

IMPROVED METHODS for ELECTROCHEMICAL
POLISHING of NIOBIUM SUPERCONDUCTING CAVITIES

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I N T R O D U C T I O N

Accelerator specialists realised the importance of the technology of working surface treatment for SC cavities long ago.

Only use of very clean SC materials and special methods of technology treatment will help to resolve the problem of higher gradients in SC RF cavities.

In this report some experimental results on different electropolishing methods for superconducting cavities from Niobium are compared: electropolishing under current oscillation control method (SIEMENS), horizontal rotation electropolishing with current density control (KEK), electropolishing with potential control method (Wuppertal, Warsaw), alternating current electropolishing and electropolishing with control by "pocket current oscillations", described by strange attractor (IHEP).

The purpose of our report is to discuss different electropolishing methods for SC cavities from Niobium.

P L A N of R E P O R T

1. Motivation, comparison and possibilities of different methods of Nb Superconducting cavities polishing.

2. Classical methods:

- Electropolishing under current oscillation control method (S I E M E N S , Germany) / 1 - 3 /
- Horizontal rotation electropolishing with current density control (K E K , Japan) / 4 - 6 /
- Electropolishing with potential control method (Wuppertal University, Polytechnical Institute, Warsaw, Poland) / 7 /

3. New methods of electropolishing:

- Method of continuous electropolishing with alternating current control (I H E P , USSR) / 8 - 10 /
- Method of final electropolishing with control by "current oscillation pockets", described by strange attractor (I H E P , USSR) / 12 - 16 /

4. Comparison of experimental results.

5. Conclusion.

COMPARISON and POSSIBILITIES of DIFFERENT METHODS

Chemical and electrochemical polishing are effective methods of suppression of emission effects in SC RF structures. Therefore presently every company dealing with SC cavities is advancing one of these methods.

This table shows advantages and disadvantages of every method.

ELECTROCHEMICAL POLISHING	CHEMICAL POLISHING
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A D V A N T A G E S

- | | |
|---|---|
| 1. Less field emission. | 1. Bigger process efficiency (to 120 $\mu\text{m}/\text{min}$, with H_3PO_4 may be 4-6 $\mu\text{m}/\text{min}$). |
| 2. Allows to avoid a chemical run-away reaction, which is a big danger to CP. | |
| 3. Higher Q. | |
| 4. Facilitates defect detecting on the polished surface. | |
| 5. Allows to use less dangerous electrolytes for alternating current EP. | |
| 6. Allows to protect Nb surface against hydrogen by screen. | |

D I S A D V A N T A G E S

- | | |
|--|--|
| 1. Lower process efficiency (to 40 $\mu\text{m}/\text{h}$) | 1. Usage of CP for large cavities is very complicated. |
| 2. Surface is contaminated with reaction products (H_2S , S). | 2. Defects detecting is hard because the surface is not very smooth. |
| 3. Large current density (300-1000 A/m^2) and, accordingly, large dissipated power (3-15 kW/m^2) in electrolyte. | 3. Surface is contaminated by a large amount of hydrogen. |

It seems to us, electropolishing methods have advantages as compared with chemical polishing. So, we will discuss this one in a more detail.

The following table shows the fundamental methods of electropolishing and typical results.

COMPARISON OF DIFFERENT ELECTROPOLISHING METHODS

Method	reduction rate	height of micro-roughness
1. Electrochemical polishing under current oscillations control method (SIEMENS).	40 μ m/h (0.1-0.6 μ m/min)	
2. Horizontal rotation electrochemical polishing with current density control (KEK).	0.4 μ m/min	0.15-0.2 μ m
3. Electrochemical polishing with potential control method (Wuppertal University and Polytechnical Institute, Warsaw)	< 120** < μ m/h	0.20 μ m***
4. Alternating current electrochemical polishing (IHEP).	2.5-3.0 μ m/min	0.05-0.08 μ m
5. Electrochemical polishing with current oscillation "pockets", described by strange attractor (IHEP).	0.01-0.87 μ m/pocket	0.05 μ m

Methods 1-3 are known well and we believe them to be classical ones because they permit to receive the height of microroughnesses of about 0.15-0.2 μ m. The motivation for the development of the horizontal rotation EP and EP with potential control methods (methods 2,3) is the possibility of continuous electropolishing. It is very important for large-scale SC cavity production.

