

Calculation of diffusion profiles of Nitrogen in Niobium to investigate the surface concentration after nitrogen treatment experiments

Student: Mario Hilbig

Hochschule RheinMain

Fachbereich Ingenieurwissenschaften, Studienbereich Physik

Report of summer student project at DESY

Supervisor: Alena Prudnikava, Ph. D.

Contents

Contents	3
List of figures	3
Abstract	4
Basics of diffusion processes	6
Binary phase diagrams	7
Equilibrium concentration.....	8
Phase growth through diffusion.....	9
Calculation of diffusion profiles	10
Results	14
Conclusion	14
References.....	15

List of figures

Figure 1: The Binary phase diagram of niobium and nitrogen [4].	7
Figure 2: Crystal lattices for the 6 main phases of niobium nitride [4].	8
Figure 3: Temperature-concentration isobars of the N ₂ - equilibrium pressure in the Nb-N-system [5].	9
Figure 4: Example for a diffusion profile with two phases [6].	10
Figure 5: Diffusion profile of the ϵ - α -phase system after the diffusion time of 10 min and temperature of 1000°C.	12
Figure 6: Diffusion profile of the ϵ - α -phase system after the diffusion time of 60 min and temperature of 1000°C.	13
Figure 7: Diffusion profile of the ϵ - α -phase system after diffusion time of 60 min and temperature of 1000°C.	13

Abstract

The improvements in the performance characteristics of superconducting niobium (Nb) cavities is a very hot topic in the superconducting radiofrequency (SRF) community. The present work is inspired by the effect of nitrogen treatment on the Nb surface properties that led to the efficiency (Q-factor) improvement of the cavities. Here, the calculation of the diffusion profiles of nitrogen in Nb are presented at the parameters of experiment which experimentally showed an increase of Q factor of Nb cavities for up to a factor of 3. During the calculations, the formation of ϵ -NbN phase at the boundary with α -Nb phase was assumed. The nitrogen atoms concentrations causing Q improvement were estimated, and were equal to 0,1-0,25 at%N.

Introduction

The electromagnetic cavity is a key component of particle accelerators used in high energy particle physics, low-energy to medium-energy nuclear physics research, and free-electron lasers. Since the energy exchange between the SRF cavity and the accelerated particle depends strongly on the quality factor Q (ratio of the stored energy in the cavity to the power dissipation from the cavity walls in one RF period) and on the accelerating field, superconducting materials have been the best choice in practice to improve their performance. The main reason for that is that the Q value strongly depends on the microwave surface resistance of the metal, and for a superconductor it is five orders of magnitude lower than that of copper which therefore raises Q five orders of magnitude correspondingly.

Niobium, the superconductor with the highest critical temperature among pure elements, good thermal conductivity and mechanical properties suitable for cavity production, has been used in SRF technology over the last two decades. During this time, great improvements have been achieved in this sphere due to collaborative efforts of numerous universities and institutes from all over the world. Recently, the nitrogen (N) doping procedure consisting in annealing in N_2 gas atmosphere at moderate (800-1000°C) temperatures followed by electro polishing has been shown to be successful to rise the Q values for up to a factor of three [1]. The phenomenon underlying such an improvement is unknown and needs further investigation. As a first step towards understanding would be reasonable to perform calculation of the concentration profile of nitrogen atoms in Nb at the experimental conditions used in the mentioned study. This is the topic of the present investigation.

Basics of diffusion processes

Diffusion processes are described with the first and second Fick's law, which are [2], [3]:

$$1. \vec{j}_{Diff}(\vec{r}, t) = -\nabla Dc(\vec{r}, t) \quad (1)$$

$$2. \frac{dc}{dt} = \Delta Dc(\vec{r}, t) \quad (2)$$

Where \vec{j} is the diffusion flux density, D the Diffusion coefficient, c the concentration of the diffusing material, \vec{r} the position vector and t the time. In terms of simplification we reduce those two laws to the one-dimensional versions, which are the equations (3) and (4)

$$1. \vec{j}_{Diff}(x, t) = -\frac{d}{dx} Dc(x, t) \quad (3)$$

$$2. \frac{dc}{dt} = \frac{d^2}{dx^2} Dc(x, t) \quad (4)$$

In order to achieve a solution we have to estimate the initial and boundary conditions.

