

PERFORMANCE OF Nb- COATED 150 MHz QWR
crippled by
ELECTRON-STIMULATED DESORPTION.

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1. Introduction.

The design of the QWR is modelled on the work by Brennan and Ben- Zvi[1]. The space inside resonator is barely able to accommodate the magnetron cathodes, which include magnetic, cooling and energy supply systems. This caused numerous complications in the realisation of the niobium sputtering project. The first superconducting resonator at ANU was produced in the beginning of 1993. Fig.1 shows dependence of unloaded Q_0 upon accelerating gradient before He conditioning. The energy calibration was determined using a beam from the

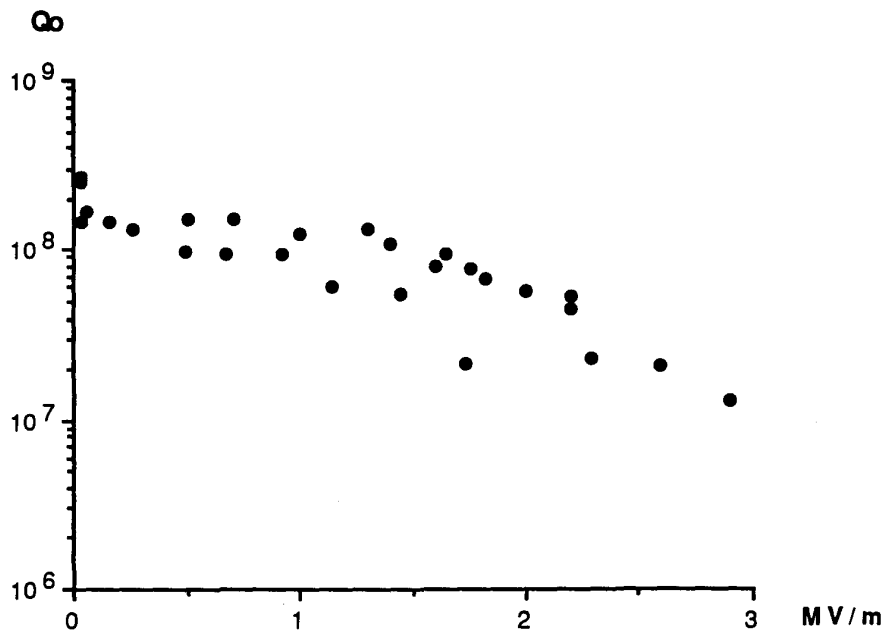


Fig.1. Performance of Nb-coated QWR

14UD Pelletron. It is:

$$E = 0.55 U_{SN} \text{ MV/m,}$$

where U_{SN} is the zero to peak amplitude in volts, of the RF on a probe.

Q was measured by the decay time method at low incident power (45 mW) as the coupling changed from almost zero to critical. At near zero coupling, the decay time is 230-240 ms. The coupling coefficient β was measured from the oscillograms of reflected power [2] and unloaded Q was calculated as

$$Q_0 = (1 + \beta) Q_L \quad \text{with} \quad \beta = 0.10 - 0.15.$$

The stored energy in the resonator was calculated from bead tests on similar resonators [3-4] by scaling the length of the accelerating gap (at $d = 2 \times 4$ cm, $\epsilon \approx 50$ mJ / MV²).

After each time the cryostat was opened, the resonator exhibited strong multipacting at field levels of $\approx 0.03-0.06$ MV/m. Routine conditioning at liquid helium temperature by pulsed RF power as high as 20-30 W for 40-60 hrs, eliminated multipacting completely.

It is clear that performance of this resonator is far from ideal. At 4.2°K, with a transitional temperature 9.2 °K and frequency 150 MHz, the surface resistance of niobium should be smaller than 10 nΩ, whereas data of Fig.1 lead to the intimidating figure of 200 nΩ. The most probable reason for that is oxygen poisoning of niobium during deposition of the film. Before analysing this phenomenon in detail, it is useful to describe the design of the sputtering system and the conditions of the niobium deposition.

2. Design of the sputtering system and deposition procedure.

A magnetron discharge in argon was used for sputtering niobium from a cathode assembly inserted inside the resonator (See Fig.2). Each cathode includes ring of Alnico 5 permanent magnets, water-cooling system, niobium shell and shielded ceramic insulators. To ensure uniform film thickness, the cathode assembly as a whole is scanned along the coax with a speed of 22.5 cm / hr for a full stroke of 18 cm in 48 minutes. In the top scanning position, shown on Fig.2, the horizontal emitting surface of cathode 1 is separated from the top plate by distance $h = 3$ cm.