The most important parameters in EP of Niobium are current density, voltage or potential, bath temperature and solution concentration.

These parameters of EP methods, used in different laboratories, are shown in the table below.

** dependent on the Nb-crystal morphology and purity

*** and the chosen electrolyte (H.Hein, Diplomarbeit, WUD 87-3 (1987))

PARAMETERS OF ELECTROCHEMICAL POLISHING METHODS, USED IN DIFFERENT LABORATORIES

Laboratory	Current density mA/cm ²	Voltage V	Potential V	Temperature C	Composition	Frequency GHZ	Mixing
SIEMENS	about 100	9-15		25-35	HF: H ₂ SO ₄ = 8.5:1		Rotating at pause
KEK	30-100	25-27		25-35	HF: H ₂ SO ₄ = 8.5:1	0.5	Rotating 0.4-1.2 r/min
WU+PIW	90-110	15-18	6.5-7.0	50-60	HF: H ₂ SO ₄ : lactic acid 17.9:20.8:61.3 18:21:61	3	Pumping
IHEP(a. c.)	50-70 j / j = 7	18-23 f(Hz) = 200		18-25	HF: H ₂ SO ₄ = 1:25	9	No need
IHEP(d. c.)	20-50		1.6-1.8	15-25	HF: H ₂ SO ₄ = 1:4 or 1:6	3	Rotating at pause

C L A S S I C A L M E T H O D S

1. Electropolishing under current oscillation control method (EP-COC).
2. Horizontal rotation electropolishing with current density control (HR-EP).
3. Electropolishing with potential control method (EP-PC).

COMPARISON of CLASSICAL METHODS

Method	Control	Rotation	Solution
EP-COC	Current oscillation	Intermittent horizontal rotation of the cavity	HF: H ₂ SO ₄ = 1: 8.5
HR-EP	Current density	Continuous horizontal rotation of the cavity 0.4-1.2 r/min	HF: H ₂ SO ₄ = 1: 8.5
EP-PC	Potential	Continuous up-down cavity stroke	HF: H ₂ SO ₄ lactic acid = 1.79: 2.08: 6.13

The regimes of cavity treatment were optimized to meet specific requirements of different laboratories, which depend on the frequency, shape and size of cavities.

Methods 1 and 2 developed by SIEMENS /1-3/ and KEK /4-6/ are known well.

So, we would like to tell some words about electropolishing with potential control method developed by L. Ponto (WPI) and M. Hein (WU).

Figure 1 shows the potential-current density curve obtained by L. Ponto and M. Hein /7/. They used a special reference electrode placed close to the anode. The optimal potential was in a range of 4.5-7 V. The authors believe the potential to be a more important characteristic than the current density.

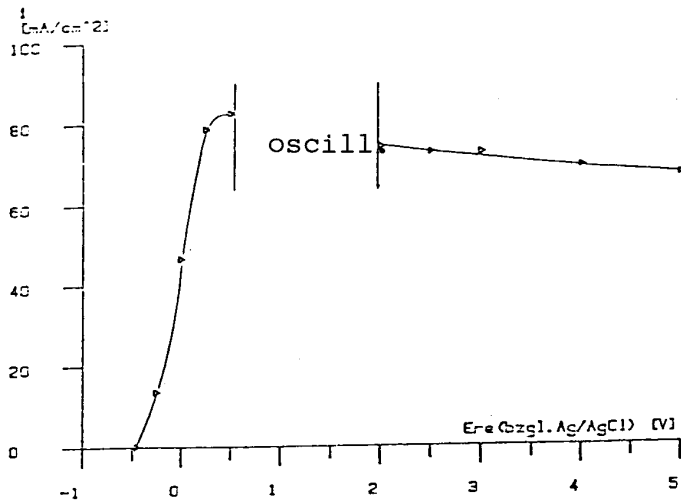


Fig.1 The potential-current density curve.

