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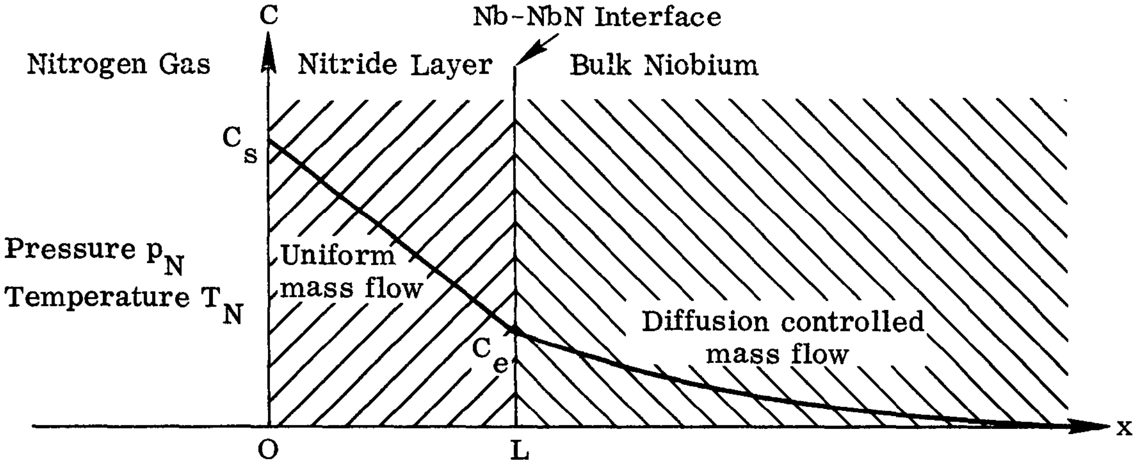
THEORY AND SUGGESTED EXPERIMENTAL PROCEDURE FOR THE PRODUCTION OF A NITRIDE LAYER ON NIOBIUM

Objectives

In this note a procedure is suggested for producing a layer of niobium nitride on the surface of a niobium rf cavity or accelerating structure. Hopefully such a layer, on the order of 100 angstroms thick, might stabilize the surface of the cavity or structure against degradation by oxidation or exposure to other contaminants. Whether this is in fact the case must be decided by appropriate rf cavity measurements. The effect of such a nitride layer on Q and breakdown fields is also open to question. Since niobium nitride is a superconductor, there is reason to hope that the cavity parameters will not be degraded significantly by a layer of the proposed thickness.

Theory

The objective in this section is to calculate the dependence of the thickness of the niobium nitride layer on temperature, exposure time to nitrogen gas, and the gas pressure. The development given here is based on a previous calculation by Pasternak.[1] A sketch showing a nitride layer with thickness L on bulk niobium is given below. The graph shows schematically how the concentration C of dissolved nitrogen varies with depth in the nitride layer and in the underlying metal.



We assume initially that the nitride layer has zero thickness and that the concentration of nitrogen gas in the bulk niobium is also zero. At time t=0 nitrogen gas at pressure p_N is introduced in the region to the left of the metal surface which lies at x=0. At some later time t the nitride layer has a thickness L. Gas diffusing through the layer arrives at the boundary at x=L, where part of the gas reacts with niobium adjacent to the boundary to form more nitride, and part diffuses on into the underlying niobium metal. Thus the boundary moves slowly to the right with velocity dL/dt. Let M be the total mass of nitrogen per unit area which lies to the right of a plane in the nitride layer. According to the law of diffusion, the mass flow per unit area per unit time is proportional to the concentration gradient. We then have

$$\frac{dM}{dt} = -D_1 \frac{dC}{dx} , \tag{1}$$

where D_1 is the diffusion coefficient for nitrogen in the nitride layer. Let C_e be the equilibrium nitrogen concentration at the NbN-Nb interface for the reaction

$$\mathrm{Nb} + \frac{1}{2} \mathrm{N}_2 \rightarrow \mathrm{NbN} \quad .$$

If we now assume that dL/dt is small, and if we assume further that the concentration is always equal to C_s at the surface (x=0) and C_e at the interface (x=L), then the mass flow must be nearly uniform throughout the layer. If this is so, then dC/dx is a constant independent of x, and C as a function of x is a straight line with negative slope. Equation (1) can then be written

$$\frac{dM}{dt} = \frac{D_1(C_s - C_e)}{L} \quad . \tag{2}$$

Now let M_1 be the mass of that part of the gas which has diffused into the bulk niobium beneath the nitride layer. From the solution to the diffusion equation, this mass flow will follow the rate [see Appendix,* Eq. (A-3)],

$$M_1 = 2C_e \, (D_2 t/\pi)^{1/2} \tag{3}$$

Here D_2 is the diffusion coefficient for nitrogen in niobium. We again assume that dL/dt is small so that the usual relations apply for the diffusion of a gas into a metal from a stationary surface.