The rings of magnets in all three cathodes are arranged with their field vertical, so they can be magnetised *in situ* by the same solenoid; the relative directions of magnetisation are shown on Fig.2 by the **B** arrows. The ring-shaped cathode 1 has a closed magnetic circuit using soft-iron pole pieces. They change the direction of magnetic flux to horizontal and concentrate it in an open gap at the top. The cylindrical cathodes 2 and 3 employ an open magnetic circuit producing axial induction alongside the cylindrical emitting surfaces.

Since about 50% of discharge power dissipates on the cathode it must be water-cooled. To avoid shorting of parallel discharge gaps, connecting water tubes are isolated from ground as well as from emitting surfaces. That permits

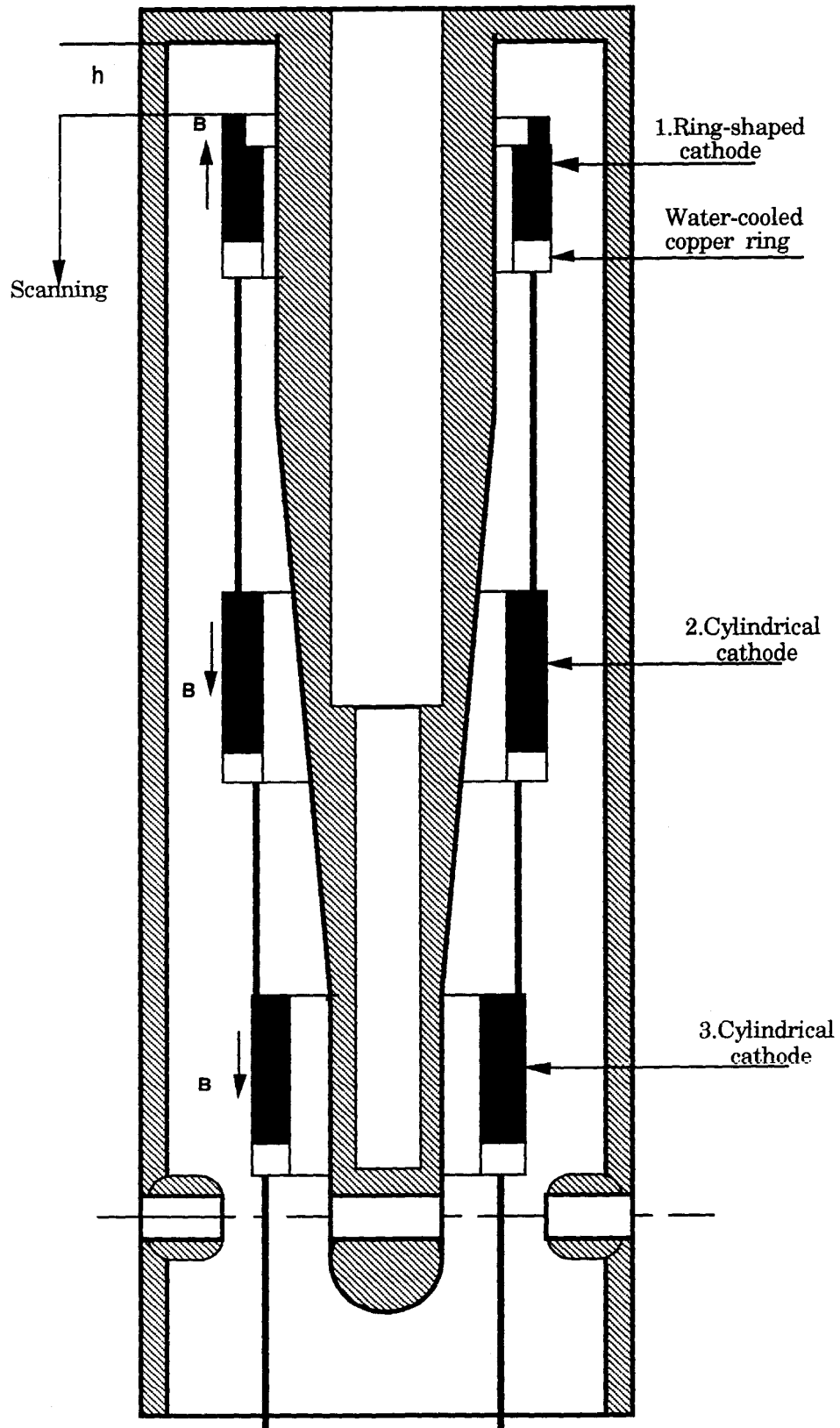


Fig.2. Cross-section of quarter wave resonator with sputtering assembly.

independent ignition of a discharge on each cathode ring. However the gaps on the outer and inner side of the same ring remain connected in parallel. The ignition potential of the outer gap is smaller than that of the inner gap and so discharge ordinarily exists in the outer gap only. A small magnetic field from an external solenoid is used to create additional leakage from electron trap in the discharge area of the outer gap increasing its ignition potential. Switching this solenoid controls on which side of the cylindrical cathode the discharge occurs.

