FEASIBILITIES OF THE METHODS OF ANODE OXIPOLISHING AND ANODIZATION IN THE TECHNOLOGY OF SUPERCONDUCTING CAVITIES

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INTRODUCTION

The practical application of RF superconductivity in accelerator technology requires the development of SC cavities having a large Q-value and capable of operating at a high level of micrfowave power.

The application of very pure SC materials and special treatment techniques helps solve the problem of higher gradients in SC cavities /1-4/.

In our previous articles /5-6/ we have considered various techniques of electrochemical polishing of SC cavities.

The goal of the present report is to present some experimental results on the study of the techniques of anode oxidation and oxipolishing of Nb cavities and samples we have obtained from 1975 until now.

PLAN OF THE REPORT

1. The application of the techniques of anode oxidation and oxipolishing in the production technology of SC cavities.

2. The requirements imposed on the experimental equipment for anode oxidation of SC cavities.

3. The technique of anode oxidation of SC cavities and samples.

4. The methods used to control the working surface of superconductor and the contents of oxide coatings.

5. The application of protective coatings by the technique of anode oxidation.

6. Optimization of the process of anode oxidation of Nb with a view to obtain the working coatings of SC cavities..

7. The study of the kinetics of high-temperature annealing of anodized SC cavities in a tight vacuum.

8. The study of the effect of electrochemical purificatilon of the working surface of Nb from admixitures of heavy elements with the help of oxipolishing technique.

9. The technique of electrochemical purification of the surface Nb layer from tantalum.

10. Conclusions.

1. The Application of Anode Oxidation and Oxipolishing in the Technology of SC Cavities

Our laboratory applies anode oxidation and oxipolishing in the following cases:

1) when it is necessary to transport SC cavities at long distances, e.g. from Protivno to Irkutsk and back. In this case prior to testing the cavities the Nb_2O_5 oxide coating is removed in hydrofluoric acid;

2) during the operation of cavities the anode coating remains the working one on the cavity surface; such cavities are used for stabilization of high-stability RF oscillatiors /7/;

3) if it is necessary to remove the carbon admixture from the working Nb surface. In this case the coating is applied prior to high-temperature ultratight vacuum annealing and is removed in the annealing process /8/;

4) when it is required to remove the admixtures of heavy elements, e.g., tantalum from the working surface of cavities at a depth of 8-10 microns /9-10/.

Of course, having clean rooms of type "100" and "10", transportation containers, very pure Nb and clean electolytes does not always need to apply these techniques. However, such studies and developments may be helpful for reducing the cost of manufacturing SC cavities.

2. Requirements on the Experimental Equipment for Anode Oxidation of SC Cavities

It should be noted that attaining the reproducible parameters of the protective coating or of the working surfaces and the effective purification from the admixtures of heavy elements during oxipolishing face certain technological difficulties.

The point is that anode oxidation is a very complicated process and depends on many techological factors such as the film formation voltage U_f, anodation current density j_a, concentration C, elejctrolyte temperature t° and the expositon time τ in the mode when U = const. In addition to that, the quality of the forming film is affected by the structure properties of the working metal surface (its texture, roughness, graininess) as wsell as by the technological conditions of the anode oxidation process (preliminary electrolyte outgassing, gas environment above the electrolyte).

It should also be noted that each goal mentioned in Section 1 is ahieved only with a certain combination of technological parameters specific for the given case and with the special conditions of oxidation observed.

The specific features of anode oxidation imposed certain requirements on the technological equipment used in this process:

1) the electrolyte bath should be placed into a thermostat that could maintain the electrolyte temperature in the 4-20°C to an accuracy of ± 0.01 degrees;

2) the setup for oxidation should be furnished with:
- systems of preliminary electrolyte outgassing and inert gas bleading-in;
- system of cavity or cathode rotation during anodation;
- special cavity holder ensuring the required movable eleklctric contact and geometric similarity of the cathode and anode.

Figure 1 shows the equipment for anode oxidation of cm-band SC cavities /11/.

Fig. 1. The view of the setup for anode oxidation.

As is seen from this figure, the setup consists of electronics (1) controlling the anode oxidation process, electrolyte bath (2) placed into temperature-controlled volume of ultrathermostat (3).

Figure 2 shows the detailed schematic view of this setup. It also contains the system of oilless pumping out (4) for outgassing the electrolyte prior to anode oxidation and the system of inert gas bleeding-in (5). The unit (6) handling and rotating cavities during treatment is shown.

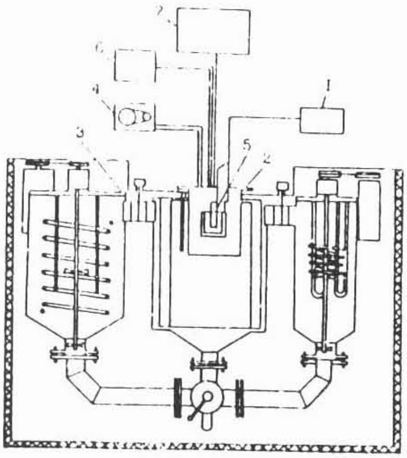


Fig. 2. The structure scheme of the anode oxidation equipment

The Technique of
Anode Oxidation of SC Cavities

In all cases the best results were obtained when anode oxidation was carried out in a mixed mode /12-14/ : first in the galvanosatstic mode until the specified voltage U_f of film formation was attained and then in the mode when U = const.

Figure 3 shows the time - dependences of anodation current density ja and formation voltage U_f.

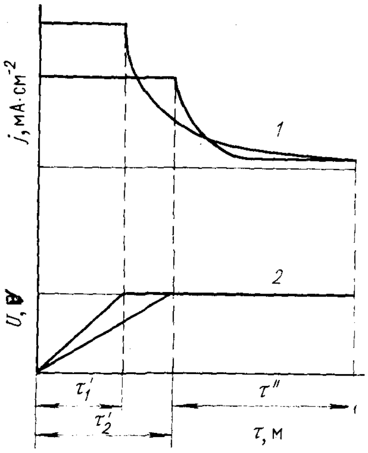


Fig. 3. The time - dependence of anodation current density j_a and film formation voltage U_f /12/.: τ' - time of formation, τ'' - time of expositon

Different purposes of applying the coating dictate the choice of different electrolytes of very pure type based on H_2SO, H_3PO , HNO_3or NH_4OH , having various additives /10/. The combination of the technological parameters of anode oxidation is different in each application case (see Section 1) and was determined as a result of multifactor optimization (see Section 6).

In order to determine the structure of the forming oxide and the conditions for higher-valence oxides to form we have measured the volt-ampere characteristics and plotted the "charging curves" shown in figs. 4 and 5.