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*In the Appendix to this note, the solution to the one dimensional diffusion equation and some related expressions are given for convenience.

The mass of gas incorporated in the nitride layer is

$$M_2 = \rho L \tag{4}$$

where ρ is the fractional density of nitrogen in the NBN compound. The total mass of gas in both the nitride layer and underlying bulk niobium is

$$M = M_1 + M_2 = \rho L + 2C_e (D_2 t/\pi)^{1/2} \quad .$$

Using this relation to eliminate L in Eq. (2) we obtain

$$\frac{dM}{dt} = \frac{\rho D_1 (C_s - C_e)}{M - 2C_e (D_2/\pi)^{1/2} t^{1/2}} \quad .$$

The solution to this equation is*

$$M = \left\{ \left[2D_1 \rho (C_s - C_e) + C_e^2 D_2/\pi \right]^{1/2} + C_e (D_2/\pi)^{1/2} \right\} t^{1/2} \tag{5}$$

At the temperature contemplated for nitridation, we will later show that the rate at which gas diffuses into the metal will be very small compared with the rate at which gas is incorporated into the nitride layer. In this case $C_e^2 \ll \rho C_s$ and Eq. (5) reduces to

$$M \approx (2D_1 C_s \rho)^{1/2} t^{1/2} \quad . \tag{6}$$

We see that the total gas uptake is proportional to the square root of the exposure time.

The concentration C_s will depend on temperature and pressure approximately** as

$$C_s \sim p_N^{1/2} \exp (C_1/T) \quad .$$

The diffusion coefficient D_1 is also an exponential function of temperature,

$$D_1 \sim \exp (-C_2/T) \quad .$$

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*The solution as given by Pasternak[1] is incorrect.

**An expression of this form is valid (e.g., see attached Fig. 3 from Fromm and Jehn[2]) for the solution of nitrogen in niobium, and we assume it will be approximately valid for nitrogen in niobium nitride.

We can therefore write Eq. (6) in the form

$$M \sim p_N^{1/4} \exp(-C_3/T)\ t^{1/2} \quad .$$

Experimental data giving M as a function of temperature and pressure is shown in the attached Figs. 1 and 2 taken from the report by Pasternak.[1] Figure 1 shows that the $t^{1/2}$ dependence is verified, at least for times that are not too long. The data are plotted as a function of 1/T in Fig. 2, showing the expected exponential dependence. It is also seen that the one-fourth power dependence on pressure is roughly confirmed. The temperature dependence of these data for $p_N = 5 \times 10^{-6}$ torr can be written conveniently as

$$\log_{10}(M/t^{1/2}) = 19.44 - 2.83 \times 10^3/T(^{\circ}K) \tag{7}$$

Thus at $T = 400^{\circ}C$ ($673^{\circ}K$),

$$M/t^{1/2} = 1.7 \times 10^{15}\ \text{atoms/cm}^2/\text{sec}^{1/2} \tag{8}$$

How many atoms/cm^2 do we need for a nitride layer 100 Å thick? Taking the molecular weight of NbN as 93 + 14 = 107 and the density as 8.4 (Handbook of Chemistry and Physics), we can calculate the molecular density of the nitride, as

$$8.4\ \frac{\text{gms}}{\text{cm}^3} \times 6.0 \times 10^{23}\ \frac{\text{molecules}}{\text{mol}} \ \div\ \frac{107\ \text{gms}}{\text{mol}} = 4.7 \times 10^{22}\ \text{molecules/cm}^3$$

The number of molecules/cm^2 in a layer 100 Å thick is therefore about 5×10^{16}. If the molecular layers are spaced about 5 Å apart, the nitride layer will be about 20 molecular layers thick.