They showed that the quality of surface polishing is dependent on the bath temperature which should lie in a range of 50-58 C.

The best results were obtained in the solution
 21.5% vol HF + 25.0% vol H₂SO₄ + 53.5% vol lactic acid.
 Agitation of the solution is obligatory.

ADVANTAGES of the CLASSICAL METHODS

1. All these methods have already been studied very well.
2. Good results for SC cavity and RF structures were obtained.
3. This process can be computerized using a fairly simple scheme.

DISADVANTAGES of the CLASSICAL METHODS

1. It is impossible to protect the working surface of the cavity against hydrogen without using special diaphragms /7/ or cathode bags /4 /.
2. All these methods apply EP solutions containing hydrofluoric acid.

In terms of large scale applications, hydrofluoric acid is an aggressive agent because it is very dangerous for people and environment and also causes corrosion of the equipment. If so, then why should we use it? Cannot we manage without it?

As is well known, hydrofluoric acid is added into EP solution in order to dissolve the oxide film Nb O. However, there are other techniques applied to dissolve this film. They will be treated in the next section of our talk.

NEW METHODS OF ELECTROPOLISHING

1. Method of continuous EP with alternating current control (CE-AC).
2. Method of final EP with control by current oscillation "pockets" described by strange attractor (EP-CPSA).

These methods have been developed by the group for Technology and Study of Superconducting Cavities of Institute for High Energy Physics.

We use method 1 for hard electropolishing. It permits to remove metal at a rate of $3 \mu\text{m}/\text{min}$.

We use method 2 for very precise removal of metal from the working surface of SC cavities. This method gives the possibility to reduce the rate from 0.01 to $0.87 \mu\text{m}/\text{pocket}$.

1. Method of continuous EP with alternating current control

In this Section of the talk we would like to draw attention to the following questions:

1. What value of voltage should be applied?
2. The features of reduction rate for metal removing at different frequencies and for Nb with different values of RRR.
3. The role of agitation.
4. The optimal content of hydrofluoric acid in EP solution.
5. The requirements imposed on the experimental setup.
6. The advantages and disadvantages of this method.

Experimental studies carried out by A. I. Ionkin (Polytechnical Institute, Novocherkassk)/17/ and by the group for technology and study of SC cavities (IHEP) /8/ showed that polishing at fixed-frequency of electric fields facilitates the destruction of oxide films Nb_2O_5 .

Therefore one may conclude that polishing at fixed-frequency alternating current may help one to avoid the use of hydrofluoric acid.

1. What value of voltage should be applied ?

Figure 2 shows the voltage-current curves recorded for the 9 GHz SC cavity at frequency from 50 to 1000 Hz. This cavity was manufactured from Niobium with RRR=15.

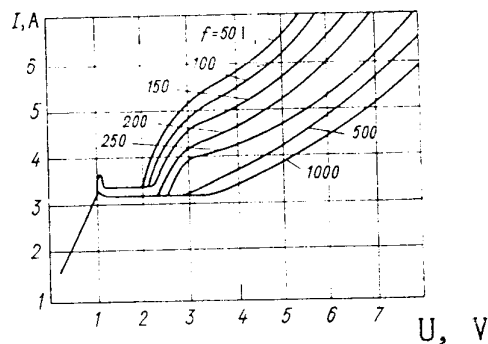


Fig.2 Voltage - current curves at EP of 3 GHz SC cavities at frequency from 50 to 1000 Hz and RRR = 15

It is seen from the figure that

- voltage-current curve is N-shaped
- with an increase of the frequency of the voltage applied the area of the horizontal part is shifted to higher voltages.

Beginning with a frequency of 300 Hz this part of curve is less pronounced.

Therefore the EP process has to be carried out at a frequency less than 300 Hz.

2. The features of reduction rate
for metal removing at different frequencies
and for Nb with different values of RRR

A very important problem is the removal of metal across the thickness of SC cavities.

In this connection, this process was studied versus the frequency of voltage applied and RRR of the initial material.