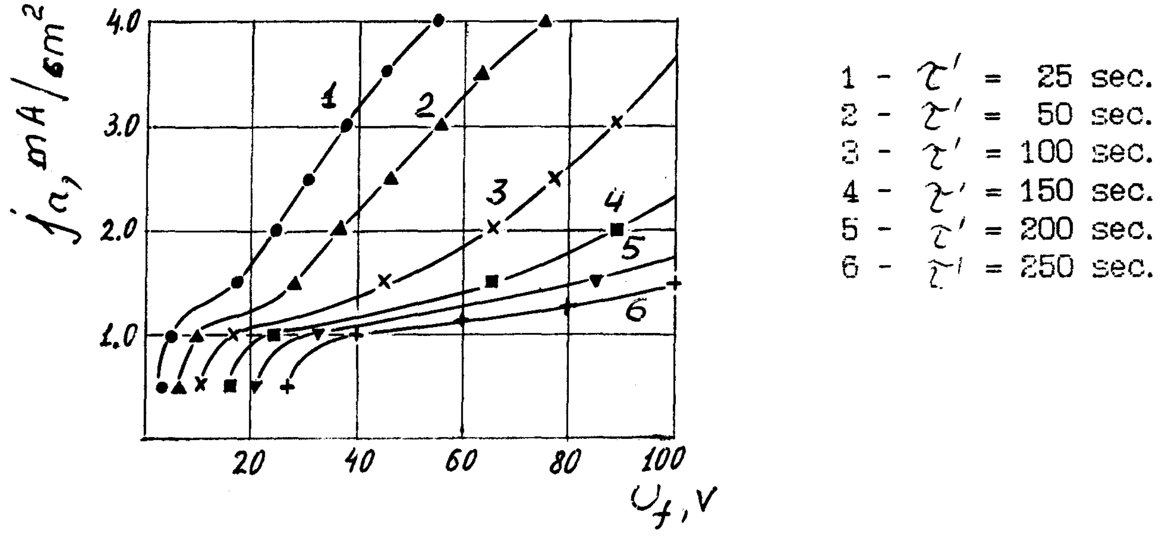


Fig. 4. The volt-ampere characteristics measured during anode Nb oxidation.

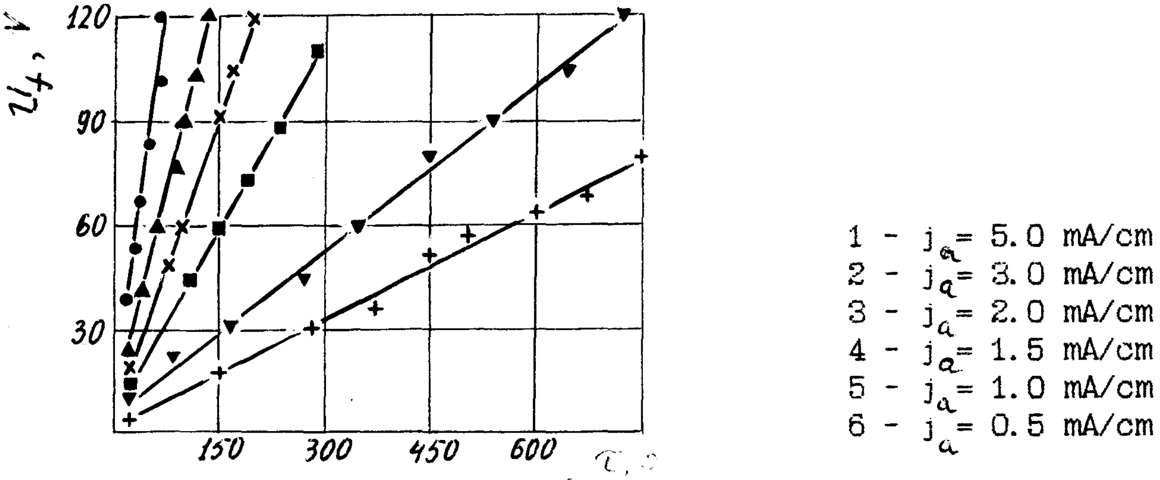


Fig. 5. The "charging curves" measured during oxidation of special Nb for cavities.

The analysis of these dependences shows that the film produced in the j = const mode is a multi-layer one. For all j_a studied there were three noticeable sections on the volt-ampere curve though they have no pronounced boundaries between them. The section of the noticeable rise correspond to the initial time period when NbO oxide is formed, the second section (the bend of the curve) corresponds to formation of oxide NbO_2, and the third section is characterized by formation of oxide Nb_2O_5 /15/.

With the time of film formation increased (growth of U), the fraction of the higher-valence oxide increases and if U = const the film contains only the higher-valence oxide /17/.

4. Techniques Used to Control the State of Superconductor Surface and Composition of Oxide Films

Different nuclear and physical methods of analysing the working surface of superconductor are applied during the development of ther technology of oxidation and oxipolishing of SC cavities. The main methods used in the process of our work are presented in Table 1 /16/.

Table 1

Methods used to analyse SC materials
(some properties)

N п/п	Method	Radiation source	Energy, particle sort	Max. thickness analysed, microns	Remarks
1	2	3	4	5	6
1.	Neutron activation analysis	Reactor ИРТ-2000	Divistion spectrum	Integral	High sensitivity if radio and chemical extraction is used 10(-7)%
2.	γ-activation	Betatron "Beam"	25 MeV	-"-	Proximate analysis
3.	Coulomb scattering	Cyclotron P-7M, electrostatic oscillator ЭСГ-2.5	He 11 MeV He from 1 до 2.0 MeV H до 1.5 MeV	<5 microns to 1-2 microns	Concentration profile 10(-3)%
4.	Backward resonance scattering of α-particles	Cyclotron P-7M	18-22 MeV	up to 10-12 microns	Concentration profile in any matrix 10(-3)%
5.	Acxtivation method using charged particles	-"-	<9-14 MeV He 16-30 MeV	up to 200 microns	Layer analysis 10(-7)%

6. Sybchrotron radiation	Synchrotron "Sirius"	Photons 5-40 eV	Unities & tens of A	Qualitative analysis, valence
7. Characteristictic X-ray radiation	Electrostatic generator ЭСГ-2.5	He up to 1 MeV	up to 0.1 microns	High sensitivity

Not all of these methods are nuclear in terms of incident radiation - matter interaction. However, they are still close to nuclear and physical ones in terms of the form of exciting radiation, techniques used to record detecting radiation and mathods used to handle the information obtained. Therefore they were considered together /20,21/.

One should also add to this Table the SIMS method /18/ and the method of Auger-electron spectroscopy /19/.