The initial conditions at $t = 0 = t_0$:

At $x=0$ (i.e. the Nb surface) the nitrogen concentration is maximum and equal c_0 for $t=0=t_0$. At $x>0$ (i.e. Nb bulk) the concentration of nitrogen represents the nitrogen impurity which might be present after the production process. As this concentration varies with the technique applied, for the simplicity we set it to zero. Thus,

$$c(x, t_0) = \begin{cases} c_0 & \text{for } x = 0 \\ 0 & \text{for } x > 0 \end{cases} \quad (5)$$

The boundary conditions at $t > 0$:

We assume that the concentration of nitrogen at the niobium surface is maximum and constant for every $t > 0$ since the atmosphere is regulated and therefore represents an infinite source. Since the thickness d of the niobium is large compared to the diffusion length, we assume that the concentration of nitrogen in the middle at $d/2$ is zero.

$$c(x_0, t) = c_0 \quad (6)$$

$$c(x_0 + d/2, t) = 0 \quad (7)$$

For these assumptions the problem can be solved by the complementary error function with the depth divided by the diffusion length as argument of the function:

$$c(x, t) = c_0 \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (8)$$

where c_0 is the concentration of the dopant at the substrate surface. How this concentration can be determined is described in the next section.

Binary phase diagrams

Binary phase diagrams are used to visualize how the structure of the compounds changes depending on temperature and the element ratio. In figure 1 the phase diagram of the Nb-N binary system is shown. The element ratio is shown in atomic percent of nitrogen. It is also shown the critical temperature for super conductivity for these phases in Kelvin.