Before sputtering, the copper surface of the resonator was tumble polished, washed with detergent, etched and rinsed. Then resonator was filled with dry nitrogen and transported to a clean room, in which a vacuum system was situated. After thorough baking (150–200 hours at 280–320°C) the residual atmosphere in the system consisted mostly of hydrogen (60–75 %) and total pressure is equal to $(0.5-1) \times 10^{-8}$ Torr. The sputtering procedure is shown in Table 1.

SPUTTERING PROCEDURE

Table 1

Cathode	Area of deposition	Argon pressure mTorr	Discharge current A	Voltage V	Sputtering time	External solenoid
1. Ring-shaped	Horizontal top plate + upper 20cm of both conductors	3–5	1.5–1.7	660–680	2.1 hrs: 30 min at the top position* + 2 strokes	Off
2 and 3 Cylinders	Outer wall	1	1.2–1.3	310–330	3.2 hrs: 4 strokes	Off
2 and 3 Cylinders	Inner stub	5	1	340–360	1.6 hrs: 2 strokes	On

* $h=30 \pm 2$ mm

"High Purity" argon was used for the discharge. According to its certificate it may contain up to 10^{-5} parts by volume of water, CO and O₂. At working Ar pressure, this amounts to a partial pressure of 5×10^{-8} Torr. To reduce this figure (by factor of 5–10 at least), the argon was passed through a moisture trap and then introduced into the vacuum system through a titanium sublimation pump. It is reasonable to assume, that before discharge ignition, the partial pressure of the combined oxygen-containing components of the residual atmosphere does not exceed $(0.5-1) \times 10^{-8}$ Torr. These figures are similar to those measured in CERN [5].

The superconducting quality of a Nb film depends strongly on its oxygen concentration, which should be less than 1 atomic % to achieve a good performance[7]. Oxidation of niobium occurs during crystallisation of the film, when deposited Nb atoms meet adsorbed oxygen-containing molecules on a substrate surface. After stabilisation of the crystalline structure, the film is insensitive to oxygen poisoning even at atmospheric pressure [6].

The amount of oxygen in a film is determined by a balance between the adsorption flow of oxygen from the residual atmosphere and the deposition rate of niobium. A rough estimation of this balance shows that at the room temperature, oxygen pressure $\approx 1 \times 10^{-8}$ Torr and the deposition rate $\approx 1 \mu\text{m/hr}$, the oxygen concentration in the film is to be less than 0.1 atomic %. In reality, it exceeds 1% in the films deposited in CERN [8] at the much higher rate and possibly reaches 3–5% in the ours.

This inconsistency in two experimental facts: low pre-discharge partial pressure of oxygen and high oxygen content in the niobium films encouraged the search for the sources of surplus oxygen. This led to the investigation of stimulated desorption which occurs as soon as the sputtering starts and the surface of the copper substrate and cathode become exposed to intense discharge impact.

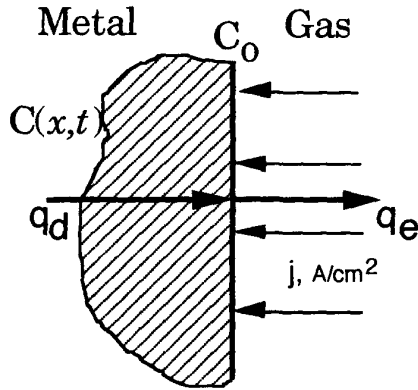
3. Oxygen desorption under electron impact.

The phenomenon of stimulated desorption exists because of specific chemical features of oxygen. Unlike hydrogen, nitrogen and inert gases, oxygen dissolved in the metal substrates can not be removed by high temperature baking. The reason is that a thin oxide layer on the surface creates an inward-directed gradient of the oxygen concentration in metal. That blocks oxygen diffusion toward the metal-gas boundary and its desorption.

The binding energy of the most oxides exceeds 6-10 eV, so their dissociation demands either hard radiation or an energetic particle impact. Even partial dissociation of the oxide layer immediately results in intense desorption and reduced surface concentration of oxygen. That starts diffusion of dissolved oxygen to the surface and continuous desorption.

A gas discharge creates a whole arsenal of stimulated desorption missiles. Electrons and negative ions strike the anode, positive ions fall upon the cathode, ultra-violet photons bombard all surfaces in view of the discharge as do neutral atoms, sputtered from the cathode. All these phenomena lead to massive desorption of oxygen. To evaluate the order of magnitude of the resulting partial pressure during the niobium sputtering, we concentrated on the clearer part of this immensely complicated picture and analysed the effect of the electron bombardment only.

