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SOME ASPECTS of DIFFUSION in NIOBIUM BY HIGH TEMPERATURE GETTERING

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INTRODUCTION

Last time most of the efforts in different laboratories were concentrated on the improvement of the surface treatment methods of superconducting Nb cavities. These efforts mainly included high temperature treatments in the presence of Ti or Y as a getter and protection material. Such firing is very important for successful performance of accelerating structures. Firstly it allows a purification and a homogenization of Nb with a subsequent improvement of its thermal conductivity and a better stabilization of the cavity against quenches. Secondly this treatment allows braking the activity of the microscopic sites where electron field emission takes place /1/.

For defining more exactly the annealing parameters and for better understanding the performances we tried to observe theoretically the procedure of the atomic diffusion at high temperatures.

On the one side Nb contains impurity atoms, in particular the interstitial impurity - O, N, C, which are most important for the material properties. During the gettering they leave the bulk Nb and move towards the surface, where they build compounds with Ti or Y (this process is schematically shown in Fig. 1). It is very desirable to know the distribution of the rest impurities in Nb after gettering. On the other side the diffusion of getter material inside the Nb takes place by heating. It is necessary to know the depth and the distribution of the getter material in Nb after treatment. The calculation methods of atom diffusion in metals and the appropriate results are described below .

THE DIFFUSION EQUATIONS

First of all we consider the basic equations, which describe the atom diffusion in metals. Diffusion occurs in the presence of a concentration gradient (ΔC) of mobile atoms. In general the atoms will move in such a way as to decrease the gradient of atoms. If the atomic jumps are random and independent of each other, it is easy to show that the flux of atoms (J) at the point x,y,z is proportional to the concentration gradient
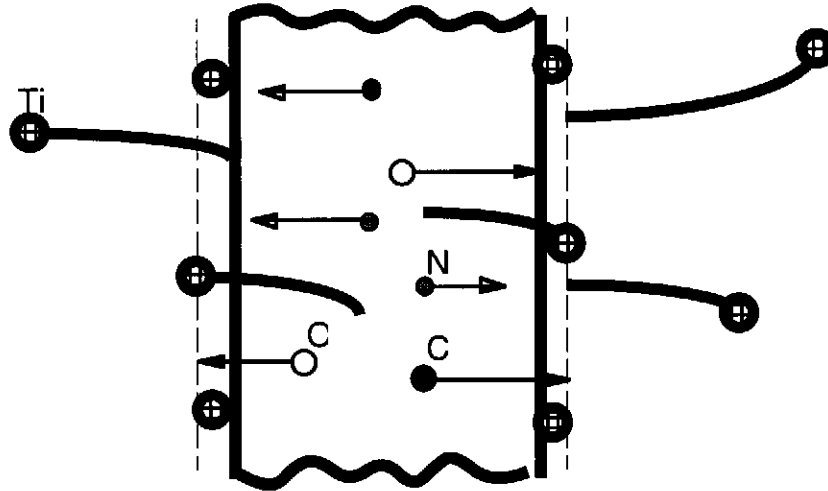
Fig. 1 Scheme of the Nb refining by high
temperature gettering

$$J = -D\Delta C \qquad (1)$$

C is the concentration at the same place and D is the constant of proportionality called the diffusion coefficient. Equation (1) is known as the first Fick's law.

The diffusion coefficient is a function of temperature and the relationship

$$D = D_0 EXP(-\frac{Q}{RT})$$

is often applied. The energy Q is the free energy required by an atom to jump from one stable position in the crystal to the next.

The second Fick's law may be derived in an isotropic medium from equation (1) if the diffusion is one-dimensional, (i.e. if there is a gradient of concentration only along the x-axis)

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (2)$$

In some systems D depends on the concentration of a diffusing substance. In this case equation (2) becomes

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}(D\frac{\partial C}{\partial x}) \qquad (3)$$

General solutions of the diffusion equation can be obtained for a variety of initial and boundary conditions. Such a solution usually has one of two standard forms. Either it is comprised of a series of error functions, which are related with integrals, or it is in the form of a trigonometric series. Some methods of solution are described in /2,3/. In most cases the solution has to be evaluated numerically.

PLANE SHEET

Firstly we consider the case of a one-dimensional diffusion in a medium bounded by two parallel planes, e.g. the planes at x=-l, x=l. In practice this applies to a diffusion substance, which goes through the plane faces and a negligible amount through the edges, and it is approximately suited for a thin enough sheet of Nb with large surface.

For us the case of interest is when the surface concentration is constant and the region -l < x < l is initially at a uniform concentration.

$$C = C_1, \qquad x = -l, \qquad t \geq 0$$

$$C = C_1, \qquad x = l, \qquad t \geq 0$$

$$C = C_0, \qquad -l < x < l, \qquad t = 0$$

We assume the surface concentration C_1 is kept constant and suppose $C_1 = 0$. This means that all impure atoms (O, N, C), which reach the Nb surface, build compounds with Ti. Concentration C_0 is the initial concentration of O, N or C impurities. We assume homogeneous initial impurity distributions in Nb.

The solution of equation (2) with the mentioned boundary conditions can be obtained either by the method of separation of the variables or by the Laplace transformation as described in /2/. Many of the results are presented by Barrer /4/, Carslaw and Jaeger /3/, Jost /5/ and summarized by Crank /2/. The general solution becomes

$$\frac{C}{C_0} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} EXP(-\frac{D\pi^2 t(2n+1)^2}{4l^2}) \cos\frac{(2n+1)\pi x}{2l} \qquad (4)$$

If M is the total amount of diffusing substance which is going through the boundary of the sheet at a time t, and M_0 the correspondent initial quantity, then

$$\frac{M}{M_0} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} EXP(-\frac{D(2n+1)^2 \pi^2 t}{4l^2}) \qquad (5)$$

The results of the calculations for Nb after annealing at a temperature of 1200°C and 1400°C and different times are given in Fig. 2-4. The profile of concentration's distribution is symmetric and the impurity distribution from the sheet center to the edge is shown in the pictures. The amount M/Mo as a function of heating time and temperature is shown in figures 5 - 7. The necessary diffusion coefficients were found in the literature / 6 / (for instance $D_O = 5.6 \cdot 10^{-3} \exp(-\frac{109600}{R \cdot T})$, $D_N = 5.1 \cdot 10^{-2} \exp(-\frac{156900}{R \cdot T})$).

It has to be remarked, that after heat treatment the impurity distribution is not homogeneous. Most of the remaining impurities are located at the center of the sheet. After 4 hours heating at 1400°C nearly all O and much more than half of the C and N atoms leave the Nb.

It is well known that the Residual Resistivity Ratio (RRR) is an excellent tool to determine impurity concentrations. The obtained results allow predict the RRR after solid state gettering. It is obvious, that because of the non uniform impurity distribution in the sheet, the RRR distribution is non uniform too. For estimation of the average RRR value we can utilize for example the empirical formula, which describes the influence of different impurity elements on RRR /7/.

$$RRR = \frac{R(300K)}{R(10K) + \sum_{i=1}^{4} \frac{\partial R_i}{\partial C_i} C_i}$$

i= 1 (=oxygen), i= 2 (=nitrogen), i= 3 (=carbon),

i=4(=rest of the impurities)

R(300K)=1,46·10⁻⁵ Ω cm, R(10K)=8,7·10⁻⁹ Ω cm

The values $\partial R_i/\partial C_i$ have been found by using of pure and doped /7/ samples: for N: 3,49 x10⁻⁹ Ω cm/wt. ppm ; C: 3,33 x10⁻⁹ Ω cm/wt. ppm; O: 2,64 x10⁻⁹ Ω cm/wt. ppm respectively.