5. Applying Protective Coatings Anode Oxidation Technique

The work on anode oxidation with a view to suppress field emission and increase acceleratying fields is described in papers /22-26/. The authors has attained good results but they noticed the bad effect of lower-valence oxides on the properties of coatings.

Our goal was to obtain an oxide coating having the minimal content of lower-order valence oxides which deteriorate the coatings and lead to increases of losses in the SC cavities.

The follo-wing requirements are imposed on the protective coating :

1) minimal content of lower-valence oxides
2) minimal content of anion admixtures
3) minimal porosity, i.e. the maximal density of the anode oxide film.

How can one obtain the minimal content of lower - valence oxides?

1.1. Application of mixed mode of anode oxipolishing because the films obtained in the mode ja = const are multi-layer ones. The exposition time τ'' in the mode when U = const (see fig. 4) is necessary to oxidize the film additionallt to higher valence.

1.2. The choice of the intervals of technological parameters should provide 100% yield of oxigen current/(η).

Fgire 6 shows the dependences of the oxigen current on the film formation voltage U_f, the anodation current density ja and electrolyte concentration. These curves were obtained using the method of standard Coulomb measurements for very pure Nb.

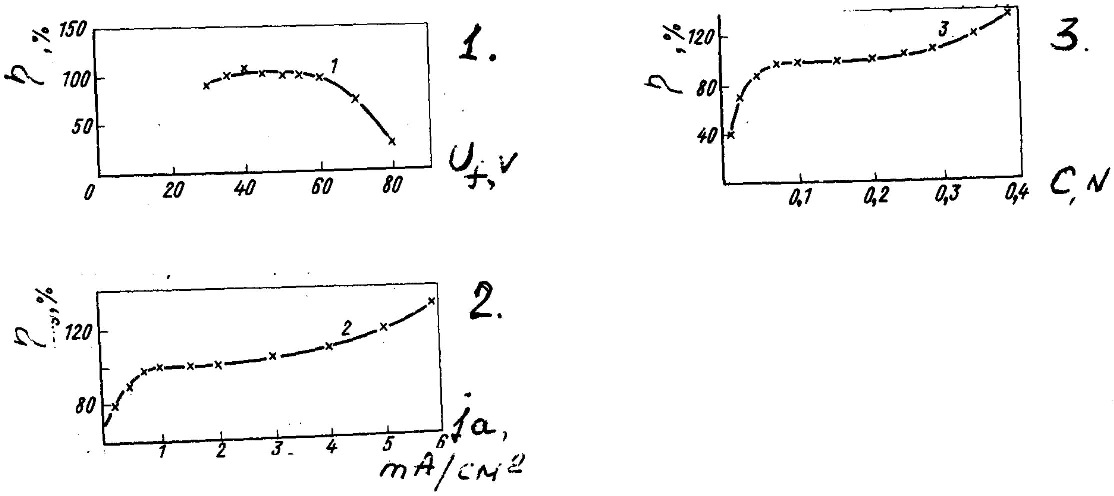


Fig. 6. The oxigen current η versus film formation voltage U_f (1), anodation current density ja (2) and electrolyte concentration (3) C.

The curves show that in our case the most dense oxide were obtained for ja = 1.5 mA/cm squared, U_f = 35-60 V, C = 0.1-0.2 N H SO . This means that in this interval just a Nb_2O_5 film is formed.

2. How can one obtain the minimal content of admixtures from the electrolyte?

Figure 7 shows the Auger-Spectra for Nb anodized at various current densities.

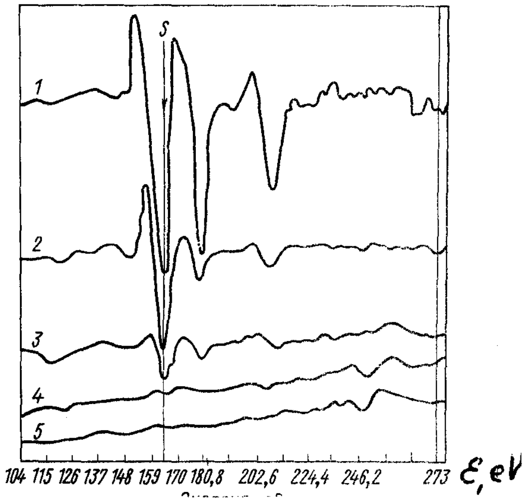


Fig. 7. The Auger-spectra for Nb anodized at ja:
1 - 10 mA/cm^2,
2 - 5 mA/cm^2,
3 - 3.5 mA/cm^2,
4 - 2 mA/cm^2,
5 - 1.5 mA/cm^2.

The figure shows that with an increase of the concentration of the S admixture in the coatings increases. **Therefore** to obtain films with the minimal content of anion admixtures from the electrolyte one should choose ja = 1-2 mA/cm^2 . In addition to that, one should also take into account the effect of the electrolyte temperature and concentration.

3. How can one obtain the maximal possible density of oxide film?

It should be stressed that in galvanostatic mode the film thickness grows proportionally to U :

$$D = k U \ , \text{ where } k = 22.5 \text{ Å/V}.$$

The film thickness keeps growing also if U = const only if the time periiod is <20 min and makes up about 300 Å for 100 V. Then in the mixed mode we get

$$D = (k U_f + 300) \text{ Å}.$$

Fig. 8 shows the oxygen content in the surface layer of anodiezed Nb and the film thickntss versus the exposition time for U_f= 100 V.

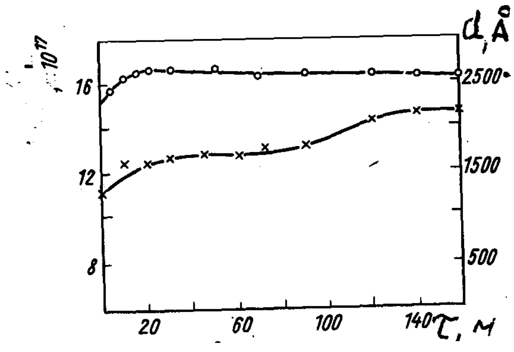


Fig. 8. The oxygen content in the surface layer of anodiezed Nb (1) and the film thickness (2) versus the exposition time for U_f= 100 V /12/.

As is seen from the curves, within the first 20 min. a good correlation is observed between the film thickness and oxygen concentration. Later the concentration increases without changes in the film thickness. This means that for t>20 min the effect of film density increase is observed.

The calculations showed that the density of the protective film varies within the time period τ''= 20-40 min from 4.71 to 5.2 g/cm^3 . A higher film density decreases the current leaks through the oxide layer and reduces porosity.