As is seen from fig. 3, the reduction rate for a single crystal Niobium cavity and for Niobium one with $RRR > 300$ decreases monotonously with the frequency of the field applied and RRR of the initial material.

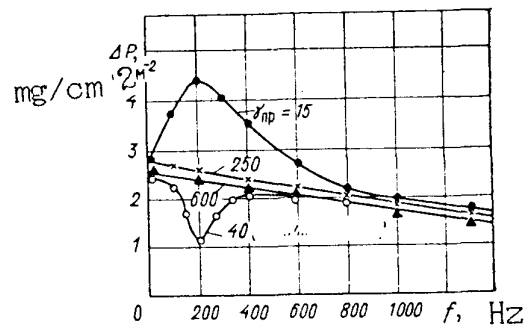


Fig.3 Reduction rate for a single crystal Niobium cavity and for Niobium with different RRR.

As is seen from fig.3, the reduction rate for a single crystal Niobium one with $RRR > 300$ decreases monotonously with the frequency of the field applied.

However, for cavities manufactured from Niobium with RRR from 5 to 20 an anomalous increase of the reduction rate is observed at a frequency of 200 Hz. It may be due to an intensive dissolution of impurities at grain boundaries. The maximum specific surface grain boundaries are observed just for Niobium with this RRR.

The lower curve was obtained for the SC cavities made from single crystal Niobium with $RRR < 40$. It still remains an enigma for us why it is a mirror reflection of the curve for the cavity made from polycrystal Niobium.

3. The role of agitation

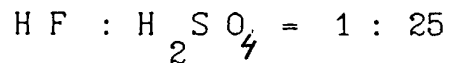
As was shown in ref. / 8 / EP of cavities causes the reaction products to accumulate to the electrode. Therefore in order to have a uniform diffusion layer the electrolyte should be agitated, which is a very complicated thing to do especially with complicated shapes of cavities and a high aggressivity of the electrolyte.

During alternating current EP of cavities a pulse of the reverse polarity plays the role of agitation. A variation in the ratio between the amplitudes of the cathode and anode constituents of the polarity current is equivalent to variations in the rotation velocity of one of the electrodes.

The best quality of the surface is obtained for the ratio $i_k / i_a = 7$.

4. What is the optimal content of hydrofluoric acid in EP solution ?

Our studies showed that for alternating current EP the following ratio of electrolyte constituents is quite sufficient:



It is known that the amount of hydrofluoric acid can be decreased by increasing the EP voltage /3 /.

Our preliminary experiments with samples showed that one can manage without hydrofluoric acid. But in this case one should be very careful when choosing the amplitude of alternating current voltage. In our case this amplitude is 18 - 25 V. The lower limit is bounded by the conditions of etching the boundaries of grains while the upper one is bounded by the formation of pittings on the working surface.

The mentioned above value of EP voltage differs for different shapes and dimensions of SC cavities.

5. The requirements imposed on
the experimental setup

Alternating current EP of SC cavities in a solution without hydrofluoric acid (or with a very small amount of it) necessitated the development of a precision power source.

The requirements on the setup are as follows :

-Capability to maintain the frequency deviation to an accuracy of ± 0.01 Hz within the whole range of voltages.

-The ratio between the cathode and anode constituents should be adjusted from 1 to 15.

We have developed such a power source jointly with Corporation " Standard " according to our request /19/.

Figure 4 shows a schematic of the setup used for EP of SC cavities.

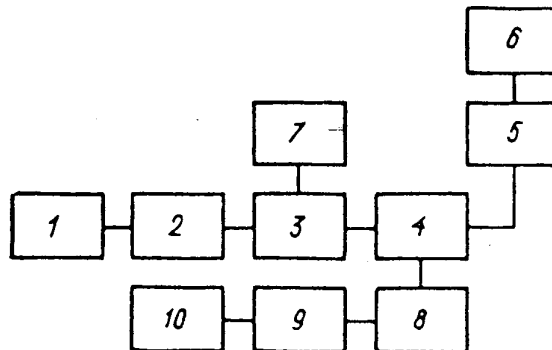


Fig.4. Block - diagram of setup for EP with alternating current control (CE-AC).