The RRR prediction can be demonstrated on an example. We consider the Nb_{300} with contents of O=4 wt. ppm, N=2 wt. ppm, C =2 wt. ppm and rest of impurities=10 wt. ppm, and assume, that $\partial R/\partial C$ for the rest is 0,12 /7/. Then the value of RRR is 430. Taking into account our calculations concerning the amount of removed impurities O, N, and C after gettering we have RRR = 1030. The last result is in sufficient agreement with a row of experiments, which show that the RRR increases after gettering by factor 2,5 - 3 /8,9/.

O in Nb, 1400°C
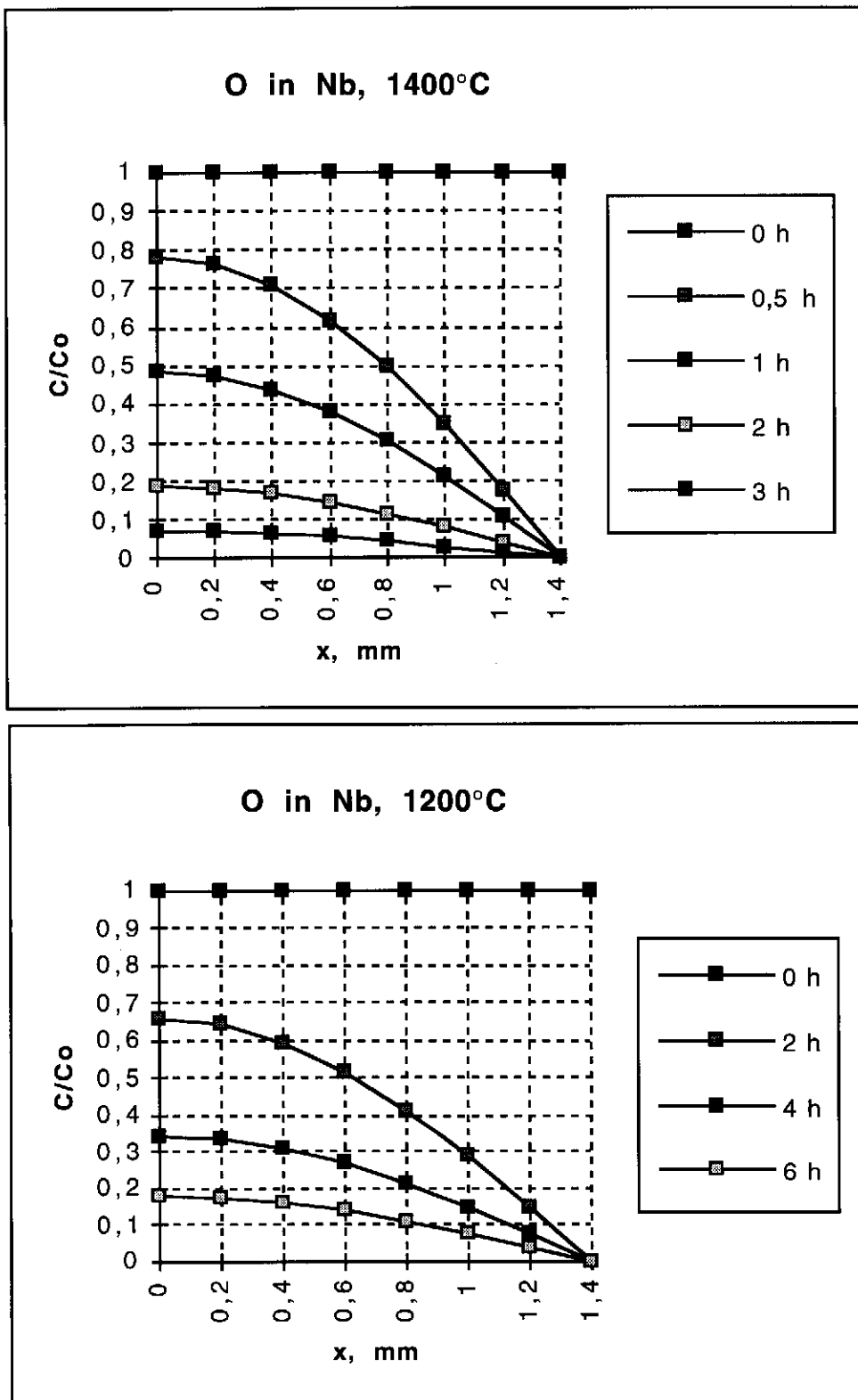

O in Nb, 1200°C

Fig. 2 The oxygen distribution in Nb sheet after refining
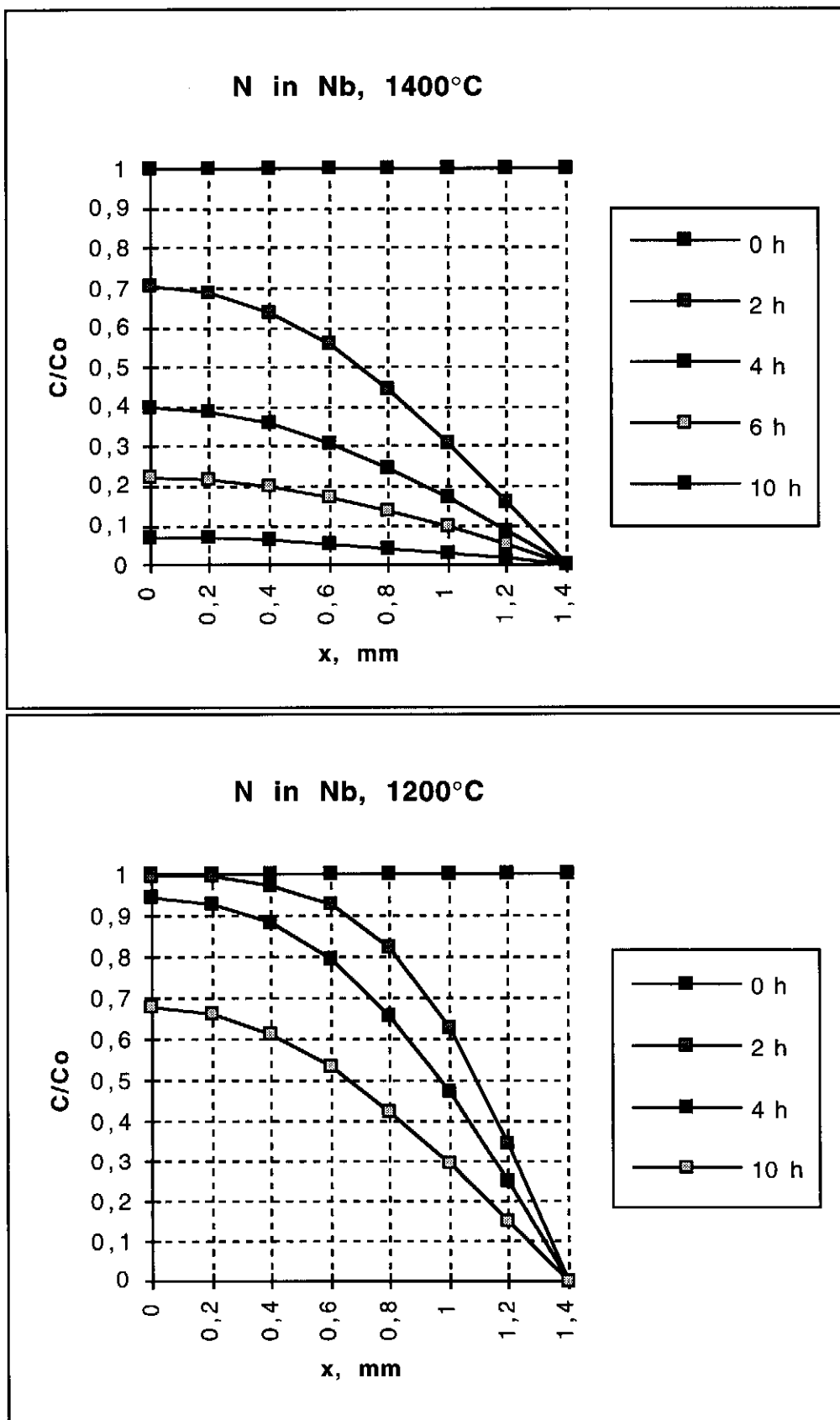
Fig. 3 The nitrogen distribution in Nb sheet after refining
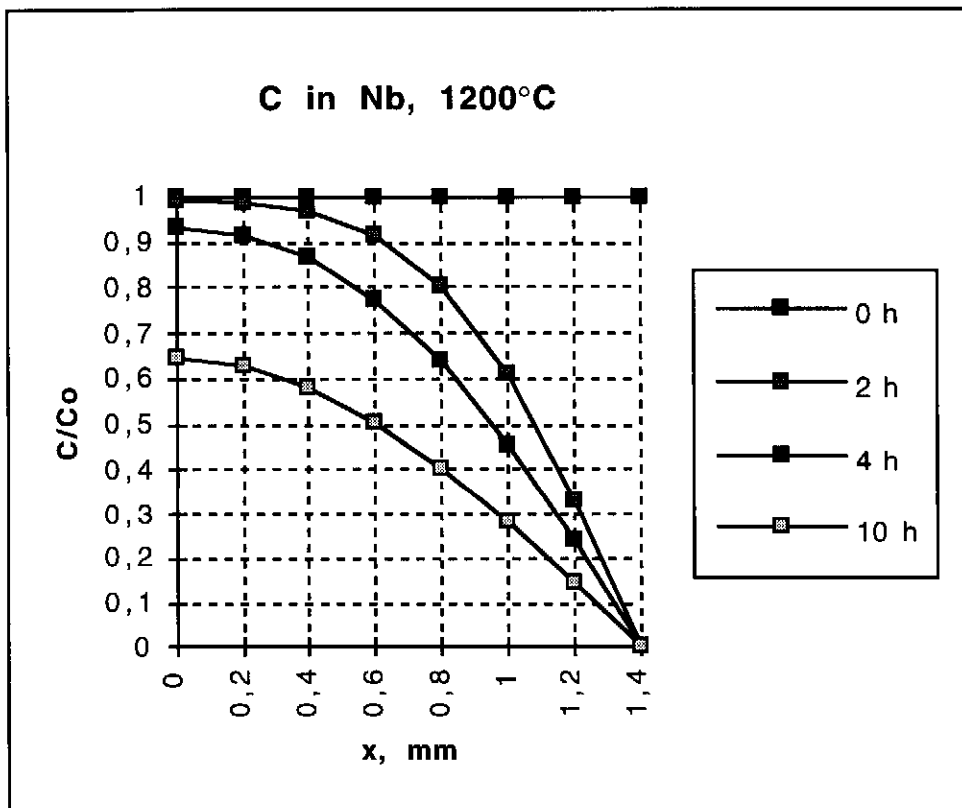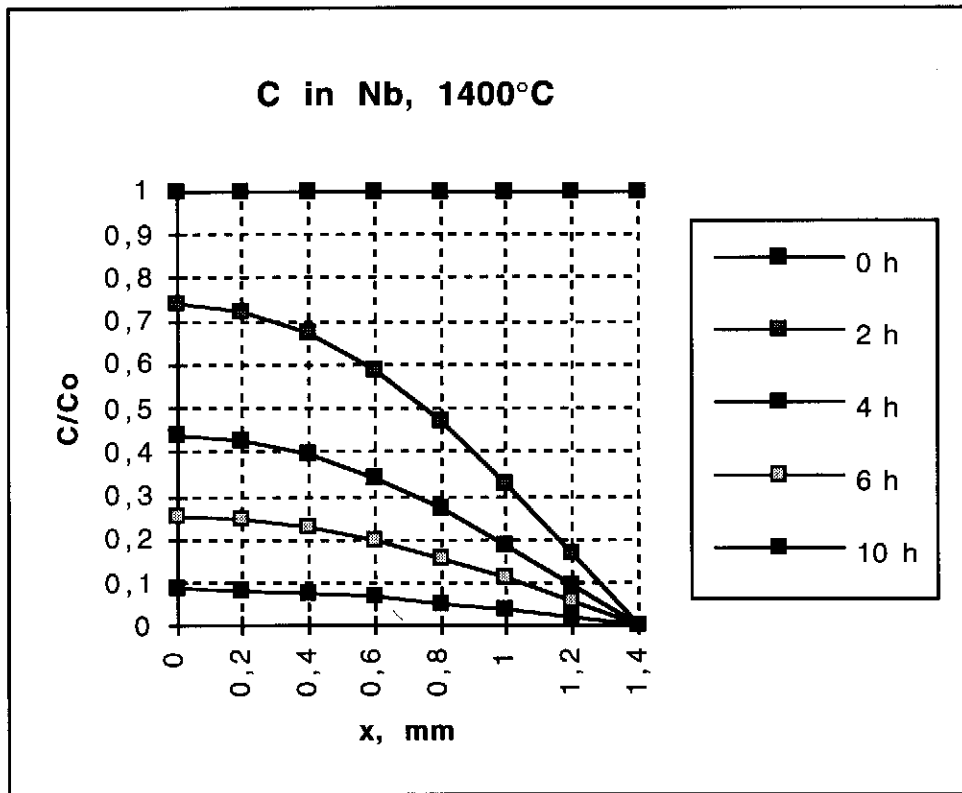
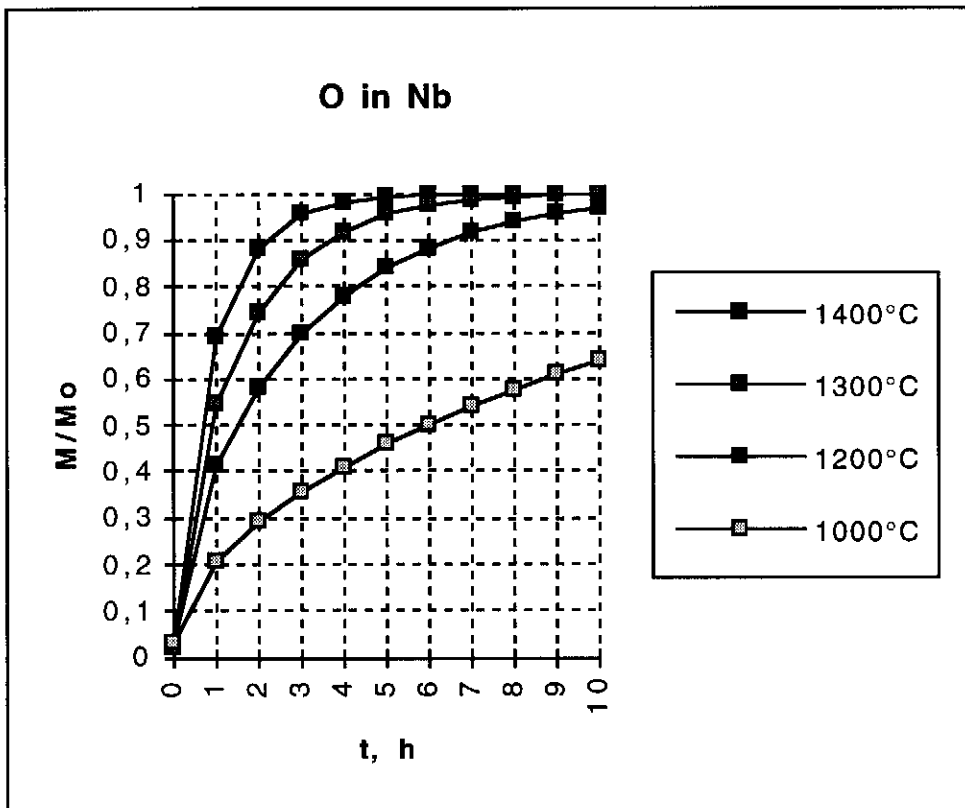Fig. 4 The carbon distribution in Nb sheet after refining