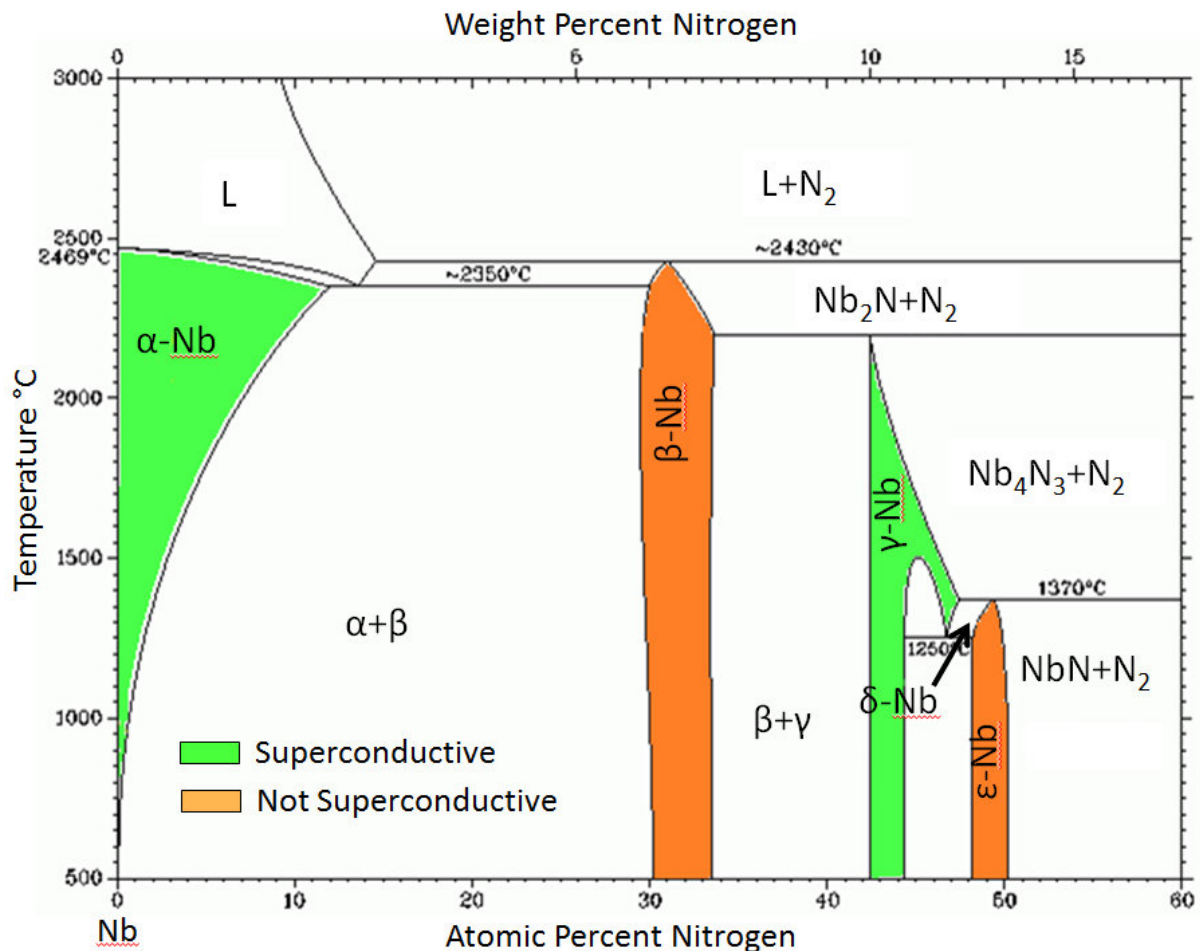


Figure 1: The Binary phase diagram of niobium and nitrogen [4].

As we can see the material consists of different phases depending on the amount of nitrogen and the temperature. There is an interval of the nitrogen concentration for every phase in which it can be formed, this interval is called homogeneity range. Between the main phases we find a mixture of the two phases which are bordering to this field.

There are 6 different main phases of niobium nitride. The crystal lattices of these phases are shown in figure 2.

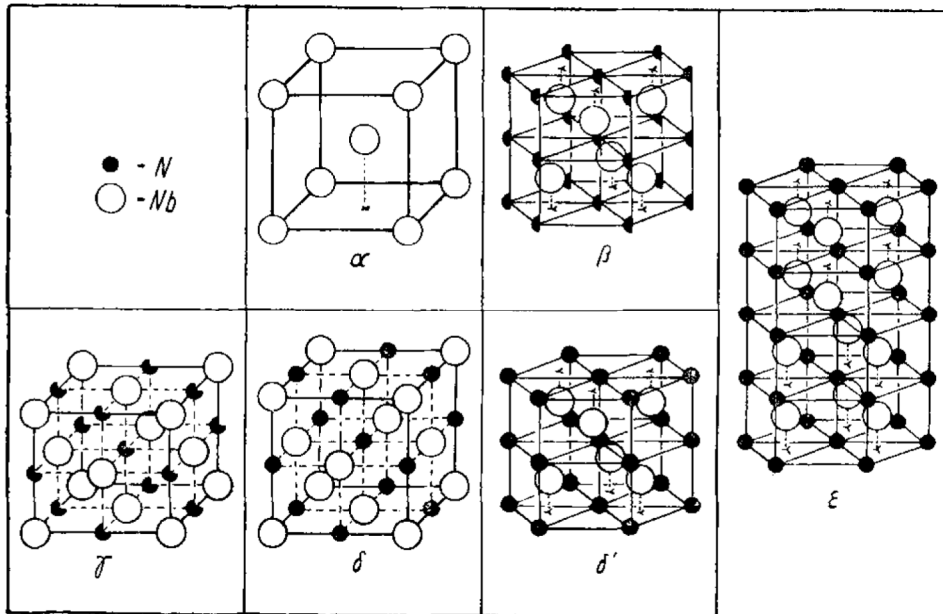


Figure 2: Crystal lattices for the 6 main phases of niobium nitride [4].

It is considerable that the critical temperatures of cubic crystal lattices are higher than those of hexagonal lattices. Therefore only niobium nitride materials with cubic crystal lattice are used as superconductors.

Equilibrium concentration

The equilibrium concentration of a gas in a liquid or solid material is the concentration at which absorption from the atmosphere and desorption into the atmosphere is in equilibrium. Furthermore there is maximum amount of dopants that a material can absorb. If this amount is exceeded the phase changes. This is called terminal solubility.

The equilibrium concentration depends on the temperature, pressure of the atmosphere and the elements involved in the process. In figure 1 concentration-temperature plot for nitrogen niobium system is depicted. From this plot one can read which nitrogen concentration a sample will have when heated to a certain temperature, as well as the temperatures and pressures at which the nitride phase is formed.