Using the result in Eq. (8), we can now calculate the exposure times needed to produce a 100 Å thick layer of nitride,

$$t = \left(\frac{5 \times 10^{16}}{1.7 \times 10^{15}}\right)^2 = 865\ \text{sec} \approx 15\ \text{min} \quad .$$

Diffusion of Gas into the Underlying Niobium

It will also be of interest to consider the diffusion of gas into the niobium underlying the nitride layer. The gas concentration and gas pressure at equilibrium in the niobium — niobium nitride system are given as a function of 1/T in the attached Fig. 3 from a paper by Fromm and Jehn.[2] The data at equilibrium can be represented analytically by

$$\log_{10} C_e(\text{ppm}) = 7.3 - \frac{5.1 \times 10^3}{T(^oK)} \quad , \tag{9}$$

$$\log_{10} P_e(\text{torr}) = 12.8 - \frac{2.9 \times 10^4}{T(^oK)} \quad . \tag{10}$$

At $T = 400^oC$ we calculate from Eq. (9) that the nitrogen concentration is about one part per million immediately adjacent to the nitride layer.

The diffusion coefficient for nitrogen in niobium is given by Ang[3] as

$$\log_{10} D_2(\text{cm}^2/\text{sec}) = -1.0 - \frac{8.4 \times 10^{-3}}{T(^oK)} \quad . \tag{11}$$

At $T = 400^oC$ this gives $D_2 = 3 \times 10^{-14}$ cm^2/sec. From the Appendix (Eq. (A.2)), the distance at which the gas concentration has fallen to 16% of the value at the interface is given as

$$x_N = 2\sqrt{D_2 t} \quad .$$

Using the above value of D_2 and $t = 865$ sec, we calculate that $x_N = 1 \times 10^{-5}$ cm = 1000 Å. At higher temperatures the penetration distance increases rapidly.

The preceding result points out the fact that for reasonable temperatures and exposure times the distance for diffusion into the metal will be greater than the superconducting penetration depth. The equilibrium concentration will therefore be present throughout the penetration depth, and this concentration should not be too high or the rf properties of the cavity might be degraded. If we assume that up to 10 ppm of nitrogen is acceptable, then from Eq. (9) we calculate that the nitridation temperature must be held to 540^oC or less. Also, at this temperature the exposure time drops to only a few seconds. On the other hand, at 300^oC, the exposure time becomes 10 hours, and at lower temperatures would rapidly become unreasonably long. Thus the nitridation must be done in a fairly restricted temperature range from about 300 to 500^oC.

Similar remarks apply to the gas pressure. For p_N less than about 10^{-7} torr, the partial pressures of contaminants can become a significant fraction of the total pressure. Pressures greater than 10^{-4} torr are difficult to measure and control. Since we plan to make initial tests using induction heating, ionization and rf breakdown will also impose a limitation on the gas pressure. The quality of the nitride layer may be pressure dependent. Finding the optimum pressure would be an objective for future experiments. But as a set of parameters which seem reasonable for a first attempt let us take

$$T_N = 400^{\circ}\mathrm{C}$$

$$p_N = 5\times 10^{-6}\ \mathrm{torr}$$

$$t_N = 15\ \mathrm{min}$$

Experimental Procedure

First the cavity is outgassed at about 1850°C in a good vacuum, following the usual procedure. The temperature is then lowered to the value T_N under ultrahigh vacuum conditions (pressures less than 10^{-9} torr for temperatures less than 1750°C) so that residual gases will not be reabsorbed. It is probably best to drop the temperature rapidly by cutting off the furnace power and allowing the cavity to cool at a rate determined by the cooling curve. When the temperature has reached T_N, sufficient heat is applied to stabilize the temperature at that value. Pure nitrogen gas is then admitted until the pressure reaches p_N. The pressure is held constant at this value for time t_N. The gas source and furnace heat are then cut off, and the cavity allowed to cool to room temperature.

Several refinements of this basic procedure might be considered. For example, it might be reasonable to allow the cavity to sit for several hours in nitrogen gas at one atmosphere pressure at a temperature somewhat below room temperature. At room temperature, the region of the nitride layer immediately adjacent to the surface will then be super-saturated with nitrogen. In the event of an exposure to air, the ability of the layer to absorb oxygen would be reduced, at least for a short time.