Fig. 5 Amount of oxygen which has left the Nb sheet

Fig. 6 Amount of nitrogen which has left the Nb sheet
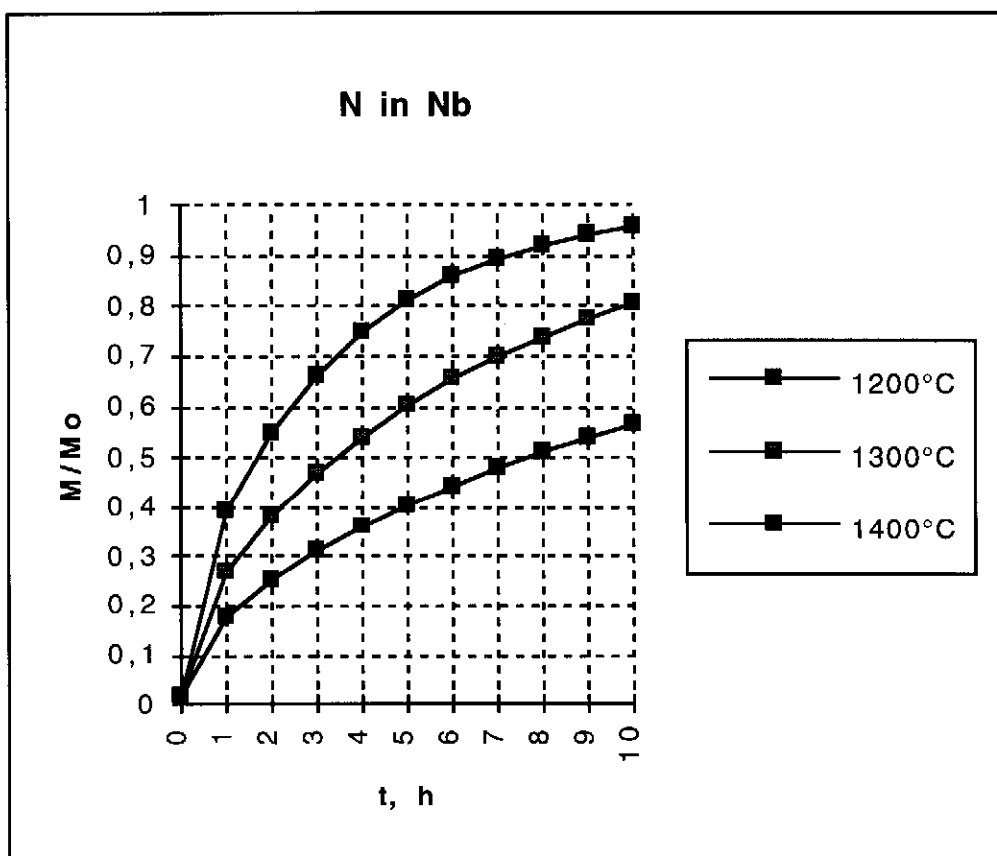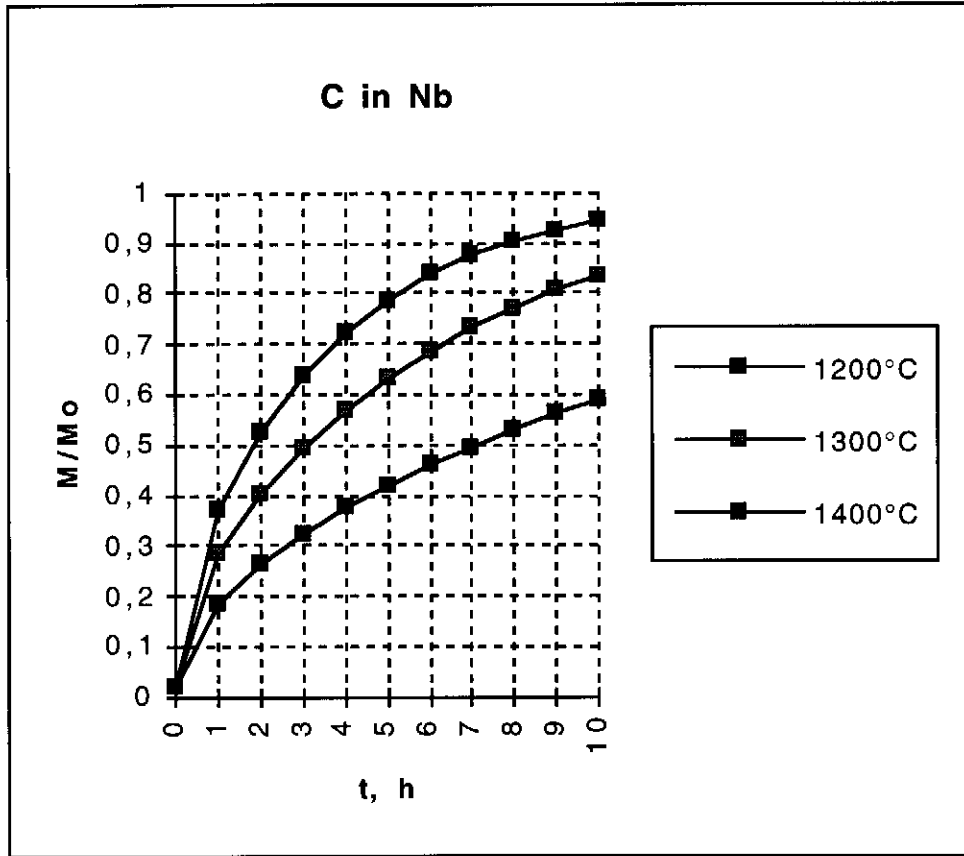
C in Nb