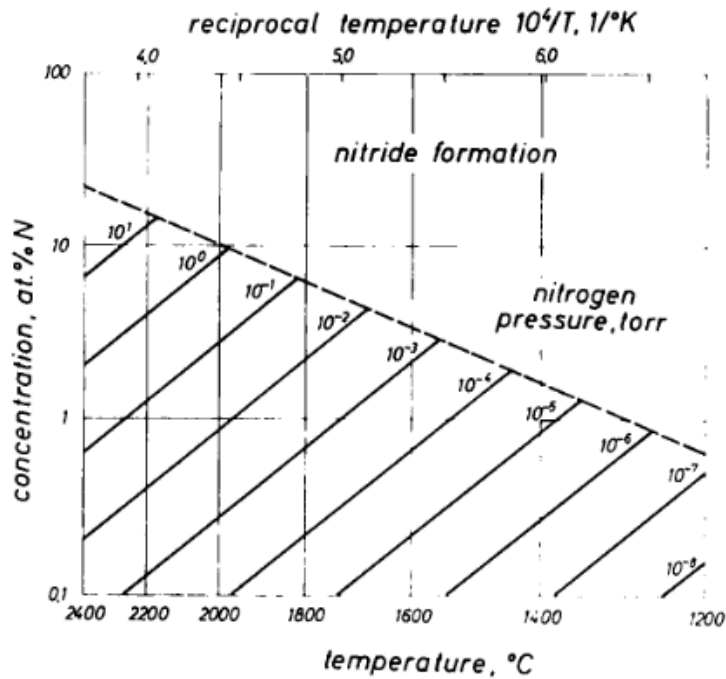


Figure 3: Temperature-concentration isobars of the N₂- equilibrium pressure in the Nb-N-system [5].

The process parameters of the heat treatment used in the present calculations are taken from ref. [3] i.e. 800 and 1000°C at $2 \cdot 10^{-2}$ Torr. If we extrapolate the dashed line we can assume that at these conditions the terminal solubility is exceeded and the nitrides are formed at Nb surface. This means that a single error function cannot describe the diffusion profile, since the diffusion coefficient varies with the phase.

Phase growth through diffusion

Let's describe how the diffusion profile is calculated when the growth nitride phases is considered. An important parameter of a diffusion process is the diffusion length x_{diff} :

$$x_{diff} = 2 \cdot \sqrt{D \cdot t} \quad (9)$$

As equation (8) shows, the x-coordinate, i.e the diffusion depth, of a distinct concentration is proportional to the diffusion length. If we assume that the temperature is constant, the homogeneity ranges for the phases will be constant too. Therefore, the movement of a phase boundary ξ_n will be proportional to the diffusion length in the material. According to Wagner's assumption [6]:

$$\xi_n = \gamma_n \cdot x_{diff} = \gamma_n \cdot 2 \cdot \sqrt{D_n \cdot t} \quad (10)$$

Where γ_n is proportionality factor which is connected to the homogeneity range.

Since the homogeneity ranges are not overlapping, a phase with a higher dopant concentration can always be assumed as an infinite source. Therefore we can assume for every phase that the

concentration of dopant follows a complementary error function. Figure 4 shows the concentration profile of nitrogen in the nitride phase (index n) and niobium phase (index m).

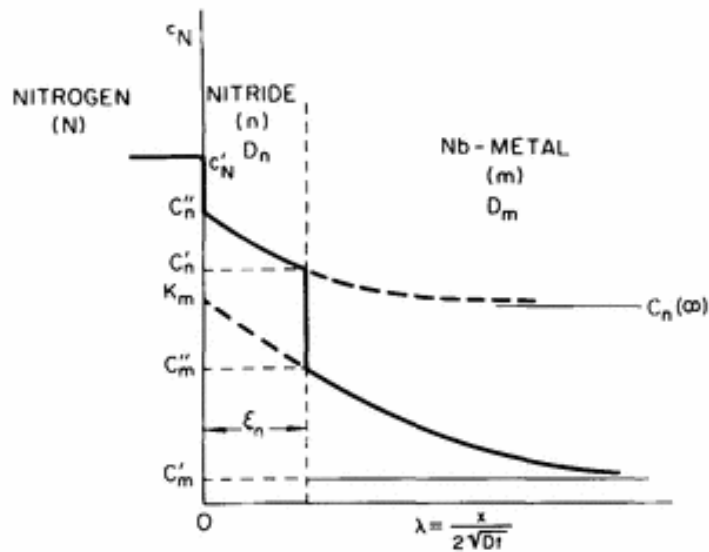


Figure 4: Example for a diffusion profile with two phases [6].