Hence, the conditions for a higher valence film of density 5.2 g/cm^3 cubed to be formed in this specific case are as follows: Uf = 35-60 V, , ja = 1-2.25 mA/cm^2
C =0.08-1.2 N H_2SO_4 , τ'' = 140 min /27/.

6. Optimization of Nb Anode Oxidation Aimed at Obtaining Working Oxide Surfaces

Some articles and books contain various controversial data on the modes of anode oxidation of cavities and the required thickness of protective coatings. Moreover, this process was studied only in terms of some single factors with other ones fixed. Therefore it became necessary to construct a mathematical model of the process of anode oxidation of cavities.

The problem of optimizing this process reduced to finding such a technological mode with parameters X_1, X_2, X_3, X_4, X_5 that would make it possible to obtain the minimal values of $tg\,\delta$ and β possible.

It should be noted that the measurement at cryogenic temperatures of the parameters of micro-wave protective coatings for a large number of cavities consisting even of one cell is a complicated and expensive process. Therefore all measurements were made for samples at the ambient temperature. The parameters of cavitiy coatings were measured only in the optimal oxidation modes.

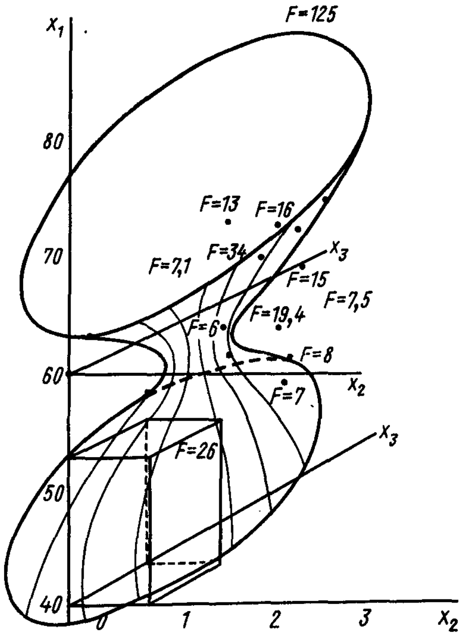


Fig. 9. Oxonometric drawing of the surface F(X X X) = const.

At the first stage, to establish the centre of experimentation area with account of the apriori information the simplex-search method /28/ with respect to varialbles $X_1 - U_f$, $X_2 - j_a$, $X_3 - C$ was applied. The values of other parameters were fixed as follows: $X_4 = 1.5$, $X_5 = 20$.

After the location of the simplex centred at point $X_1 = 60$ V, $X_2 = 1$ mA/cm^2 and $X_3 = 0.1$ N H_2SO_4 was determined its further motion became impossible. It turned out to be "stuck" on the "throat" of the hyperbolic cone (see fig. 9). In this case any extrapolation resulted in an increase of F(X) = or T(X) rather than to their minimization.

A more detailed presentation of the properties of the function T(X) can be obtained from quadratic approximation constructed from the experimental results. The quadratic polynomial in the space of the variables X_1, X_2, X_3 has the form

$$10(9)\quad F(X) = 1716.9\, X_1^2 - 908\, X_1X_2 + 529\, X_1X_3 + 2017\, X_1 + 172{,}4\, X_2^2 - 96{,}5\, X_2X_3 + 269\, X_2 + 1032\, X_3^2 - 3579\, X_3 - 450.$$

This function was tabulated within the acceptable limits and the results were used to obtain the axonometric drawing of the surface $F(X_1, X_2, X_3) = \text{const.}$ The surface shown in fig. 9 is a hyperboloid truncated by two planes. The experimental points are shown on the background of this surface and the values of F(X) are given next to them. It is clearly seen from the analysis of the location of the points that in the vicinity of point 6 whose choice as the centre of the experiment is unquestionable the function F(X) grows sharply.

Proceeding from the study of the polynomial gradient shifts of parameters of the technological process were recommended. Then the centre of experimentation and the intervals of variation by parameters were chosen finally /14/.

$X_1 = 54.0 \pm 4.00$ V
$X_2 = 1.4 \pm 0.20$ mA/cm^2
$X_3 = 0.1 \pm 0.02$ N H_2SO_4
$X_4 = 2.3 \pm 0.04$ h.
$X_5 = 15.0 \pm 5.0$ deg. C

The Hartley plan /29/ fairly close in its characteristics to the D-optimal one and requiring 27 observations only was chosen as the plan of the experiment.

Following the Hartley plan, a system of normal equations was obtained and solved by the square root method. The solution led to the following process of anode oxidation of very pure Nb "HБP", for example for tg δ:

$$10\ (3)\quad T(X) = 0.01\, X_1^2 + 31\, X_1X_2 + 1400\, X_1X_3 + 1{,}5 X_1X_4 + 50 X_1X_5 - 215\, X_1 + 23\, X_2^2 - 222\, X_2X_3 + 25\, X_2X_4 + 184\, X_2X_5 - 130\, X_2 - 412\, X_3^2 - 128\, X_3X_4 - 688\, X_3X_5 - 129\, X_3 + 5.5\, X_4^2 + 130\, X_4X_5 - 66\, X_4 + 440 X_5^2 - 623 X_5 + 282.$$

The analysis of the formules for and helped establish that they are similar. A specific feature of them is that they are not convex downwards. It turned out that there are two local minima in the region of search /14/:

1. X_1= 50 , X_2= 1.2 , X_3= 0.086 , X_4= 2.4 , X_5= 10
2. X_1= 59 , X_2= 1.24, X_3= 0.08, X_4= 1.7, X_5= 22.

After additional experiments in these modes and correction of the quadratic model from the obtained observations the problem of optimizing tg !! was solved again. Two local minima were found again:

3. X_1= 50, X_2= 1.59, X_3= 0.12 , X_4= 2.35, X_5= 10.2
4. X_1= 58, X_2= 1.2 , X_3= 0.08 , X_4= 2.7 , X_5= 10.0.

Since the problem of optimizing anode oxidation is stochastic in its nature a certain deviation from the recommended values of X is possible when the optimal modes are determined. From the viewpoint of stability /29/ modes 1 and 4 are preferable. However, judging from the values of functions T(X) and B(X) the best results were obtained in mode 3 in which film had tg δ 1.5x10(-4), a pronounced boundary between oxide-metal phases confirmed by metallographic studies and concentration distribution in the surface layer that was obtained by the method of elastic scattering of α-particles.

Hence, the results of optimization gave two local minima corresponding to anodation modes A and B given in Table 2.