Fig. 7 Amount of carbon which has left the Nb sheet
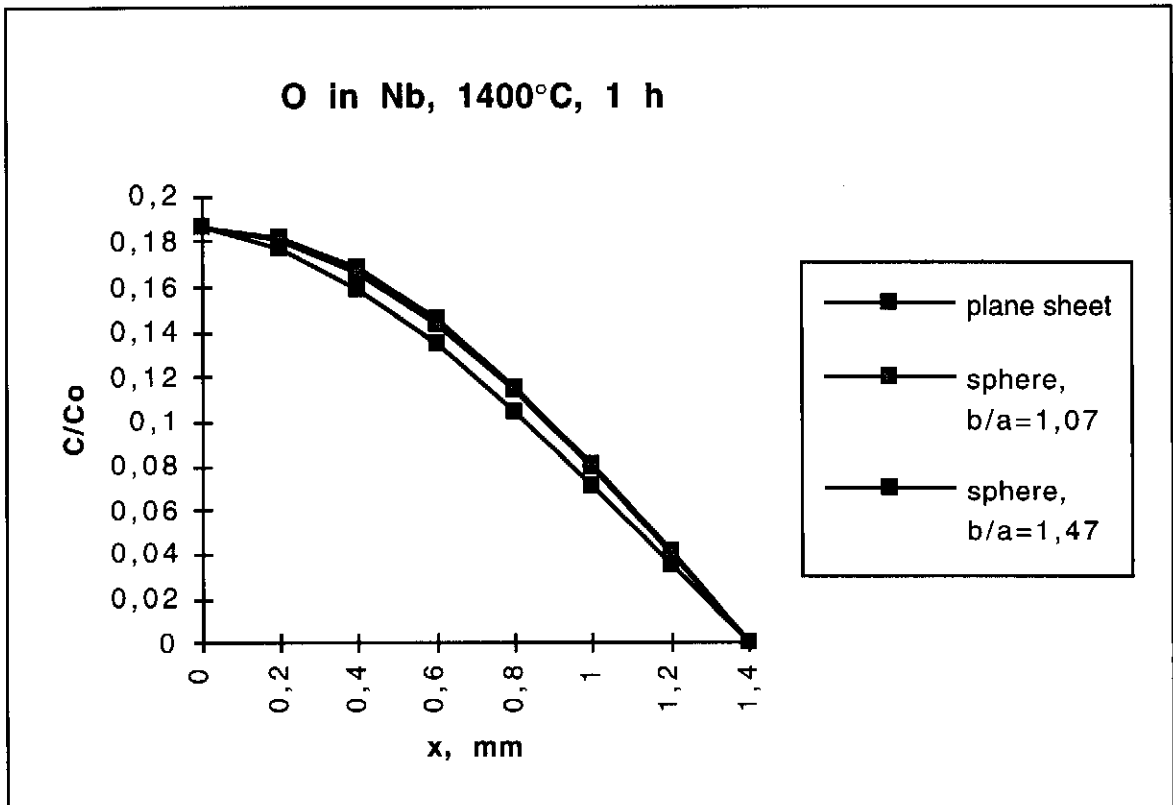
O in Nb, 1400°C, 1 h

Fig. 8 Comparison of the diffusion in plane sheet and in a sphere

SPHERE

It is reasonable to expect that in the spherical objects with the small ratio of the outer diameter to the inner diameter (<1,5 as by TESLA cavity) the conclusions may be the same as for the flat sheet. This result would be very useful for us, since the cavity cell has a shape close to a sphere. In order to check it up we now consider the diffusion in a hollow sphere.

The appropriate equation for a sphere should be obtain in terms of spherical polar coordinates r, θ, φ. By taking into account an element of volume of a sphere of sides $dr, rd\theta, r \sin \varphi d\varphi$ it is possible to get

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} (Dr^2 \frac{\partial C}{\partial r}) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (D \sin \theta \frac{\partial C}{\partial \theta}) + \frac{D}{\sin^2 \theta} \frac{\partial^2 C}{\partial \varphi^2}$$

If the diffusion is radial, the diffusion equation for a constant diffusion coefficient takes the form

$$\frac{\partial C}{\partial t} = D(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r})$$

Carslaw and Jaeger /3/ gave the general solution of the problem of the hollow sphere with the surface r = a maintained at a constant concentration C_1, and r = b at C_2, when the initial distribution is f(r) in the region a ≤ r ≤ b. In our case of a constant initial concentration, f(r) = C_0 and if C_1 = C_2 = 0, the solution is

$$\frac{C}{C_0} = \frac{2}{\pi r} \sum_{n=1}^{\infty} (\frac{b \cos n\pi - a}{n}) \sin \frac{n\pi(r-a)}{b-a} EXP(-\frac{Dn^2 \pi^2 t}{(b-a)^2}) \qquad (6)$$

The total amount of diffusing substance entering or leaving the hollow sphere in a time t is given by

$$\frac{M}{M_0} = 1 - \frac{6}{\pi^2 (a^2 + ab + b^2)} \sum_{n=1}^{\infty} (\frac{b \cos n\pi - a}{n})^2 EXP(-\frac{Dn^2 \pi^2 t}{(b-a)^2}) \qquad (7)$$

We considered the spherical cell with dimensional parameters near to the 1,3 GHz cavity for TESLA (b/a = 1,07) and compared the diffusion behavior in spheres and in plane sheets.

For instance Fig. 8 demonstrates that after one hour gettering at 1400°C the profile of oxygen distribution in sphere and in plane sheet are very similar. Even at a ratio of b/a= 1,47, that may occur in some regions of the cavity the differences between

these two sorts of shapes are negligible (Fig 8). This means that a conclusion about the diffusion of impurities in a plane sheet may be applied to a cavity.

SEMI - INFINITE MEDIUM

Now we consider the behavior of getter material in niobium. It is to expect, that the penetration depth of getter material in niobium is not very large, in any case much less than the thickness of the Nb sheet. Therefore a model of diffusion in a semi-infinite medium is appropriate. We suppose: - the Nb surface is kept at a constant concentration, C_S with the initial concentration being zero throughout the medium. We need a solution of (2) satisfying the boundary condition

$$C = C_S, \quad x = 0, \quad t > 0$$

and the initial condition

$$C = 0, \quad x > 0, \quad t = 0$$

After application of the Laplace transformation /2/ the solution is given by

$$\frac{C}{C_s} = erfc\frac{x}{2\sqrt{Dt}} \qquad (8)$$

where $erfc(z) = 1 - erf(z)$ and

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z EXP(-\eta^2)d\eta$$

a standard mathematical function - the error function. The erf function has been extensively calculated and corresponding values are given in standard tables.

Unfortunately we don't have reliable information about the diffusion coefficient of titanium and other promising getters (for instance Y, Zr, Hf) in Nb with RRR=300. It is possible to find some data about diffusion coefficients of mentioned metals in Nb, their differ is remarkable and depend on purity and structure state of Nb. Calculations of penetration profile (C/Cs as function of x), which are made by applying the dates of works /10/ (small amount of impurities) are shown in Fig. 9 - 11. It is to be noted, that the penetration depth is not large (about 5µm). For Ti and Zr the penetration depth is minimal in the frame of this point of view.