D_n and D_m are the diffusion coefficients of nitrogen atoms in the nitride s and Nb phases (α -Nb), correspondingly, ξ_n is the thickness of the nitride phase. C_n'' and C_n' are the boundaries of the homogeneity range of the nitride phase. C_m'' is the terminal solubility of nitrogen in α -Nb. C_m' is the initial concentration of nitrogen in niobium. K_m represents the value of concentration of nitrogen atoms in α -Nb at the surface, which represents no physical property. $C_n(\infty)$ represents the value of nitrogen concentration in the nitride, and has no physical meaning either. But these two values are parameters of the error functions and have to be calculated therefore.

If the homogeneity ranges and the diffusion coefficients of all the phases are known, it is possible to calculate a multiphase diffusion profile.

Calculation of diffusion profiles

Since there is lack of the required data in the literature for performing calculation of the real diffusion profile for the temperature interval of our interest, we assumed the formation of only ϵ -NbN at the boundary with α -Nb.

The data which were used for this calculation are from ref. [6]. The parameters used in the calculations are presented in Table 1.

Table 1: Summary of experimental data used for the calculation of diffusion profile of a ϵ -NbN/ α -Nb-system [6].

Table 1. Summary of Experimental Data Used for Evaluation of Nitrogen Uptake by Niobium at Different Temperatures							
Parameter	1273 K	1175 K	1083 K	1043 K	993 K	943 K	873 K
C_m' ; gN/cm ³	4.03×10^{-4}	4.03×10^{-4}	4.03×10^{-4}	4.03×10^{-4}	4.03×10^{-4}	4.03×10^{-4}	4.03×10^{-4}
C_m''	4.01×10^{-3}	2.96×10^{-3}	2.31×10^{-3}	2.07×10^{-3}	1.75×10^{-3}	1.47×10^{-3}	1.17×10^{-3}
C_n'	1.095	1.095	1.095	1.095	1.095	1.095	1.095
C_n''	1.0955	1.0955	1.0955	1.0955	1.0955	1.0955	1.0955
D_n ; cm ² /s	5.40×10^{-9}	2.22×10^{-9}	8.37×10^{-10}	5.19×10^{-10}	2.71×10^{-10}	1.32×10^{-10}	4.21×10^{-11}
$(D_n)_{av}$	7.86×10^{-9}	3.29×10^{-9}	1.37×10^{-9}	9.17×10^{-10}	5.43×10^{-10}	3.12×10^{-10}	1.34×10^{-10}
γ_n	0.01454	0.01497	0.01803	0.01371	0.02245	0.03601	0.04284

Let's calculate the missing parameters for the temperature of 800°C and 1000°C. Since the diffusion coefficients for the α -phase have a large range depending on the author, we assume a maximum and a minimum diffusion coefficient for the calculation of the profiles.

Parameters for 1000°C

$$C_m(x) = (K_m - C_m') \cdot \operatorname{erfc}\left(\frac{x}{2\sqrt{D_m t}}\right) + C_m' \quad (11)$$

$$C_m(\xi_n) = C_m'' = (K_m - C_m') \cdot \operatorname{erfc}\left(\frac{\gamma_n \cdot 2\sqrt{D_n t}}{2\sqrt{D_m t}}\right) + C_m' \quad (12)$$

$$K_m = \frac{C_m'' + C_m'(A-1)}{E} \quad \text{with} \quad A = \operatorname{erfc}\left(\frac{\gamma_n \sqrt{D_n}}{\sqrt{D_m}}\right) \quad (13)$$