The semi-quantitative description of the desorption under electron bombardment was made 20 years ago by one of the authors [9].



The gas flow from the electron-bombarded surface is determined by the diffusion equation.

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

with the boundary condition which results from the continuity equation:

$$q_d = q_e; \quad -D \frac{\partial C(0,t)}{\partial x} + 0.175 \beta \frac{J}{F} \frac{C(0,t)}{C_0} = 0,$$

where:

- q_d is the gas flow diffusing from metal, Torr l / cm² s,
- q_e is the gas flow desorbed by electrons, Torr l / cm² s,
- D is the diffusion coefficient, cm² / s,
- β is the desorption efficiency, mol/el,
- J is bombarding current, A,
- $C(x,t)$ is the gas concentration, Torr l / cm³,
- F is the bombarded area, cm².

With the uniform initial condition

$$C(x,0) = C_0,$$

the solution of the diffusion equation gives the time dependence of the desorption gas flow:

$$Q(t) = 0.175 \beta J \psi(\eta \sqrt{Dt}), \quad (1)$$

where the function

$$\psi(z) = \exp z^2 (1 - \text{erf } z). \quad (1a)$$

$$\text{At } z < 0.3, \psi(z) \cong 1 - z \text{ and at } z > 3, \psi(z) \cong \frac{1}{\pi \sqrt{z}}. \quad (1b)$$

The gas exchange constant is:

$$\eta = \frac{0.175 \beta J}{C_0 D F}, \quad (2)$$

where F is a bombarded area, cm² and Q is measured in Torr l / s.

Stimulated desorption is regulated by both dissociation and diffusion. So in the initial phase of bombardment ($\eta \sqrt{Dt} < 0.3$), the desorption rate is proportional to current, but with time, this dependence gets weaker until it almost disappears during the diffusion phase ($\eta \sqrt{Dt} > 3$). The degassing rate then is:

$$Q_d = C_o F \sqrt{\frac{D}{\pi t}} \quad (3)$$

Experimental studies of electron-stimulated desorption confirm that the amount of released gases (it is mostly oxygen-containing gases: O₂, CO, CO₂ and water) can not be appreciably reduced by high-temperature baking. At relatively low temperature (300–600 °K) where diffusion is slow, all processes leading to stimulated desorption take place in the thin surface layer with its high concentration of oxygen, carbon and other contaminants.

The parameters of stimulated desorption from oxygen-free copper after baking at 400 °C were calculated from experimental degassing curves [9]:

$$\beta = 3 \cdot 10^{-3} \text{ mol / el}, \quad C_o = 450 \text{ Torr l / cm}^3, \quad D = 10^{-19} \text{ cm}^2 / \text{s}.$$

The bombarded area on a resonator wall is a mirror image of the emitting surface. For the cylindrical cathode it is a ring with length $2b = 6 \text{ cm}$. The distribution of current density, in the first approximation, is uniform. The pumping speed of the sublimation pump ($\approx 1000 \text{ l/s}$) reduces, inside resonator volume, to $S = 300 \text{ l/s}$.

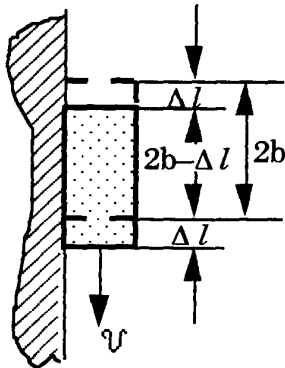
Then the initial burst at the discharge ignition ($t = 0$) of a current of 2.5 A is as large as

$$p_o = \frac{Q_o}{S} = \frac{0.175 \beta J}{S} = 4 \times 10^{-6} \text{ Torr}. \quad (4)$$

Fortunately, after a short transition time t_o defined by eqs.(1b) and (2) ($t_o \approx 0.05 \text{ s}$ in our conditions), the diffusion processes prevail and the degassing rate reduces quickly according to equation:

$$p_d = \frac{Q_d}{S} = \frac{C_o F}{S} \sqrt{\frac{D}{\pi}} \frac{1}{\sqrt{t_o + t}}. \quad (5)$$

When the cathode is stationary, the pressure of oxygen-containing gases reduces below the pre-discharge level in 10-15 minutes (Fig.3). However, as the cathode scans the resonator wall, the bombarded area moves slowly ($v = 0.00625 \text{ cm / s}$), exposing to electron impact new parts of the copper wall.