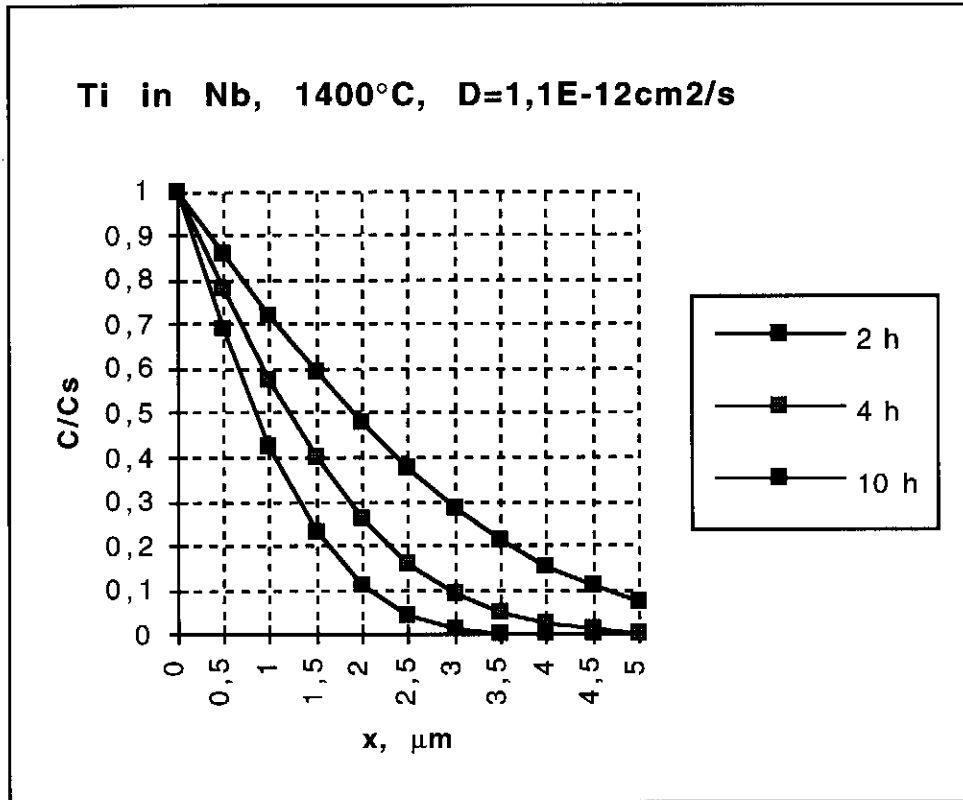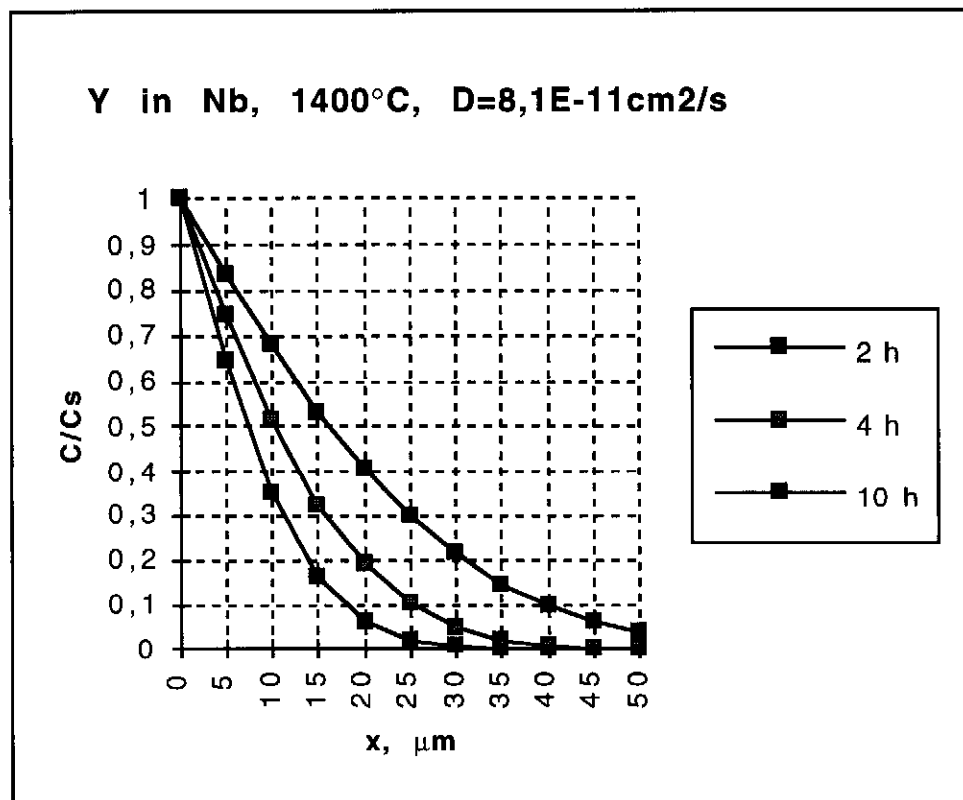**Fig. 9 Penetration profile of Ti in Nb**

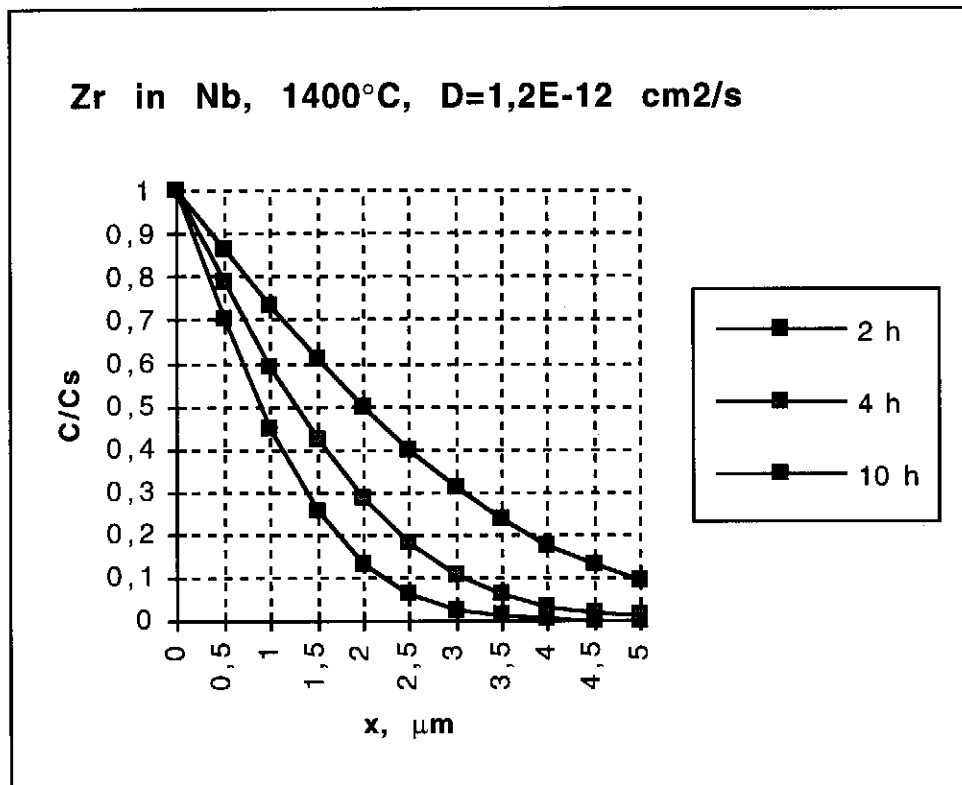**Fig. 10 Penetration profile of Y in Nb**

Fig. 11 Penetration profile of Zr in Nb

CONCENTRATION DEPENDENT DIFFUSION. SEMI- INFINITE MEDIA

The mathematical solutions of problems where the diffusion coefficient is taken as a constant were presented above. A case of special interest for us is that one in which the diffusion coefficient depends on the concentration of the diffusing substance. Fig. 12 can explain this situation. Of course, it is to expect a higher concentration of getter material near to the Nb surface than far away from it. This means that the diffusion coefficient (it depends on the concentration) has a dependence on the penetration depth into the medium. In this case such a dependence is not negligible.

A number of methods have been developed to obtain numerical solutions in this complex situation. One type of diffusion coefficient dependence, namely exponential dependence is suited for us.

If a substance diffuses from the interior of a sample with uniform initial concentration Co to the surface (or vice versa) we need the solution of (3) with the initial and boundary conditions

$$C = C_o, \qquad x > 0, \qquad t = 0,$$

$$C = C_s, \qquad x = 0, \qquad t > 0,$$

where x is the distance from the surface and Cs is the surface concentration for t > 0.
We assume that D is given by

$$D = D_s EXP\{\beta(C - C_s)\} \ ,$$

where D_S is the diffusion coefficient for the surface concentration C_S.

Wagner /11/ has given the method of dealing with the diffusion coefficient which varies exponentially with concentration. After inserting the auxiliary variables

$$y_s = \frac{\frac{1}{2}x}{\sqrt{D_s t}} \qquad (9)$$

$$c = \frac{C - C_s}{C_0 - C_s} \qquad (10)$$

$$\gamma = \beta(C - C_s)$$

into (3) it is obtain

$$\frac{d}{dy_s}(e^\gamma \frac{d\gamma}{dy_s}) + 2y_s \frac{d\gamma}{dy_s} = 0$$

and with the help of the new auxiliary variable

$$u = e^\gamma$$

we have

$$u\frac{d^2u}{dy_s^2} + 2\frac{du}{dy_s} = 0$$

A solution of the transformed equation, which satisfies the boundary conditions is obtained by numerical integration in /2/.
The concentration C at any distance x and any time t follows from (10)

$$C = C_s + (C_0 - C_s)c$$

and y_S is given by (9).