The setup consists of audio-signal generator 1, amplifier 2, unit 3 for controlling the ratio of cathode and anode current constituents, electrochemical resistor 4, solution bath 5 for EP of SC cavities, scope 6 for observing the shape of the signals from polarized currents, measuring units 7 for recording the currents and voltages, matching block 8, commutation block 9 and recording potentiometer 10.

6. Advantages and disadvantages of the continuous EP method with alternating current control

Advantages

1. Saving of expensive materials due to removal of the high-corrosive component from solution.
2. Reduction of corrosion degradation of the ventilation ducts and equipment.
3. EP solution is not very dangerous for people.
4. No need to agitate solution.
5. It is possible to use horizontal rotational EP of SC cavities like at KEK together with alternating current control.

Disadvantages

It is impossible to prevent hydrogen from reaching the cavity surface, but it may be corrected by high temperature treatment

II. Method of final EP with a control by current oscillation "pocket" described by strange attractor

The technological process of DC EP of Niobium SC cavities has been developed proceeding from a very interesting phenomenon, i.e. self-excitation of low frequency current oscillations after applying constant voltage.

Such oscillations develop in the range of the voltage current curve having a negative differential conductivity.

Figure 5 shows a voltage - current curve recorded for EP of the 9 GHz SC cavity.

The figure shows that this curve is N-shaped and that periodic current oscillations are observed in the strictly determined range. It is very important, that this curve has a few ranges of current oscillations.

This phenomenon became the underlying idea to control the method of EP of SC cavities according to the shape of current oscillations.

The employees of the " S I E M E N S " Company /1, 2-/were the first obtain packet -shaped oscillations shown in fig.6

Fig. 5. The voltage-current density curve for anodical dissolution of Niobium with $RRR > 600$

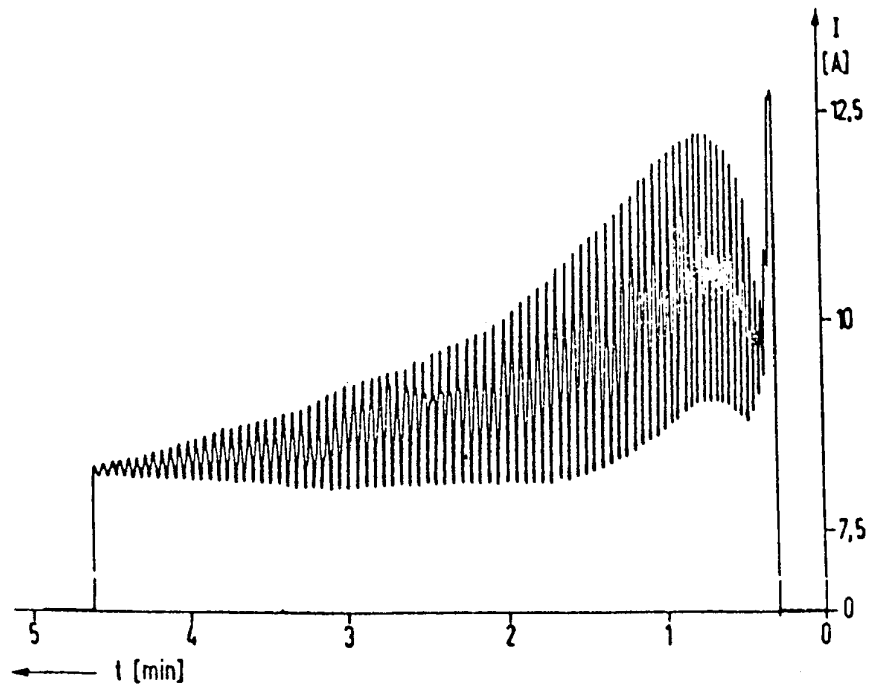
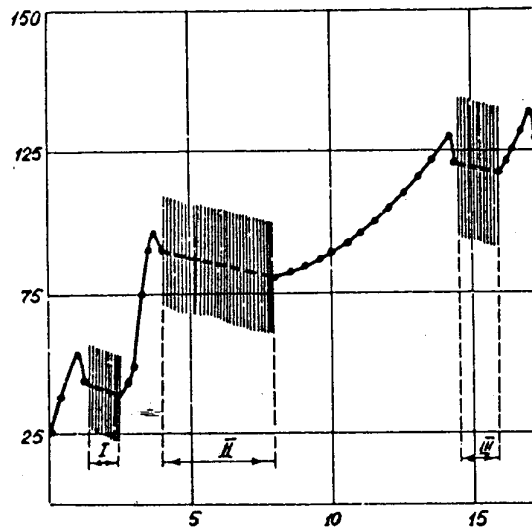