Earl Hoyt has suggested that after the nitride layer has been produced by exposure to nitrogen at about 400°C, the cavity might then be heated to a temperature on the order of 1000°C for a brief period (after pumping out the remaining nitrogen gas). The homogeneity and stoichiometry of the nitride layer would perhaps be better after "flashing" the cavity in this manner.

APPENDIX

SOLUTION TO THE ONE DIMENSIONAL DIFFUSION EQUATION

For reference, a brief discussion of the one dimensional diffusion equation and its solution for a semi-infinite medium is given here. The solution presented will be approximately valid for the absorption of gas in a metal structure for which the radii of curvature of the surfaces and the wall thicknesses are large compared to the expected depth of diffusion.

Inside the metal the mass flow rate Γ(atoms/cm^2/sec) is proportional to the concentration gradient and the diffusion coefficient

$$\Gamma = -D \frac{\partial C}{\partial x}$$

The equation of continuity demands, in addition, that

$$\frac{\partial C}{\partial t} = -\frac{\partial \Gamma}{\partial x} = D \frac{\partial^2 C}{\partial x^2} \quad .$$

The solution to this equation for the case C=0 at t=0 for x > 0, and C=C$_0$ at x=0 for t ≥ 0 is,[4]

$$C = C_0 \left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] = C_0 \, \mathrm{erfc}\left[\frac{x}{2\sqrt{Dt}}\right]. \tag{A.1}$$

Here erf α is the error function defined as

$$\mathrm{erf}(\alpha) \equiv \frac{2}{\sqrt{\pi}} \int_0^{\alpha} e^{-\theta^2} \, d\theta \quad ,$$

and erfc(α) = 1 - erf(α) is the complement of the error function. A short table of the error function and its complement is given below.

α	erf(α)	erfc(α)
0	0	1
0.10	0.11	0.89
0.50	0.52	0.48
0.64	0.63	1/e
1.00	0.84	0.16
1.16	0.90	0.10
1.82	0.99	0.01
2.37	0.999	0.001
2.75	0.9999	0.0001
∞	1	0

Some additional useful properties of the error function and its component are:

$$\int_0^\infty \text{erf}\,\alpha\, d\alpha = 1 \qquad \frac{d}{d\alpha}(\text{erf}\,\alpha) = \frac{2}{\sqrt{\pi}}\, e^{-\alpha^2}$$

$$\text{erfc}(\alpha) \approx \frac{e^{-\alpha^2}}{\alpha\sqrt{\pi}} \quad \text{if } \alpha \gg 1 \qquad \text{erf}(\alpha) \approx 2\alpha/\sqrt{\pi} \quad \text{if } \alpha \ll 1$$

From Eq. (A.1) and the preceding Table we see that

$$x = 2\sqrt{Dt} \tag{A.2}$$

gives the depth at which the concentration has fallen to 16% of its value at the surface. Beyond that depth the concentration falls off very rapidly ($\sim e^{-x^2}/x$).

The total mass of gas absorbed in the metal at any given time is obtained by integrating Eq. (A.1) over x,

$$M(t) = C_0 \int_0^\infty \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) dx = 2C_0 \left(\frac{Dt}{\pi}\right)^{1/2} \tag{A.3}$$

The mass flow rate at the surface of the metal is then

$$\frac{dM}{dt} = C_0 \left(\frac{D}{\pi t}\right)^{1/2} \tag{A.4}$$

References

1. R. A. Pasternak, "High temperature oxidation and nitridation of niobium in ultrahigh vacuum," Interim Report, June 1, 1962 to July 1, 1963, Stanford Research Institute, Menlo Park, Calif. (also, AEC Report TID-19489).
2. E. Fromm and H. Jehn, Vacuum 19, 191 (1969).
3. C. Y. Ang, Acta Metallurgica 1, 123 (1953).
4. J. Crank, The Mathematics of Diffusion (Oxford University Press, London, 1957).