For the diffusion coefficients D_{m1} , D_{m2} and D_n this gives in at/m³ the following values:

$$K_{m1} = 8,674 \cdot 10^{25} m^{-3} \quad \text{with} \quad D_{m1} = 2,2 \mu m^2/s \quad \text{and} \quad D_n = 0,54 \mu m^2/s$$

$$K_{m2} = 8,7346 \cdot 10^{25} m^{-3} \quad \text{with} \quad D_{m2} = 0,786 \mu m^2/s \quad \text{and} \quad D_n = 0,54 \mu m^2/s$$

$$C_n(x) = (C_n'' - C_n(\infty)) \cdot \operatorname{erfc}\left(\frac{x}{2\sqrt{D_n t}}\right) + C_n(\infty) \quad (14)$$

$$C_n(\xi_n) = C_n' = (C_n'' - C_n(\infty)) \cdot \operatorname{erfc}\left(\frac{\gamma_n \cdot 2\sqrt{D_n t}}{2\sqrt{D_n t}}\right) + C_n(\infty) \quad (15)$$

$$C_n' = (C_n'' - C_n(\infty)) \cdot \operatorname{erfc}(\gamma_n) + C_n(\infty) \quad (16)$$

$$C_n(\infty) = \frac{C_n' - C_n'' \cdot B}{1-B} \quad \text{with} \quad B = \operatorname{erfc}(\gamma_n) \quad (17)$$

$$C_n(\infty) = 2,214 \cdot 10^{28} m^{-3} \quad \text{with} \quad \gamma_n = 0,01454$$

Parameters for 800°C

K_m -values in at/m^3 for the diffusion coefficients D_{m1} , D_{m2} and D_n

$$K_{m1} = 5,0423 \cdot 10^{25} \text{m}^{-3} \quad \text{with} \quad D_{m1} = 0,137 \mu\text{m}^2/\text{s} \quad \text{and} \quad D_n = 0,0837 \mu\text{m}^2/\text{s}$$

$$K_{m2} = 5,07819 \cdot 10^{25} \text{m}^{-3} \quad \text{with} \quad D_{m2} = 0,063 \mu\text{m}^2/\text{s} \quad \text{and} \quad D_n = 0,0837 \mu\text{m}^2/\text{s}$$

$C_n(\infty)$ in at/m^3 :

$$C_n(\infty) = 2,30674 \cdot 10^{28} \text{m}^{-3} \quad \text{with} \quad \gamma_n = 0,01803$$

With these parameters the diffusion profile for three different cases has been calculated. The results are shown in figures 5, 6 and 7, respectively. In addition, the layer removal of the investigation conducted in ref. [1] is marked with arrows. The green arrows are marking the removal which led to a Q-factor improvement, the red arrows mark the layer removal with lower Q-values.

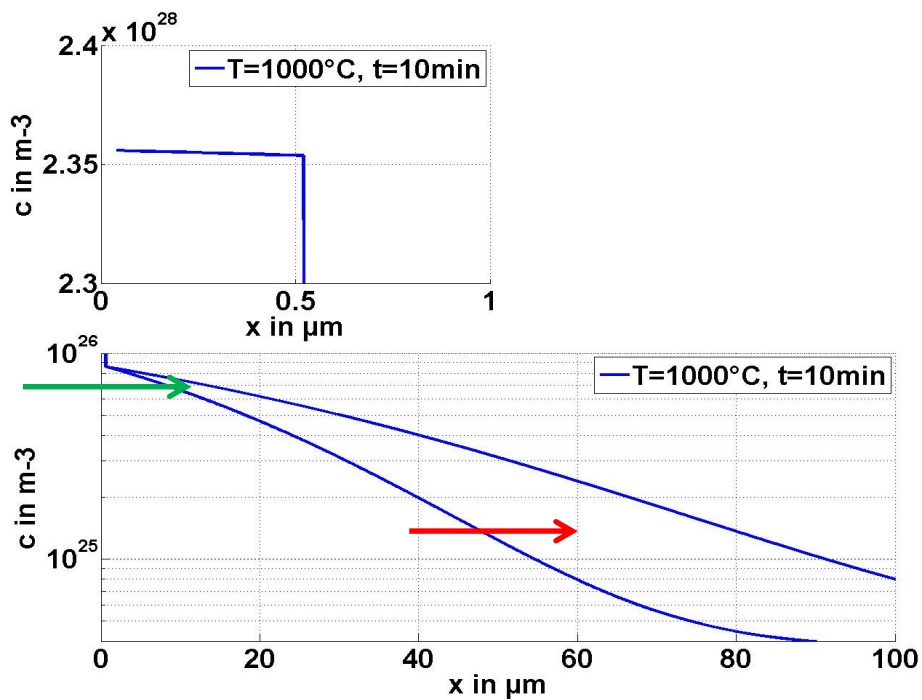


Figure 5: Diffusion profile of the ϵ - α -phase system after the diffusion time of 10 min and temperature of 1000°C.