Fig.6. Electropolishing niobium current oscillations obtained by using "SIEMENS" method.

Figure 7 shows the oscillations "pocket" obtained at our laboratory. Each pocket has quite a specific shape and duration and also quite a specified frequency of oscillations filling it.

In addition, each pocket corresponds to quite specific metal removal across the cavity thickness.

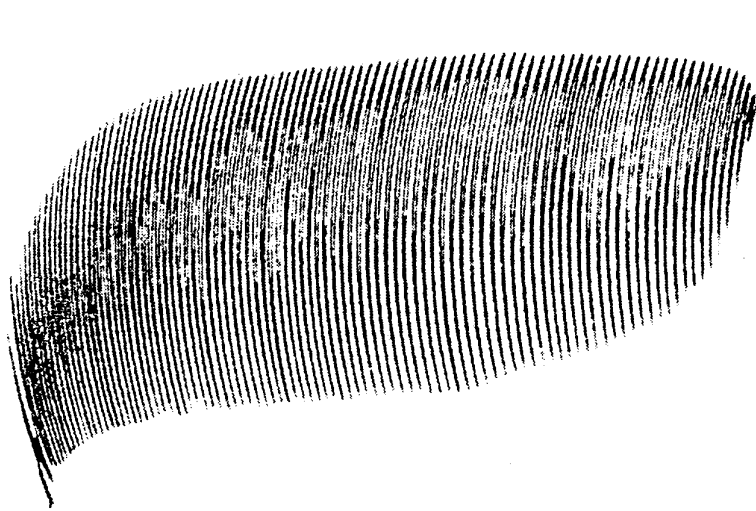


Fig. 7. Oscillations "pockets" at electrochemical polishing of Niobium SC cavity.

How may we receive such pockets ?

To answer this question we need to consider in more details the first current oscillations area of the curve shown in Fig. 8.

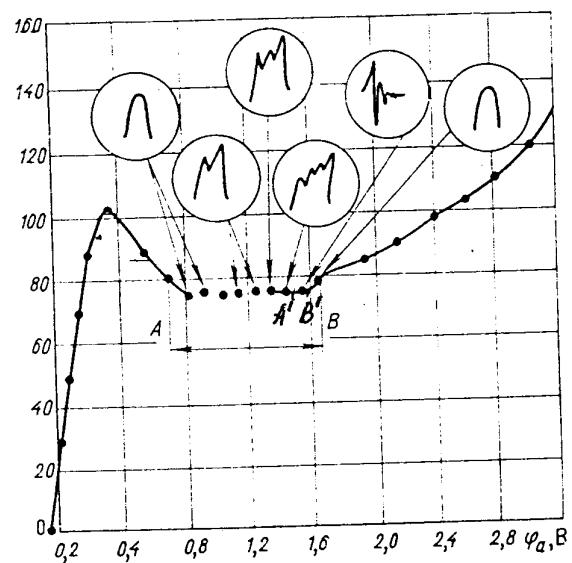


Fig. 8. Potential-current curve at electrochemical polishing of Niobium.

So, as was obtained experimentally, the current oscillations arise at point A. First, oscillations have a quasisinusoidal shape, then the oscillation period doubles, quadruples, etc.

A further increase of the voltage applied causes the oscillation process to transform into quasistochastic one.