Table 2

Technological modes of applying protectivce coatings on the surface of Nb cavities

Technological factors	X	Modes					
		A	B	C	D	E	F
U, V	X_1	50	58	40	30	20	10
j, mA/cm	X_2	1.59	1.2	1.59	1.59	1.59	1.59
C, n	X_3	0.12	0.08	0.12	0.12	0.12	0.12
, h	X_4	2.35	2.7	2.35	2.35	2.35	2.35
t,°C	X_5	10.2	10.0	10.2	10.2	10.2	10.2
d, Å		1425	1600	1200	975	750	515

From the viewpoint of losses introduced into the cavity by a dielectric coating more preferable is mode A becasuse of a decrease of the value of tg δ. But the volume of the dielectric in the cavity should be decreased. Therefore the oxidation modes (c, d, e, f) corresponding to the optimal combination of parameters X_2, X_3, X_4, X_5 but with different decreasing X_1 were tested.

The best results were obtained during studying modes d and e in which the dielectric coating was 975 Å and 750 Å /30/ thick.

Hence, on the one hand it is necessary to protect the cavity surface reliably and, on the other hand, to decrease the dielectric volume. The trade-off was found in the mode with the following parameters:

X_1 = 30 V, X_2 = 1.59 mA/cm^2, X_3 = 0.12 N H_2SO_4,
X_4 = 2.35 h, X_5 = 10.2 °C.

It should be noted that optimization of anode oxidation aimed at decreasing field emission is not complete yet though the variation law for the function T(X) has been established.

Two stages of finishing optimization of the anode oxidation process with the view of minimizing β are planned:

1) at the ambient temperature at the setup of field emission measurements /7, 31/ - 1994

2) at cryogenic temperatures at the setup of low-temperature field emission measurements /7/ - 1995.

7. The Study of the Kinetics of High - Temperature Annealing of Anodized Cavities

In this Section we would like to discuss very briefly the problems related to high-temperature annealing of anodized cavities. The results on studying the state of the superconductor surface by Auger-electron spectroscopy are presented in /17, 19, 21/, those by applying vacuum ultraviolet spectroscopy are treated in /32/ and the ones obtained by the method of elastic scattering of ions are discussed in /16/.

The most interesting results were obtained in /19/.
The conditions of annealing (temperature rise rate, annealing temperature, cooling modes) were simulated in the vacuum chamber of the Auger-spectrometer.

The most ingteresting Auger-spectra are shown on fig.10.

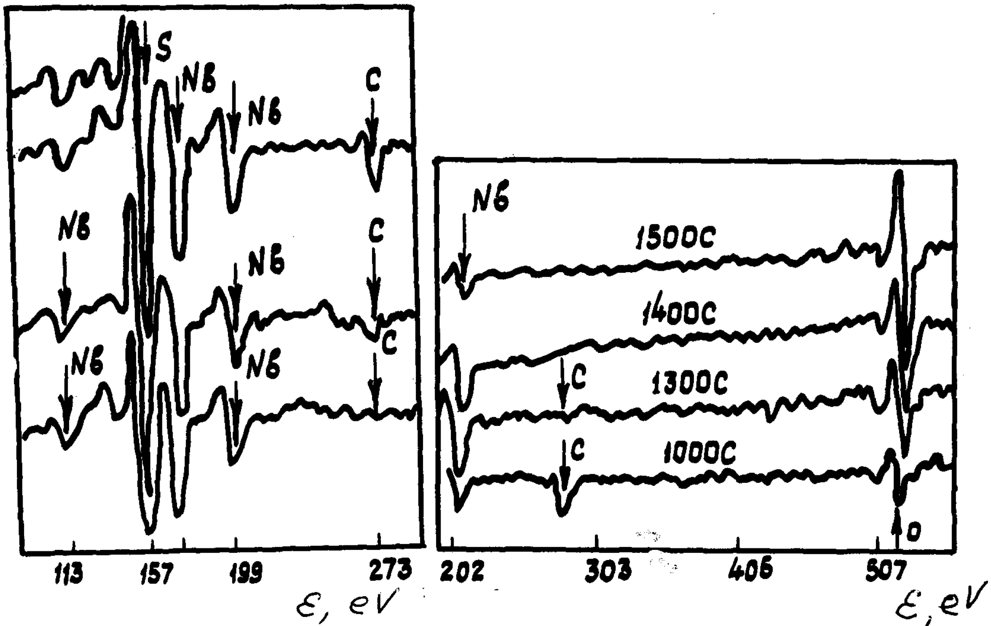


Fig.10. The Auger-spectra of Nb recorded during high- temperature annealing:
a) a - for electropolished Nb,
b) for anodized Nb.

The experiments showed that the carbon can be removed from the Nb surface layers only when its volatile compounds with oxygen, fluorine and hydrogen are formed. However, diffusion of carbon to the surface becomes rather fast at t>1300 K whereas carbon and fluorine are already desorbed. Therefore the only way of cleaning Nb from carbon is its interaction with oxygen.

Figure 10a shows clearfly the effect of carbon accumulation in the surface layers of the Nb annealed just after elctropolishing. It was established that a longer annealing time in the absence of oxygen in the residual atmosphere leads to carbon accumulation and its deposigtion on the crystal defects. This deteriorates the homogeneity of the Nb surface layer and reduces noticeably both the Q-value and the value of the critical RF field.

The developed mode of anode oxidation providing reduction of carbon content in the Nb surface layer by a factor of 5-6 /16/ was developed to be used for cleaning Nb from carbon in the process of annealing.

The effect of the oxide coating of Nb O on the carbon content is shown in fig. 10b. The figure shows that at $t > 900$ C the intensity of the oxygen peak intensity starts growing as a result of sequential decomposition of oxide Nb O - NbO - NbO. At this time the carbon is removed in the form of oxides CO and CO_2.

Hence, the oxygen content (on the surface!) should be increased somewhat in order to facilitate cleaning from carbon. Therefore we anodized the samples prior to high-temperature annealing.

Table 3 presents the data on the carbon content and microhardness versus the thickness of oxide coating on Nb. It should be noted that the microhardness of samples was measured after annealing and storing them in He atmosphere during a month.

Table 3

Thickness of anode oxide film, Å	Carbon content after annealing, %	Microhardness, g/cm
0	0.03	56.2
450	0.0327	51.1
900	0.018	50.6
1350	0.012	46.0
before annealing and without coating	0.05	139.8

The table suggests that with an increase of the thickness of oxide film the carbon content and microhardness decrease. Owing to decomposition of the oxide film /10/ starting with 1170 K annealing takes place in the oxidizing atmosphere and removing t he oxide film from the surface the second stage, i.e. tight-vacuum annealing starts.

The results on the experiments on studying the diffusion and desorption of carbon, oxygen and sulphur on the Nb surface layer obtained by the Auger-spectroscopy method are in a good agreement with the ones obtained by electron microscopy.