The newly bombarded area is equal to:

$$\frac{F}{2b} \Delta l = \frac{F}{2b} v \Delta t$$

Desorption from that area consists of two components: the initial phase of desorption and the subsequent diffusion phase. The first term is time-independent and equal to :

$$\frac{p_o v}{2b} t_o.$$

The second term is similar to eq. (5):

$$p_d(t) = \frac{C_0 F}{2b S} \sqrt{\frac{D}{\pi}} \int_0^t \frac{v dt}{\sqrt{t_0 + t}} = \frac{C_0 F}{2b S} \sqrt{\frac{D}{\pi}} 2v (\sqrt{t_0 + t} - \sqrt{t_0}).$$

The area on the tail of the ring is:

$$\frac{F}{2b} (2b - v t).$$

Taking into account the degassing rate from this area one can find the time dependence of the partial pressure of oxygen, created by electron impact from the moving cathode:

$$p(t) \cong p_0 \frac{v}{2b} t_0 + \frac{C_0 F}{2b} \sqrt{\frac{D}{\pi}} \left(\frac{2b - vt}{\sqrt{t_0 + t}} + 2v \sqrt{t} \right). \quad (6)$$

Eq. (6) is valid until $2b - vt \geq 0$. Thereafter the desorption rate remains constant till the end of the first scan.

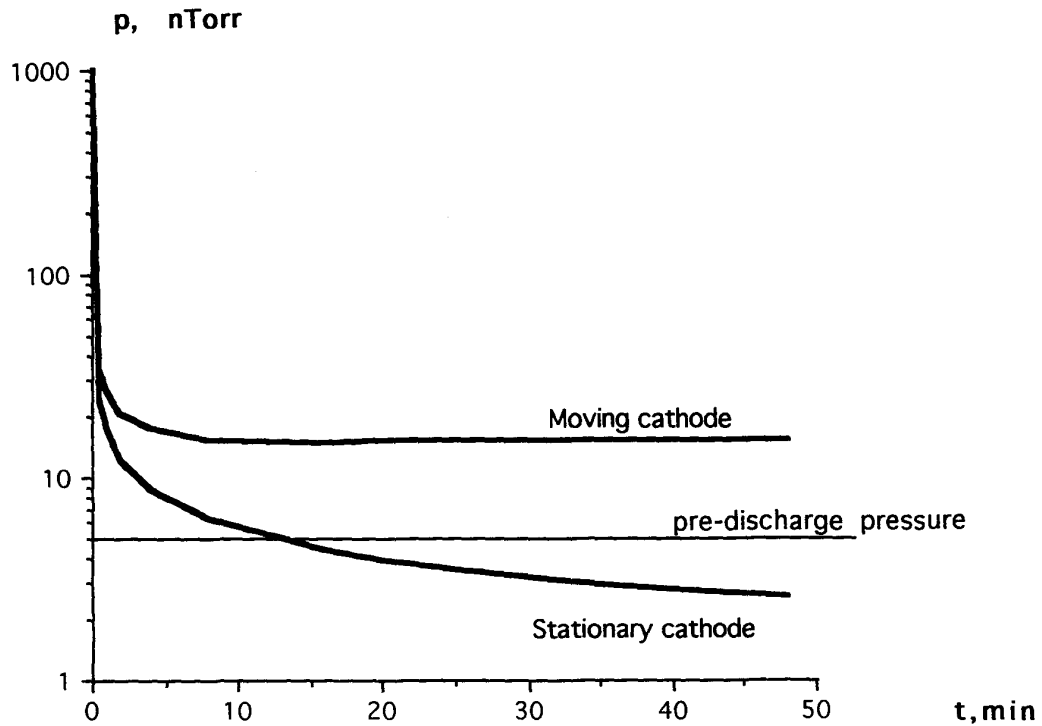


Fig.3. Pressure of oxygen-containing gases released by electron impact on resonator wall during deposition of Nb film. ($J=2 \times 1.2$ A)

The curve marked "moving cathode" in Fig.3, shows the results of the calculations. In 2 to 3 minutes after the initial peak, the pressure stabilises at

≈ 20 nTorr. This exceeds the pre-discharge level by a factor of 3–5. During second scan the desorption rate slowly reduces proportionally to $t^{-\frac{1}{2}}$.

Of course, these calculations show a very simplified picture. Other than taking into account electron impact only, it was assumed as well, that the substrate surface is pure copper and that it remains unchanged. In reality, sputtered niobium quickly covers the copper, thus influencing the dynamics of desorption. The full interaction of the surfaces of the resonator and the cathode assembly with all the energetic components in the discharge, probably results in considerably higher oxygen pressure than shown on Fig.3 – up to an order of magnitude or even higher.