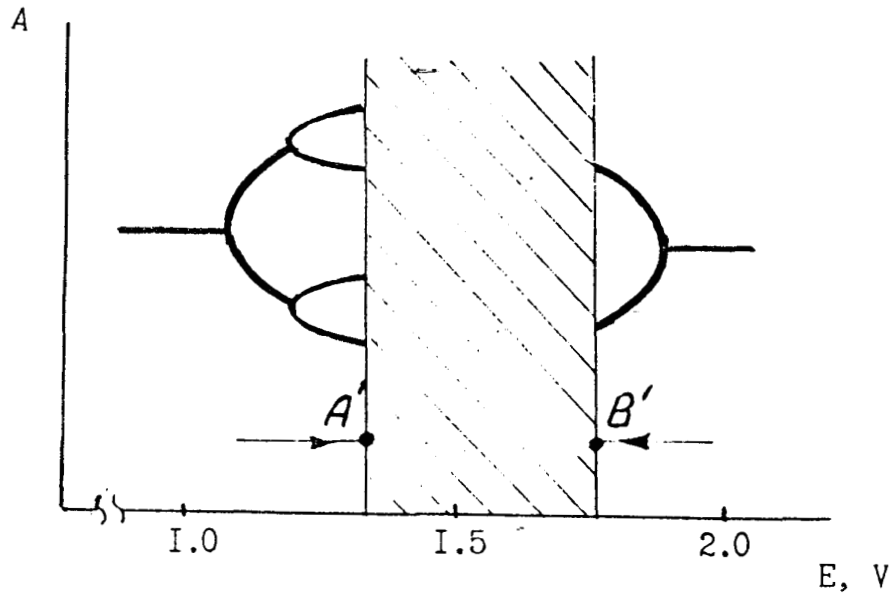


Fig. 9. Doubling scheme of current oscillations period

Fig. 9 shows the doubling scheme of current oscillations period

We see that after sequential doubling and quadrupling under specific potential our system transforms into the field of oscillations described by a strange attractor.

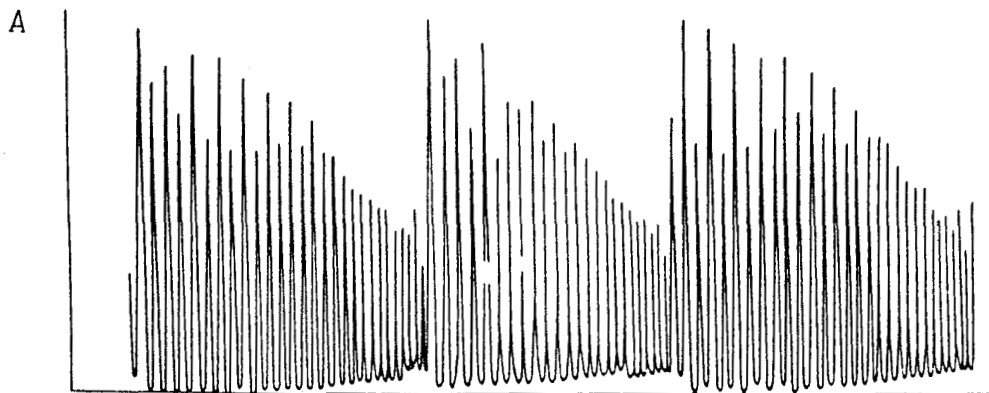


Fig. 10. Shape of current oscillations in the area A-B.

Current oscillations in the area A-B are shown in Fig: 10.