It was possible to find in literature the diffusion coefficients of Ti for two different concentrations in Ti-Nb alloys at 1300°C (10% Ti in Nb: D= 3,48 $\cdot 10^{-11}$cm^2/s and 90% Ti in Nb: D=3,8.10^{-10}cm^2/s). The results are represented in Fig. 13 and 14.

It should be noted, that for example after heating at 1400°C for 4 hours the penetration depth is approximately 100μm. This conclusion is in agreement with experimental results obtained by means of SIMS (Secondary Ion Mass Spectroscopy) /12/ and AES (Aueger electron spectroscopy) /13/ for Nb with the same annealing parameters.

Furthermore we are in a position to draw a useful conclusion from our calculations. The comparison of Fig. 2,13,14 shows, that the same results of Nb refining from oxygen can be achieved for example after its titanisation during 4 hours at 1400°C or after 8 hours at 1200°C, but the penetration depth is different. In the first case it is roughly 100μm, and in the second case only 25 μm. This means we can, in principle, get satisfactory refining from impurities and relatively small penetration of getter material in Nb by correct choice of the heating parameters.
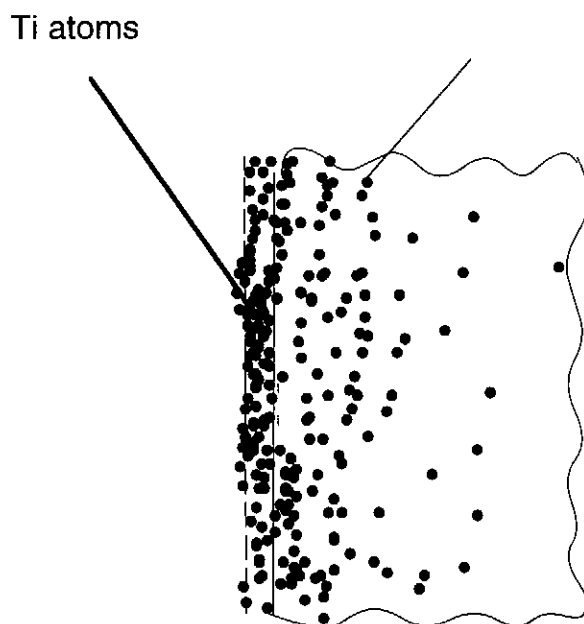
Ti atoms

Fig. 12
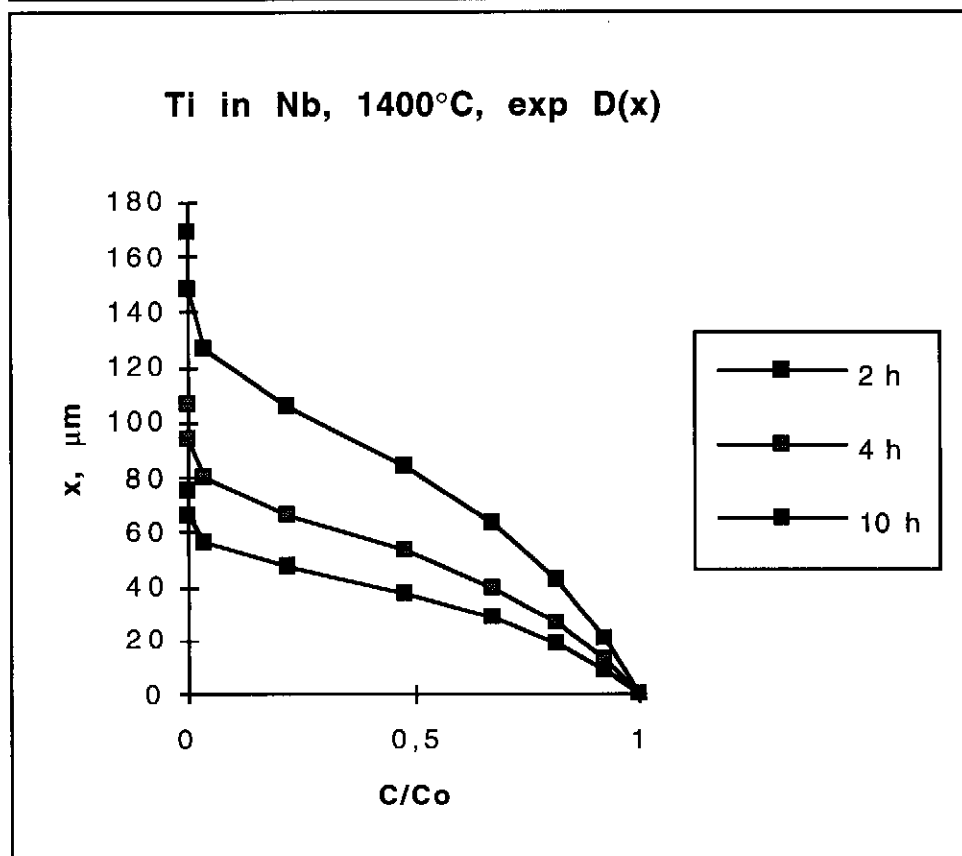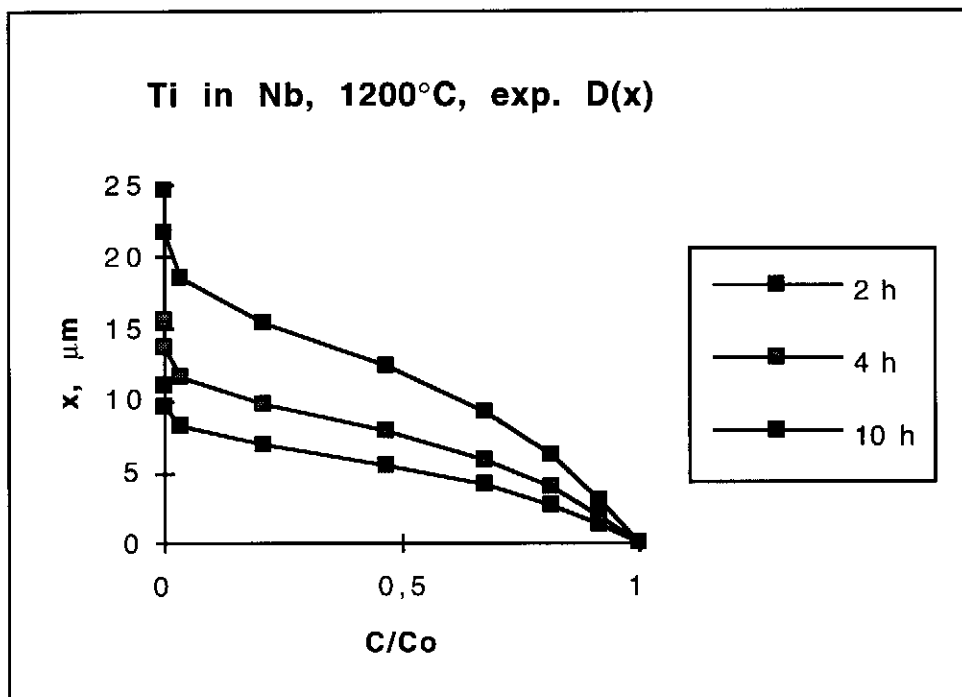The Ti distribution in Nb during the high temperature treatment

Fig. 13-14 Penetration profile of Ti in Nb in case of concentration dependent diffusion

THICK FILM SOLUTION

Actually it is not necessary to sputter Ti onto the Nb surface during heating. It would also be very interesting to consider the case that the appropriate layer of getter is deposit onto the Nb surface before the treatment. Then we have a definite thickness of getter layer which is changeable during the high temperature treatment because the getter penetrates into the Nb. The question is, whether such a procedure can be successful.