Because oxygen desorption and Nb deposition occur in the same place and at the same time, it is not too gross an overstatement to say, that the niobium film is formed in a cloud of toxic gases. That makes the poisoning effect even stronger.

4. Deposition rate of niobium.

A critical deposition rate of niobium was adopted, rather arbitrarily, equal to $2 \mu\text{m/hr}$ on the basis of CERN data [5,6] and a rough evaluation of the adsorption flow of oxygen from the residual atmosphere.

The geometry of the entire inner surface of the resonator is quite complicated and so the deposition rate is far from uniform. The shape and position of the cathodes, distances between emitting surfaces and substrate, as well as the discharge parameters, had to be chosen in such way, that over the whole surface of resonator, the deposition rate exceeds the critical magnitude. That had been done using a relatively simple and reliable method of calculation.

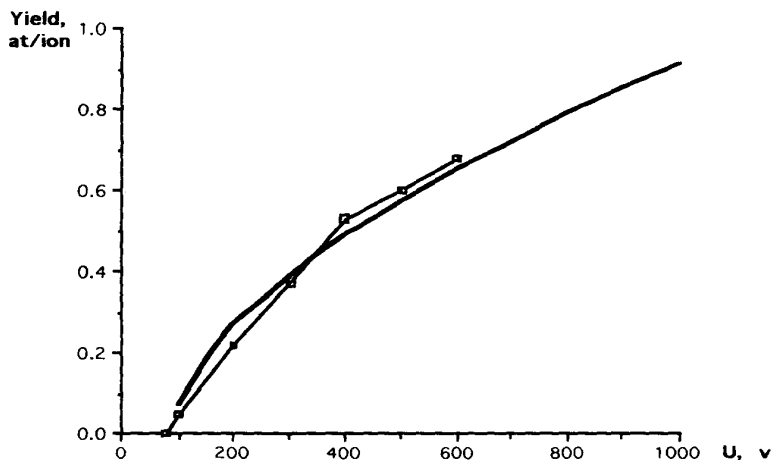


Fig. 4. Sputtering yield of Nb in Ar

Experimental data on the sputtering yield of Nb in an Ar discharge [10] are shown on Fig.4. They can be approximated by an empirical formula:

$$\gamma = 0.025 j_c (U - 90)^{0.58} \mu\text{m} / \text{hr} ,$$

where γ is sputtering rate, U is discharge energy, V , and j_c is the discharge current density in the cathode, mA/cm^2 .

The angular distribution of sputtered Nb is described by Knudsen law [11].

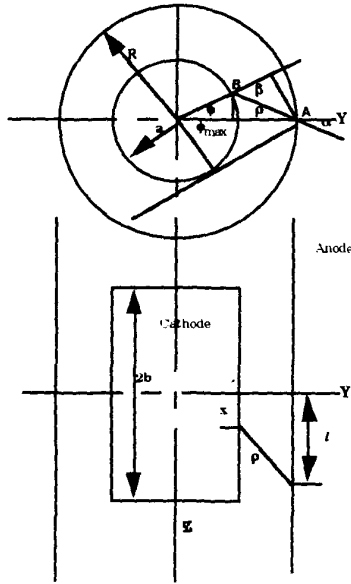


Fig.5. Schematic diagram of a simple cylindrical cathode in hollow co-axial anode.

The deposition rate from an infinitesimal surface source dS_c onto a small area around arbitrary point A on a substrate is:

$$d\delta = \frac{m}{\pi S_c} \frac{\cos \alpha \cos \beta}{\rho^2} dS_c, \quad (7)$$

where:

- ρ is a distance between dS_c and point A,
- α is two-dimensional angle between ρ and surface element of substrate around point A,
- β is similar angle between ρ and surface element of emitting surface dS_c ,
- m is the full sputtering rate from the cathode.

An integral of eq.(7) gives the distribution of the deposition rate along the substrate. For example, the running coordinates of emitting surface of the cylindrical cathode are length x and central angle ϕ , as it is shown on a schematic diagram Fig.5.

Then

$$\delta(l) = \frac{0.05 J (U - 90)^{0.58}}{\pi^2 b} \int_{-b}^b \int_0^{\phi_{\max}} \frac{\cos \alpha \cos \beta}{\rho^2} \left(1 - \frac{|x|}{b}\right) d\phi dx, \quad (8)$$

where:

- $2b$ is a full cathode length,
- ϕ_{\max} is the coordinate of the extreme point on the emitting surface, visible from the point A,
- l is linear coordinate along the resonator wall,
- J and U are the discharge current and voltage.

