{-111\,530/RT} \text{ (cm}^2/\text{s)}, \quad (4)$$

where T is the temperature in kelvin and R is the molar gas constant in J/(mol K). The one-dimensional diffusion equation which includes a time- and temperature-dependent source is given by

$$\frac{\partial u(x,t)}{\partial t} = D(T) \frac{\partial^2 u(x,t)}{\partial x^2} + q(x,t,T), \quad (5)$$

where $u(x,t)$ represents the oxygen concentration. $q(x,t,T)$ is the source term given by

$$q(x,t,T) = u_0 k(T) e^{-k(T)t} \delta(x). \quad (6)$$

The exponential time dependence is due to the first-order reduction kinetic and the source is concentrated at the niobium-oxide interface at $x=0$. u_0 is the total amount of oxygen per unit area from the Nb_2O_5 decomposition. Equation (5) can be solved by Fourier transformation and the solution is given by the following function:

$$u(x,t) = \frac{u_0}{\sqrt{\pi D(T)}} \int_0^t \frac{k(T) e^{-k(T)s}}{\sqrt{t-s}} e^{-x^2/[4D(T)(t-s)]} ds. \quad (7)$$

Besides the diffusion of oxygen generated by the dissociation of the oxide layer, the diffusion of the interstitial oxygen

FIG. 2. Oxygen concentration as function of depth obtained from BCS surface resistance measurements (Ref. 2) and calculated with Eq. (10) with $T=145$ °C and $t=45$ h.

initially present at the niobium-oxide interface needs to be considered. The diffusion equation for the oxygen concentration $v(x,t)$ is given by

$$\frac{\partial v(x,t)}{\partial t} = D(T) \frac{\partial^2 v(x,t)}{\partial x^2}, \quad v(x,0) = v_0 \delta(x). \quad (8)$$

The total amount of oxygen per unit area v_0 was measured to be approximately 10 at. % nm.¹⁴ The solution of Eq. (8) is the following Gaussian distribution:

$$v(x,t) = \frac{v_0}{\sqrt{\pi D(T)t}} e^{-x^2/[4D(T)t]}. \quad (9)$$

The total oxygen concentration $c(x,t)$ is given by the sum of the two solutions given by Eqs. (7) and (9),

$$c(x,t) = u(x,t) + v(x,t). \quad (10)$$

Due to the lack of accurate quantitative data on the total oxygen contribution from the oxide layer (u_0), we estimate the scaling factor u_0 from a comparison between Eq. (10) and the oxygen concentration calculated from depth measurements of the Bardeen-Cooper-Schrieffer (BCS) surface resistance of a superconducting cavity baked at 145 °C for 45 h (Refs. 2 and 9) (Fig. 2). u_0 is found to be of the order of 1 at. % μm .

A calculation of the oxygen concentration at the niobium-oxide interface ($x=0$) with Eq. (10) for baking at different temperatures for 48 h (Fig. 3) shows that there is a minimum in the temperature range of 120–150 °C. At lower temperatures the oxide layer does not dissociate significantly and the main contribution comes from the interstitial oxygen originally present, while at higher temperatures the concentration at the interface increases due to stronger oxide dissociation. At temperatures above 200 °C, the diffusion is faster than the oxygen production, so that the concentration at $x=0$ starts to decrease again.

The oxygen diffusion model discussed above can be linked to the Q drop and the baking effect in superconducting niobium cavities by considering the role of impurities on the lower critical field of niobium (B_{c1}). A reduction of B_{c1} and of the surface barrier in Nb due to interstitial oxygen was clearly measured by Van der Mey *et al.*¹⁵ In agreement with

FIG. 3. Oxygen concentration at the niobium-oxide interface ($x=0$) as function of baking temperature. The functions v and u represent the contribution due to the interstitial oxygen originally present and as a result of the oxide decomposition, respectively.

these results, Koch *et al.* measured an increase of the Ginzburg-Landau parameter (κ_{GL}) due to higher interstitial oxygen content.¹⁶ We propose that the very high concentration (≈ 10 at. %) of interstitial oxygen in the 1 nm layer at the niobium/oxide interface may reduce the surface B_{c1} by changed boundary conditions and therefore yields enhanced rf losses. (An oxygen concentration of 0.25 at. % decreases the thermodynamic critical field of Nb at 2 K to $B_c = 172$ mT while increasing k_{GL} to about 1.6.¹⁶ This corresponds to $B_{c1} = 100$ mT, as calculated with the Ginzburg-Landau theory.) The subtlety of baking at optimum temperature and time could be the dilution of oxygen over lengths greater than 40 nm by diffusion. This model shows that, even though the total oxygen concentration in Nb is increased by baking, if the baking temperature is below 150 °C, the main effect is the reduction of the highly contaminated region at the metal/oxide interface (Fig. 3). In agreement with these hypotheses are recent results¹⁷ showing that the baking effect on the Q drop is limited to changes in a 20 nm depth from the surface. Secondary ion mass spectroscopy (SIMS) measurements on samples show that the oxygen concentration up to that depth is reduced by baking.

Measurements on polycrystalline niobium cavities prepared by electropolishing show, on average, a higher onset field for the Q drop than cavities prepared by buffered chemical polishing (BCP).¹⁸ Cavities prepared with BCP have a rougher surface than those prepared by electropolishing and this could also reduce the surface barrier.¹⁹

The presence of interstitial oxygen concentrations well above the estimated solubility limit, as found in Ref. 14, might cause some precipitation into suboxides by baking and

this effect was not considered in the simplified model proposed in this letter. Topological effects, such as grain boundaries, where the diffusion parameters could be significantly different from the ones we used, are also neglected in this model, due to the lack of experimental data. More accurate quantitative measurements of the kinetic of the oxide dissociation are auspicious to improve the accuracy of this model. Also, it is necessary to find a clear experimental evidence for fluxons in the niobium surface at high rf fields and to clarify their nature.

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