It is easier to consider the case of the film sandwiched between two semi-infinite bars. The film occupies the space $-h < x < h$ and the bars occupy $-\infty < x < h$, $h < x < \infty$ respectively. The picture is symmetrical relative $x=0$. The boundary conditions may therefore be expressed by $t=0$

$$C=C_0; \qquad -h < x < h$$

$$C=0, \qquad -\infty < x < h, \ h < x < \infty$$

The equation (2) has the analytical solution for this case /14/

$$\frac{C}{C_0} = \frac{1}{2}(erf\frac{h+x}{2\sqrt{Dt}} + erf\frac{h-x}{2\sqrt{Dt}})$$

The calculations are carried out with the annealing conditions 1300°C, 4 hours. The curves $C/C_0(x)$ are shown in Fig. 15. It is clear, that the layer thickness must be not smaller than 30 μm. In this case the quantity of titanium atoms is sufficient for formation of TiO_x, TiN_x and TiC_x compounds on the Nb surface. Even at a 30 μm initial thickness of Ti only 70% Ti remain on the Nb surface after heat treatment, which is already critical.

SUMMARY

The process of Nb refining can be successfully considered by using the second Fick's equation with the appropriate boundary and initial conditions. It allows to understand the main aspects of solid state gettering.

In particular it is possible to get information about the profile of the impurity distribution after gettering, about the amount of impurities leaving the Nb and in this context to calculate the final RRR. This calculations are rather simple and allow

to get the final RRR as function of initial RRR, annealing time, temperature, sheet thickness.
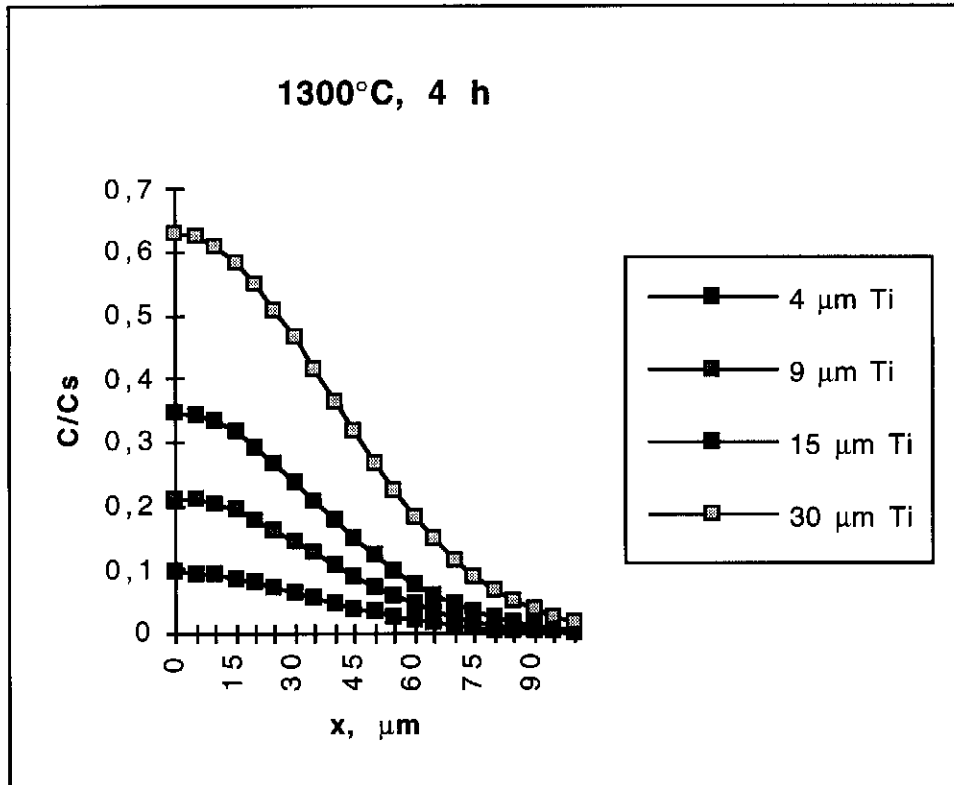

Fig. 15   Penetration profile of Ti in Nb in case of Ti layer on Nb surface

It is also possible to calculate the penetration depth and the getter material distribution in Nb after the treatment.

By choice of the diffusion coefficients from the literature should be taken into account, that the material transportation in the polycrystals occurs both grain volume and grain boundary. Speeds of the volume (Dv) and grain boundary (Dg) diffusion are differ and the experimental diffusion coefficient depends on the grain size, Dv and Dg values. By temperatures near to the melting point the volume diffusion determines the total D, while by rather low temperatures the grain boundary diffusion determines the transportation process. It is difficult to separate the relative influence of both type of the diffusion in most cases. In our case the annealing temperature is by factor two less than the melting point and the grain boundary diffusion is more likely.

As usual the calculation contains some idealization of the real situation. In particular it is assumed, that all those impurities which came from inside to the niobium surface bound compounds with getter material. This means: firstly the amount of the getter atoms on the Nb surface is always bigger than the value of impurity atoms; secondly the getter has a high chemical activity towards the Nb impurities.

The promising getter material (Y, Ti, Zr, Hf) can be analyzed from this point of view.

The first assumption is plausible if the getter vapor pressure during the purification is sufficient. Yttrium has the highest evaporation speed and the necessary vapor pressure of 10^{-5} - 10^{-6} mbar can be achieved already at 1200°C. The evaporation speed of Ti is smaller roughly by a factor of 10, the required pressure is reached at temperature, of about 1350°C. The evaporation speed of Hf and Zr is smaller by a factor of 10^5-10^6 , which makes the gettering procedure possible only above 1700°C.

The analysis of the impurity diffusion in the Nb has shown, that already temperatures above 1200°C and a reasonable annealing duration (6-10 h) are sufficient for improving the RRR by a factor of 2-3. The obstacle for application of these parameters is the insufficient vapor pressure at the main getters. Therefore the idea to increase the evaporation speed by additional heating of the getter, for instance by means of the electrical currency /9 / is very perspective. Application of this procedure would be give the opportunity to reduce the gettering temperature to about 1200°C and bring some advantages, namely a) reduce the penetration depth of Ti, because of the calculation results in this case it is by a factor of 4 smaller b) spread the opportunity of using new getter materials c) make possible the purification of complicated structures without risk of deformation d) reduce the activity of the Nb softening.

The second assuming is the closer to the assumption reality the bigger is the positive difference between the enthalpy getter-impurity compound from one side and niobium-impurity compound from another side. Besides during the heating cycle the getter material should additionally intercept the impurity from the furnace vacuum. The enthalpy of Nb and some getter materials with interstitial impurities was analysed in the reference 15. Yttrium is most effective in regard to purification from oxygen, but it is not in a position to remove carbon from Nb. Titanium is 10 times cheaper than yttrium, can remove most of all impurities, but has a average affinity to the main interstitial impurities. In principle the last point can mean, that the time of solid state gettering procedure is limited not by the time of impurity diffusion from inside to the surface, but by the kinetic of the reaction between Ti and impurity components, which is hardly known now. From this position the extension of the gettering time can be more favorable. Hafnium and zirconium have a better affinity to the main impurity, than titanium, nevertheless they are not applied in practice because of low vapor pressure.

For conclusion it is also worth to note that the achievement of high gradients frequently is not limited by small RRR of the whole material, but by some spots with small RRR present in the Nb even at rather high average RRR values. The annealing

at the high temperatures itself as a part of the solid state gettering procedure improves the homogeneity of the metal (distribution of the components becomes more unified) which has a positive influence on the thermal stability (quench).

ACKNOWLEDGMENTS

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