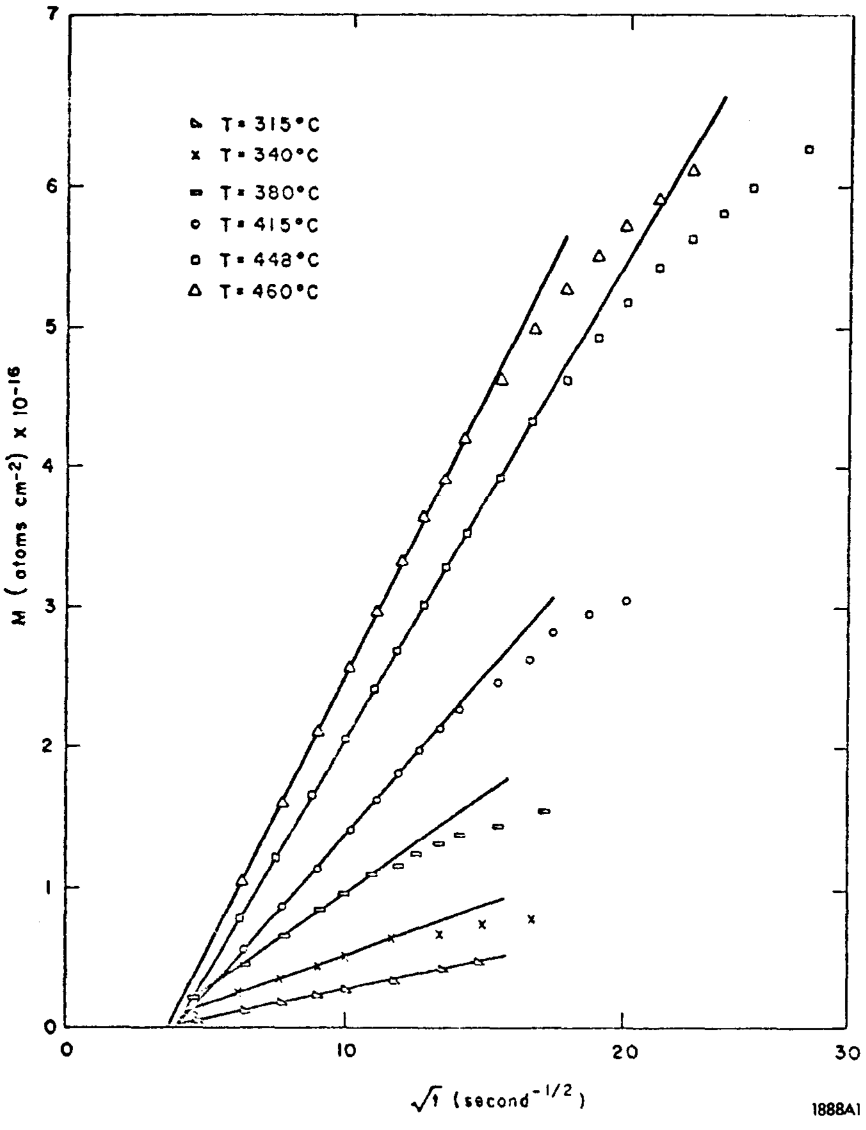

FIG. 1--Sorption of nitrogen by a niobium filament at 5×10^{-6} torr at temperatures between 315 and 460°C (plot of amount sorbed M versus $\sqrt{t}$). After R. A. Pasternak.[1]