The factor $\left(1 - \frac{|x|}{b}\right)$ takes into account reduction of discharge current from the centre to the borders of the emitting surface. The parameters of eq. (8) for the cylindrical cathode may be calculated by the elementary, although rather tedious, geometrical analysis. They are:

$$\rho^2 = a^2 + R^2 + (l-x)^2 - 2aR \cos \phi,$$

$$\cos \alpha = \frac{R - a \cos \phi}{\rho}, \quad \cos \beta = \frac{R \cos \phi - a}{\rho}.$$

Similar expressions were written for different cathode - substrate geometries. Integration was carried out by "Mathematica" software [12].

Fig.6 shows the deposition rate from the ring-shaped cathode in the stationary top position. It is easy to see, that it exceeds the critical magnitude on the whole covered area. The average deposition rate is equal to 4.5 $\mu\text{m/hr}$. Table 2

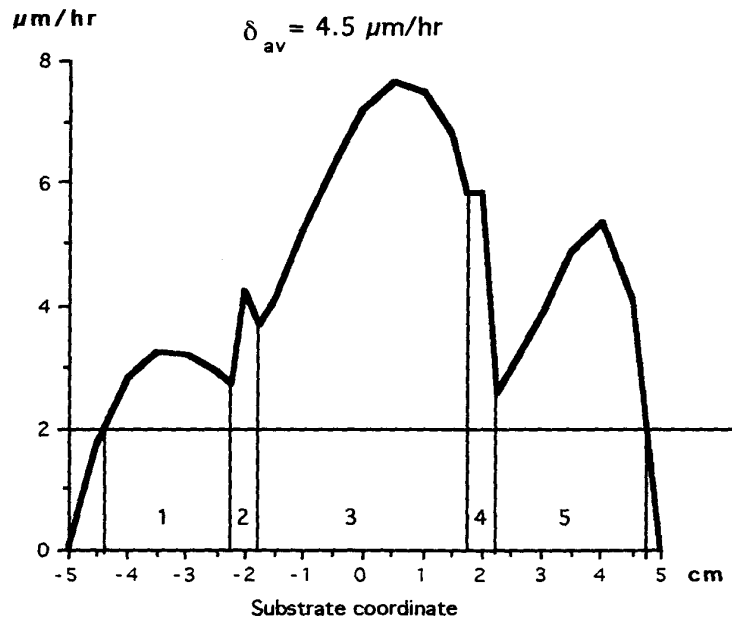


Fig.6 Deposition rate from stationary cathode along the top part of resonator . $h=3 \text{ cm}$, $I=1.6 \text{ A}$, $U=680 \text{ V}$. Sputtering time, 0.5 hr

gives more detail information about sections 1–5 of the top part of the resonator.

PARAMETERS OF THE TOP PART OF THE RESONATOR

Table 2

Section	1	2	3	4	5
	Outer cylindrical wall	Rounded corner. Outer	Horizontal top plate	Rounded corner. Inner	Inner cylindrical wall
Length	2.25 cm	R=0.25 cm	7.5 cm	R=0.25 cm	2.5 cm
Average rate, $\mu\text{m/hr}$	2.5	3.5	5.0	5.0	4.0
Average film thickness, μm	1.25	1.75	2.5	2.5	2.0

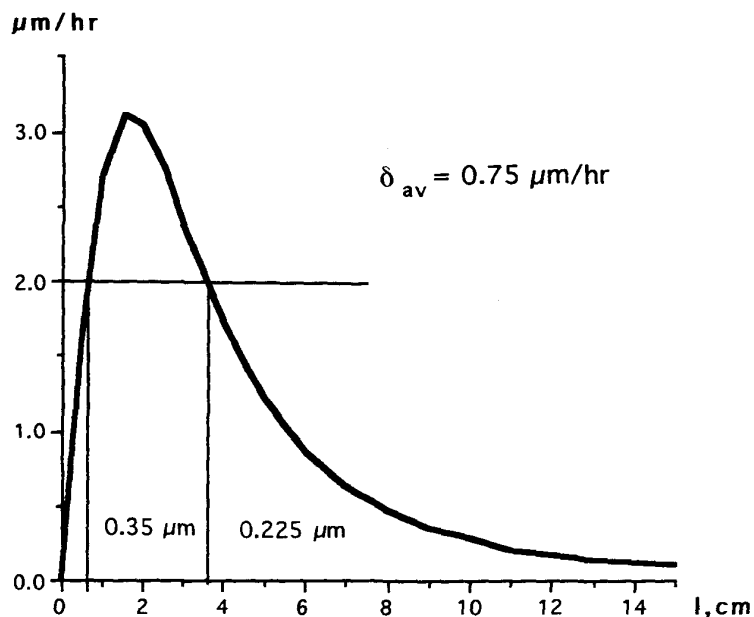


Fig.7 Distribution of the deposition rate from the ring-shaped cathode onto the outer wall. $I=1.6$ A, $U=680$ V.