Electrochemical Purification of Nb Working Surfaces from Admixtures of Heavy Elements Using Oxipolishing Technique

In was shown in paper /32/ that the surface resistance of pure Nb after removing various admixtures by prolonged electrolysis or tight-vacuum annealing in supertight vacuum can be expressed as the sum

$$R(T) = 5.14 \cdot 10^{-12} T^{3} + 10^{-5} C_{N} + 2.5 \cdot 10^{-7} C_{Ta} + 1.1 \cdot 10^{-6} C_{W},$$

where the first term is the resistance caused by electron scattering by thermal oscillations of the lattice and the rest three terms are caused by atomic concentrations of nitrogen, tantalum and tungsten. The value of C_N is determined completely by the partial pressure of nitrogen in the vacuum system when Nb is purified. Admixtures of such refractory metals as tantalum and tungsten are the most difficult to be removed.

Table 4 shows the results of neutron & activation analysis of the tantalum and tungsten concentration for Nb with RRR = 15, 300, 600 and 1000 that was supplied by "GIREDMET" /33, 34/ and also the Q-values of cylinder -shaped cavities /35/.

Table 4

The effect of the initial Nb quality on the Q-value of 3-cm band SC cavities

R R R of Nb	Admixture content		Q-value at 2 K /36,37/
	Tantalum	Tungsten	
15	0.095	0.02	2.0 x 10 (8)
300	0.005	0.007	5.0 x 10 (8)
600	0.003	0.003	1.5 x 10 (9)
1000	0.0005		-
			4.0 x 10 (9) - - calculated

Though this tantalum is a limiting admixture in Nb, still it is still difficult to be removed. The point is that the atomic radius of tantalum is close that of Nb and can replace any nodes of the Nb lattice.

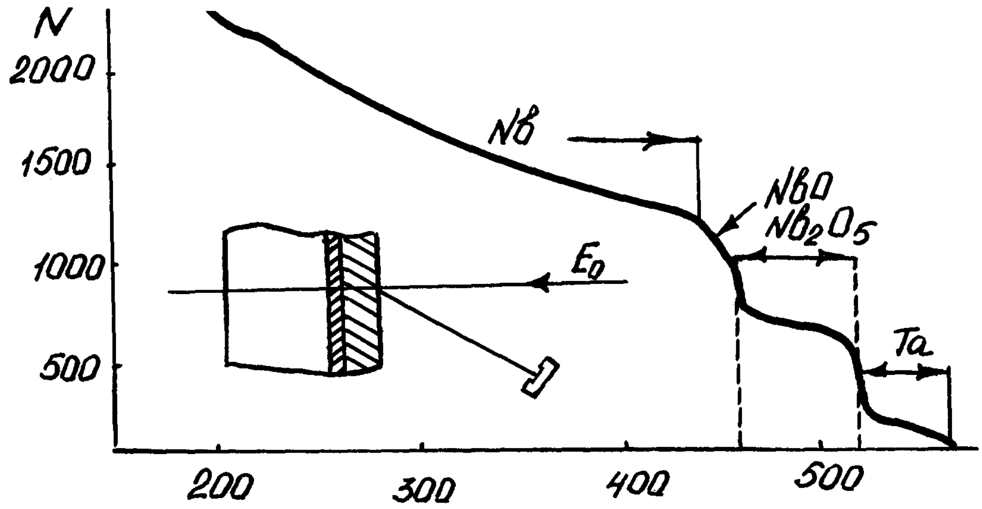
However, is more active chemically as compared with other admixtures. Therefore complex inclusions of tantalum atoms are formed as a result of their interaction with admixtures of light elements. These inclusions have the form of "clusters" in the defective places of Nb /13/ and, on the one hand, hamper recrystallization, and on the other hand, impede the motion of dislocations.

With account of these factors the method of purifying the Nb surface layer from tantalum admixtures /9, 10/ was offered. The known method of power transfer, whose particular case is deep purification of metal by electrotransfer through the oxide layer /38/, was chosen.

It tunred out to be convenient to integrate this method with anode oxidation to obtain a mixed mode within which transfer of tantalum ions into the oxide film under the action of electric field takes place. Then the film is removed in hydrofluoric acid together with the tantalum contained in it. Multiply repitition of these operations, i.e. oxipolishing ensures effective purification of the Nb surface layer up to a depth of 10 microns.

To analyse the admixture content of Nb and its oxides the methods of Rutherford backward scattering, X-ray fluorescence spectroscopy and neutron-activation analysis were applied /39-41/.

Figure 11 shows the amplitude spectrum obtained by the method of Rurtherford scattering of α-particles on the anodized Nb.



Figf. 11. The amplitude spectrum of anodized Nb /40/.

As is seen from the figure, such spectra allows one to determine the thickness of oxide layer, its phase content and also the concentration of the tantalum admixtures in the film.

The concentration of admixtures at further stages of purification was determined with the help of X-ray fluorescence analysis by exciting X-ray radiation by accelerated ions /40/. Further neutron - activation analysis /41/ was applied. The mose isotopes for this analysis are Ta(182) and Ta(181). Radioisotope Ta(182) has a half-life peiod of 116 days and emits 9 groups of γ -quanta in energy range from 42 to 1458 MeV. The minimal concetration of Tantal in Nb that can be discovered by this technique is 10(-6) — 10(-7)% /41/.

Figure 12 the concentration of microimpurity of Ta in the oxide versus the exposition time for U_f = const and for different thicknesses of the oxide coating.

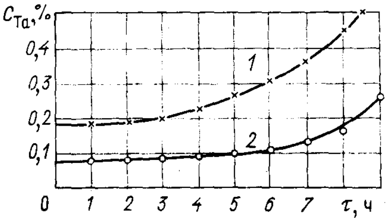


Fig. 12. The concentration of Ta microimpurity in the oxide film versus the exposition time for different film thicknesses: 1 - 400 Å, 2 - 1120 Å.

As already noted, if the mode with j = const is applied without exposition for U_f = const the film produced is a multilayer one. In this case we have the structure of oxide NbO - NbO_2 - Nb_2O_5 but with exposition for U = const one may obtain NbO - Nb_2O_5 or just Nb_2O_5.

The experiments showed that exposition for U_f = const results in the growth of the Ta concentration in the film, and in the laboratory conditions it varies very weakly at the first stage. This is in a good agreement with the data of paper /12/. At the first stage the film gets more dense due to elimination of the complicated structure of the oxide and the Ta concentration level is weakly dependent on exposition, then a sharp growth of the Ta concentration is observed.

In addition, the most pronounced effect of Ta extraction into the oxide film was always observed for small thicknesses of the oxide layer. This is confirmed by the experimental data presented in fig. 13 showing the Ta concentration in the Nb oxide film versus the thickness.