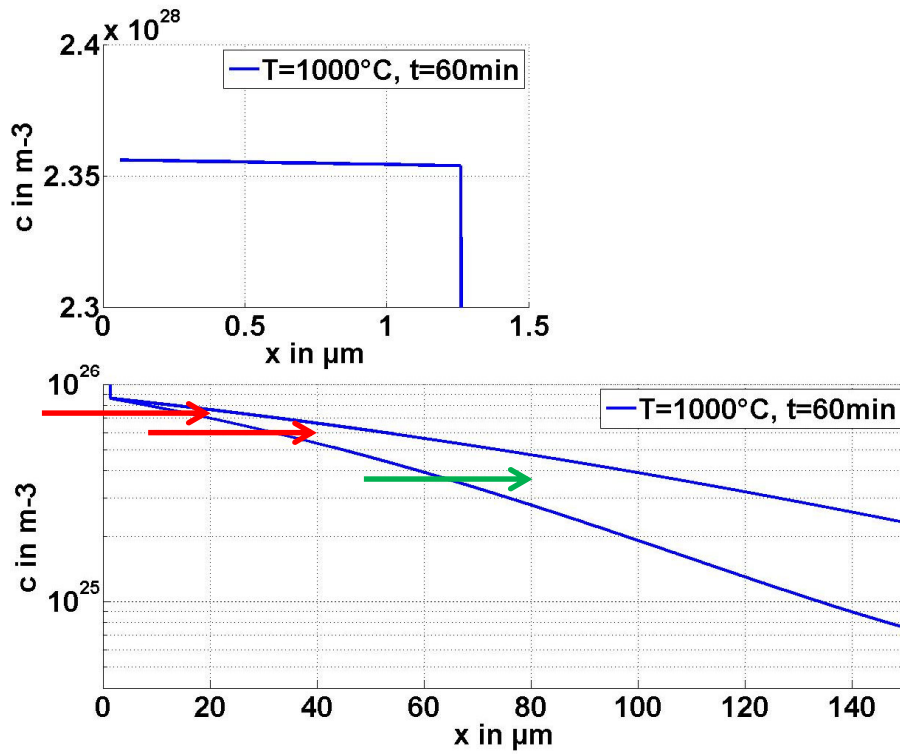


Figure 6: Diffusion profile of the ϵ - α -phase system after the diffusion time of 60 min and temperature of 1000°C .