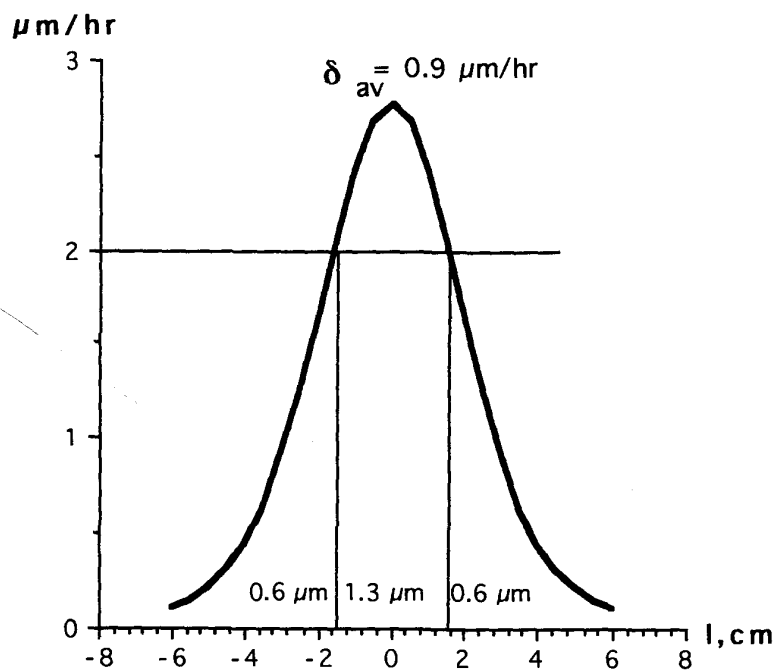


Fig.8 Distribution of the deposition rate from the cylindrical cathode onto the outer wall. $I=1.25$ A, $U=320$ V.

Fig. 7, 8 demonstrate similar curves for deposition from the scanning cathodes onto the outer wall of the resonator. It is evident that these distributions produce less favourable conditions for the creation of superconducting Nb film.

The maximum deposition rate describe by these curves, exceeds the critical magnitude of $2 \mu\text{m/hr}$, but the average is a factor of 2–3 smaller. In the tails of distribution, the probability of oxygen poisoning increases significantly. Up to 50% of the deposited film consists of "bad" niobium, deposited with $\delta < 2 \mu\text{m/hr}$. After several scanning strokes a "sandwich" of good and bad layers is produced. Not surprisingly, the surface resistance of such structures exceeds significantly the theoretical figure for pure niobium. Conditions of deposition onto the inner conductor are similar to that on Fig. 7, 8.

5. Conclusions.

The performance of the niobium-coated 150 MHz QWR can be significantly improved by simply raising the discharge current to the average level used in CERN [5,6]. This corresponds to 3.5–4 A on the ring-shaped cathode and 1.7–2 A on the cylindrical ones. That will increase the percent of "good" Nb in the film to 85-90 as well as allow sputtering time to be reduced to one scan thus eliminating "sandwich effect". Another possibility for improvement is to increase the resonator temperature during deposition to 200–250 °C. That would reduce the residence time of adsorbed molecules on the surface and thus their probability of reacting with a Nb atom. Deposition on a heated surface results in a better characteristics of niobium films [13].

Still, these standard ways of improvement of the Nb-sputtering technology, when implemented, solve only part of the problem. At the best they allow achievement of the level, which the best performers in the field have already reached [13]. Although at low fields this level ensures a surface resistance close to the theoretical value, it rises steeply with RF field inside the resonator. This behaviour is caused by oxygen contaminated "spots" with low transition temperature (or not superconducting at all) inside the niobium film [8]. The average oxygen concentration in such films is as high as 1-2%. The analysis made in this paper shows, that with very high probability, oxygen released due to discharge-induced desorption play the critical role in forming these spots.

Proper surface treatment, reducing significantly the amount of oxygen available on the surface at the start of Nb coating, will dramatically improve quality of the niobium films. In fact, the existing sputtering technology lacks any attempts to reduce discharge- stimulated desorption. In the industrial production of electron tubes, where the problems caused by stimulated desorption were recognised long ago, the basic rule is that all surfaces have to be outgassed at least in the same conditions under which they will be working.

To apply this rule to the sputtering technology, one has to introduce some sort of electron and/or ion bombardment during the process of baking. At first sight, a magnetron discharge in He seems a quite acceptable solution. Desorption in helium and argon discharges has to be almost identical, while the sputtering yield in He discharge is less than 5–10% of that in Ar [14].

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