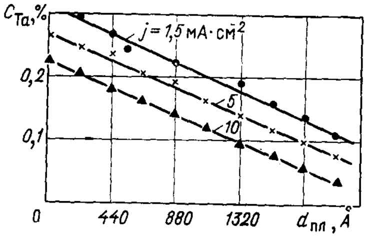


Fig. 13. Ta microimpurity concentration versus the thickness of the anode film on Nb for different anodation current densities:
1 - j = 1.5 mA/cm^2, 2 - j = 5 mA/cm^2
3 - j = 10 mA/cm.^{2}

The Ta concentration left in the main metal after a series of oxipolishing was studied by the SIMS method /18/ at the setups described in /36,7/.

9. The Technique of Electrochemical Purification of the Surface Nb Layer from Ta

The cost of Nb is known to be determined by its RRR and, consequently, by the Ta concentration as a limiting impurity /43, 44/. If there is a possibility to purify the working surface of a cavity to a depth exceeding the depth of microwave field penetrating superconductor then the following question arises: can one use a cheaper material for manufacturing cavities? This is rather a complicated question because for raising the gradients in SC RF structures not only the surface Nb layer and its Rs are important but also the whole thickness of walls as the conditions of heat removal from scattered microwave power into the helium bath are important as well /44/.

But still, proceeding from the studies described in Section 8 we have developed the technique of manufacturing SC cavities /10/, allowing one to fabricate cavities having a high Q-value from Nb with an increased concentration of Ta.

This technique is based on the oxipolishing method and helps reduce the Ta concentration by 6-10 times up to a depth of 67-8 microns that is much larger than the one of microwave penetration into superconductor.

Figures 14 ands 15 show the concentration of Ta impurity in the oxide film versus U and ja. The films were made in electrolytes of various chemical composition.

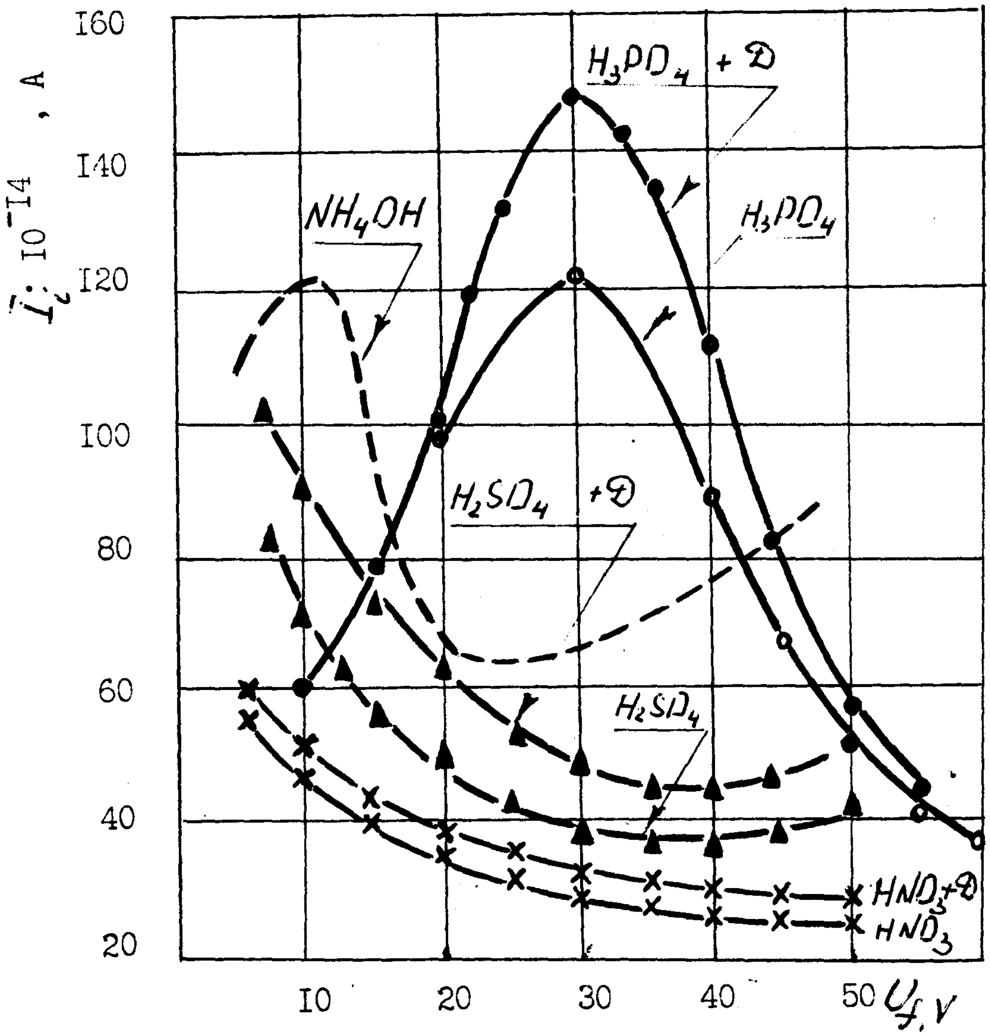


Fig. 14. The concentration of Ta(+181) ions in the oxide film obtained in different eletrolytes versus the film formation voltage..

Figure 15 shows the concentration of Ta impurity extracted into the oxide film versus the anodation current density.