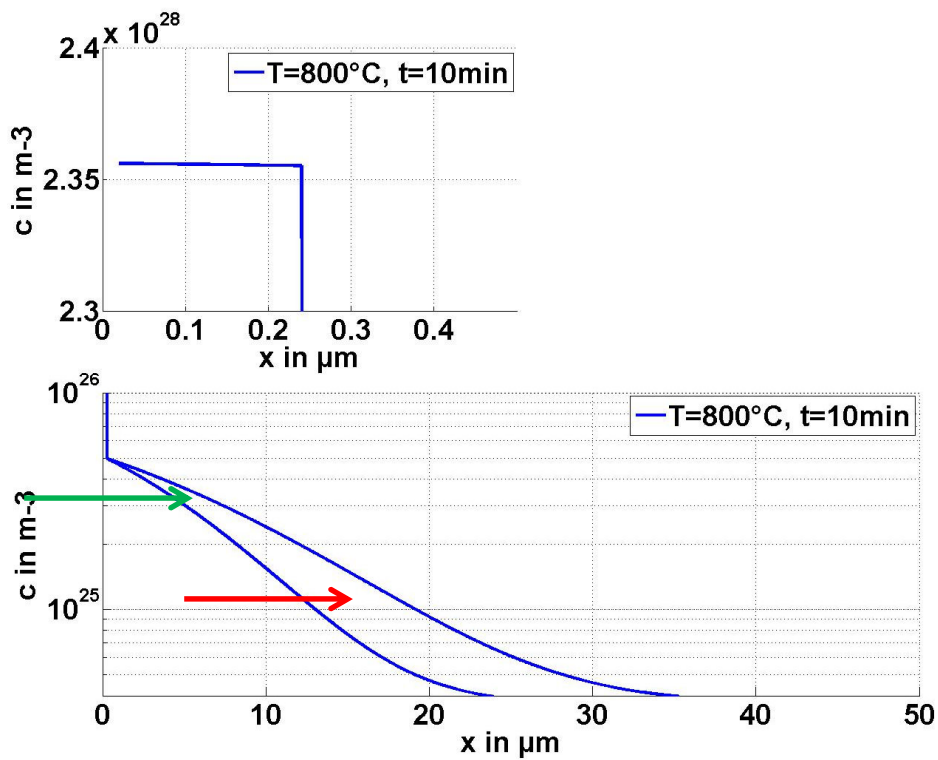


Figure 7: Diffusion profile of the ϵ - α -phase system after diffusion time of 60 min and temperature of 1000°C .

Results

The calculated profiles show first of all that the ϵ -phase layer is much thinner than the layer removal in all three cases. Therefore, we can conclude that the skin layer is not consisting of highly doped ϵ -phases.

The calculated profiles show nitrogen concentrations in the skin layer from $3 \cdot 10^{25}$ to $7 \cdot 10^{25} \text{ m}^{-3}$ for improved Q-factors. These are concentrations of 0,1 to 0,25 at%N, which means the skin layer represents the α -phase.

As revealed in the former investigation the Q-factors of cavities 1 and 3 are reduced to the values of normal treated cavities in case of further removal. This acknowledges the assumption that a lower interstitial concentration leads to a lower Q-factor.

Figure 2 shows that if the removal is not deep enough the Q-value will be still lower. This indicates that there might be some mixed α -nitride-phases within the skin layer which suppresses superconductivity and lowers the Q-factor.

Conclusion

The calculation of the diffusion profiles of nitrogen atoms into niobium was performed. Assuming the formation of ϵ -NbN phase at the boundary with α -phase it was revealed that, no highly doped nitride layer exists after the layer removal steps. Therefore, we can preliminary conclude that in the cases of improved values of Q-factor the top layer represents α -niobium phase. One should point out that the depth of best Q values couldn't be estimated precisely in the work we have been referring [1] because of the method used for this purpose (i.e. electropolishing removes outer layers of Nb not uniformly within the cavity surface because of its complex shape, therefore just average values were given). More precise diffusion coefficients of the other phases of niobium which are missing in the literature are also needed for a more precise calculation of the diffusion profile. Therefore, the experimental work should be conducted in order to estimate the missing parameters for the modelling of such processes which would let lit more light on the phenomena of efficiency improvement by nitrogen treatment of the Nb cavities.

References

- [1] Nitrogen and argon doping of niobium for superconducting radio frequency cavities: a pathway to highly efficient accelerating structures; A Grassellino¹, A Romanenko¹, D Sergatskov¹, O Melnychuk¹, Y Trenikhina², A Crawford¹, A Rowe¹, M Wong¹, T Khabiboulline¹ and F Barkov¹ (1: Fermi National Accelerator Laboratory, Batavia, IL 60510, USA. 2: Illinois Institute of Technology, 3300 S Federal St, Chicago, IL 60616, USA.)
- [2] Melchers, Fritz: Gase und Kohlenstoff in Metallen. Softcover reprint of the original 1st ed. 1976. Wiesbaden: Springer Berlin Heidelberg, 2011.
- [3] Baehr, Hans Dieter ; Stephan, Karl: Wärme- und Stoffübertragung. 8. Aufl.. Berlin Heidelberg New York: Springer-Verlag, 2013.
- [4] (G. Brauer, R. Esselborn, Nitridphasen des Niobs, Zeitschrift für anorganische und allgemeine Chemie, Volume 309, Issue 3-4, pages 151–170, April 1961)
- [5] Reactions of niobium and tantalum with gases at high temperatures and low pressures; E. Fromm and H.Jehn, Max-Planck-Institut für Metallforschung , Institut für Sondermetalle, Stuttgart, West Germany
- [6] Nitridation Kinetics of Niobium in the Temperature Range of 873 K to 1273 K; James T. Clenny and Casimir J. Rosa