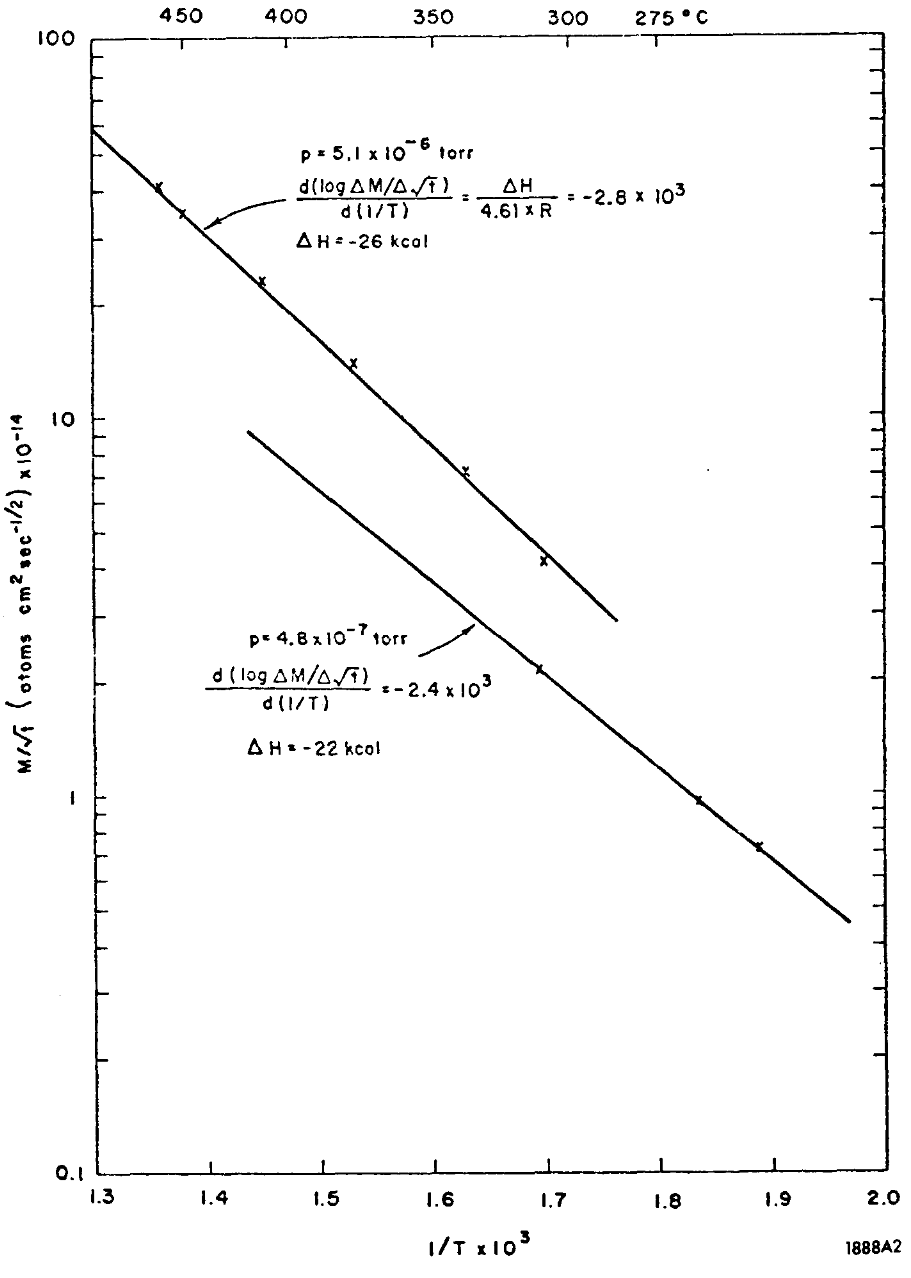

FIG. 2--Diffusion of nitrogen through a niobium nitride layer (plot for evaluation of activation energy). After R. A. Pasternak.[1]

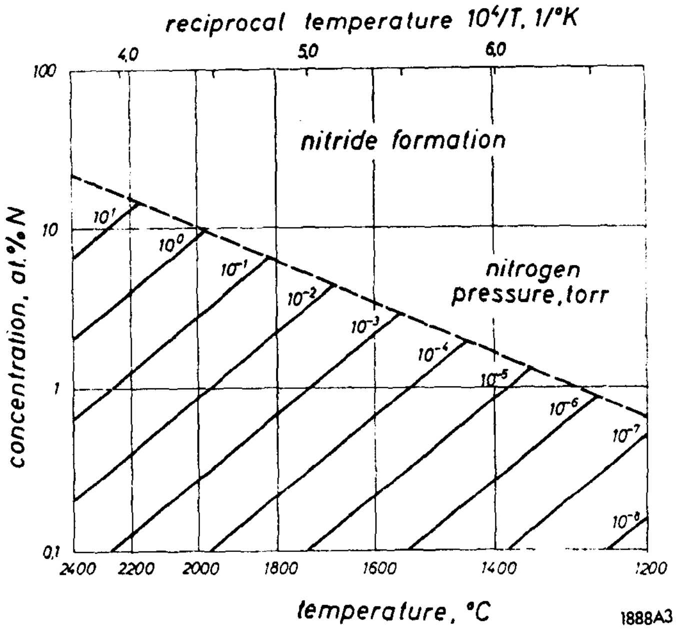

FIG. 3--Temperature-concentration isobars of the N_2-equilibrium pressure in the Nb-N system. After E. Fromm and H. Jehn.[2]