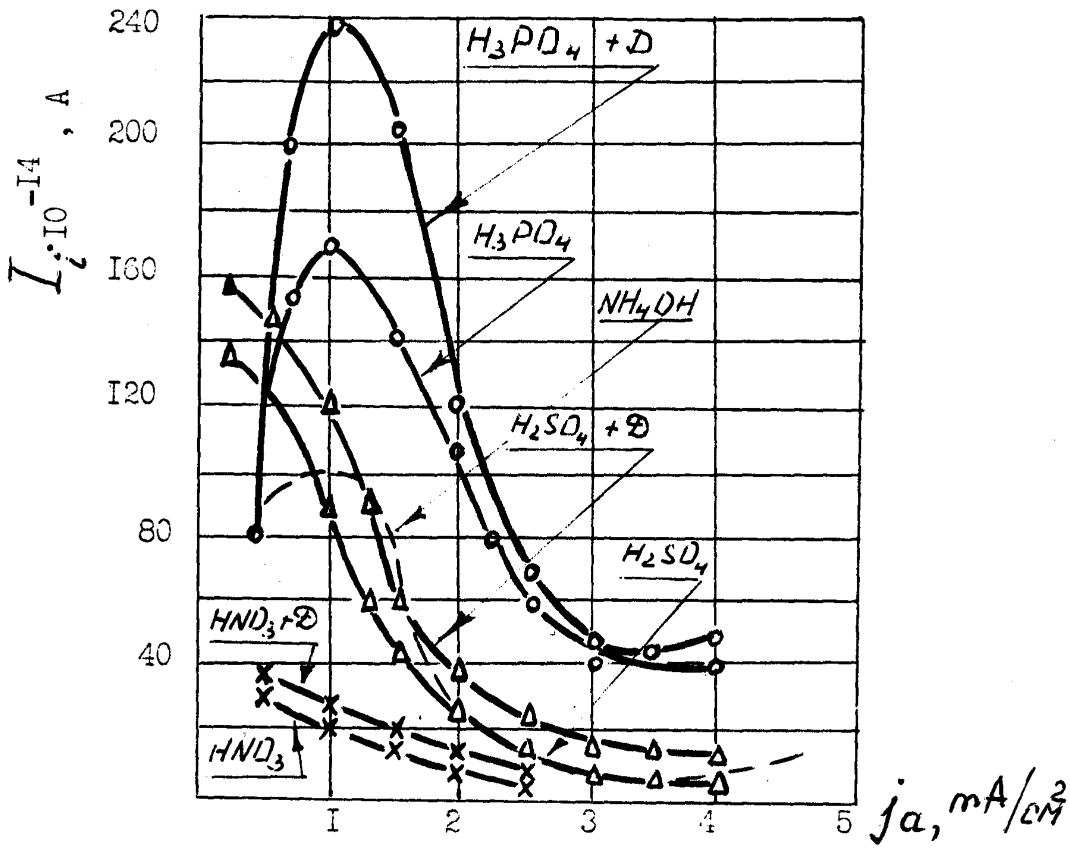


Fig. 15. The concentration of Ta impurity vedrsus anodation current density.

It is seen from these figures that the purification effect manifests itself in the case of using an electrolyte based on orthophosphoros acid with additives in the narrow region of their concentrations, (0.1-0.15)%.

A disadvantage of the method we developed earlier is a prolonged cycle of cavity treatment especially at the exposition stage for Uf = const that lasted 5-8 hours. For 10-fold oxipolishing it takes 50-80 hours to treat each piece of the cavity! It is just the exposition time within which for U = const the required diffusion processes take place and the impurities are transferred under the action of electric field from the metal depth into the oxide film.

Therefore we faced the following problem: how can one make this treatment cycle shorter?

When applying protective coatings we always had to control mechanical stresses in the film. These stresses were the cause of cracks in the dielectric coating on the cavity surface especially during temperature drops from 300 K to the operating temperature of the cavity, 4.2-2.1 K. However, as it turned out, the effect playing a negative role in one case may have a positive effect in another one.

The analysis of experimental and theoretical data on mechanical stresses in anode oxide films and their dependence on the anodation current density (see fig. 16) suggested us the idea of developing the maximal mechanical stresses in the Nb_2O_5 film.

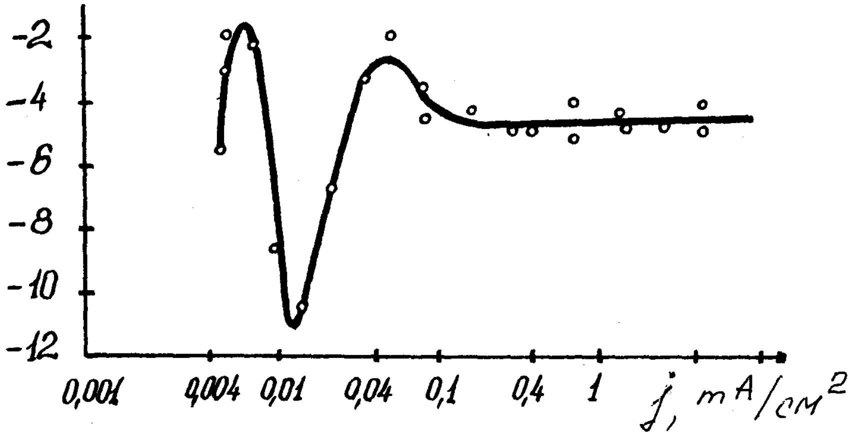


Fig.16. Mechanical stresses in the anode oxide film versus the anodation current density /4/.

As is seen from the figure, the maximal mechanical stresses are observed in current region the 0.01-0.02 mA/cm!!.

To enhace this effect, it was decided to cooldown the oxide instantaneously in liquid nitrogen after applying the coating and then to continue exposition at U_f = const. This had a positive effect on the diffusion processes and electrotransfer of impurities and also made it possible to cut the duration of each operation from 50-80 hours down to 10-15 min.

With 10-fold oxipolishing it takes just 100-150 min insted of 50-80 hours to treat each piece of the cavity.

Figure 17 shows the Ta and TaO ion current versus the bombardment time defining the profile of the concentration of these impurities in the surface Nb layer to a depth of

7.5 microns /18, 45/.

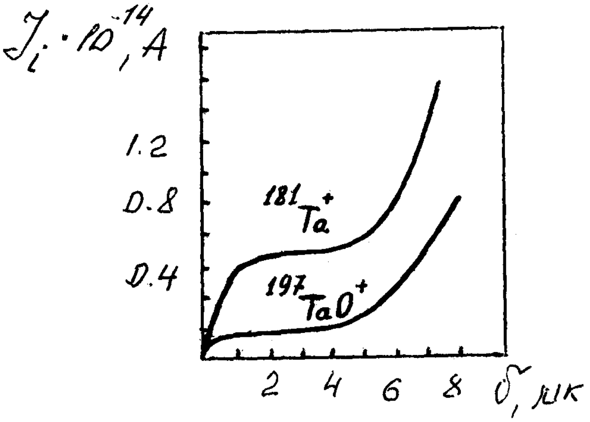


Fig. 17. The profile of Ta and TaO concentration in the surface Nb layers after a few oxipolishings.

The figure shows that in this case the Ta impurity in the surface Nb layer is distributed almost uniformly at a depth of 4 microns whereas in deeper layers an exponential growth is observed at a depth of 6.5 microns followed by a flattop.

All results presented here point to the existence of the eeffect of purification of Nb from Ta through the oxide layer.

10. Conclusions and the Future

The study of anode oxidation of Nb cavities has not yet been finished.

Surface oxidation influence onto the different types of emission (field emission, acoustic, secondary and exoelectronic) is being planned to study , and optimization of anodizing process is to be completed with the purpose to obtain the minimal fild emission coefficient.

The study of cleaning surface process using oxipolishing to the heat conductivity and Kapitza resistance seems to be of a definite interest.

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