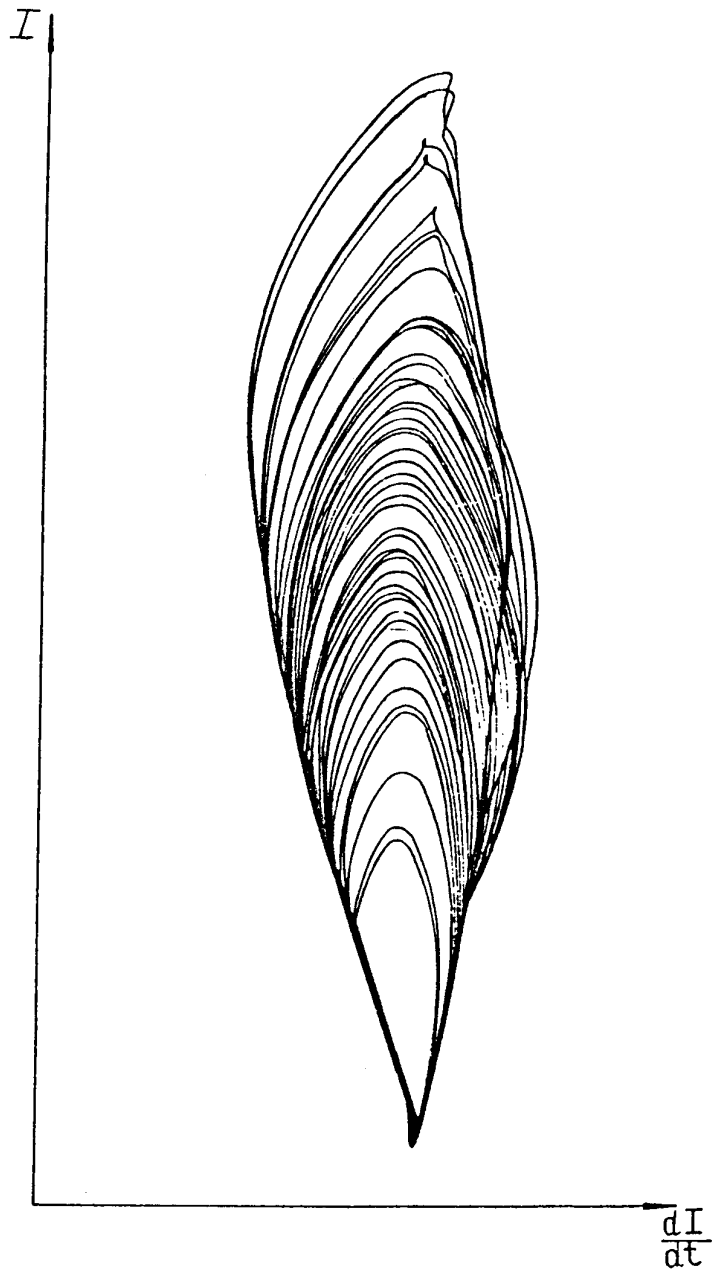


Fig. 11. Phase portrait of the strange attractor.

In Fig. 11 one sees the phase portrait of the strange attractor at point B.

It is a very important point for this process !
with The location of the boundary points A and B is very stable
with respect to the fluctuation of the external conditions. Our
experiments showed that with EP of SC cavities at this point
there are no flaws caused by pittings.

So, using special conditions of the experiment, a voltage - current curve with 3 areas of electric instability was obtained

Practically, this means the possibility to conduct the EP process at three levels with metal removal varying in thickness ($0.01 \mu\text{m/p}$, $0.1 \mu\text{m/p}$, $0.87 \mu\text{m/p}$). The current oscillations described by the strange attractor are at every level.

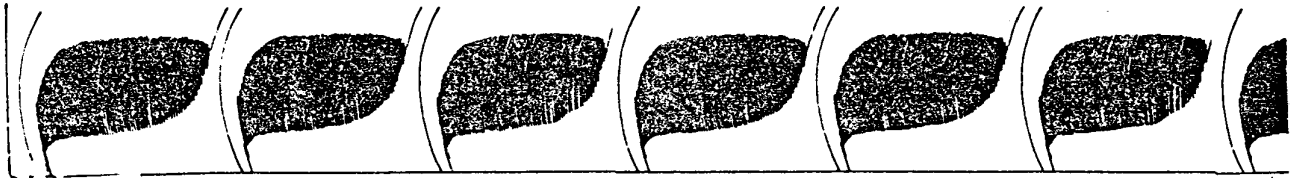


Fig. 12. "Pockets" at pauses of 5 min.

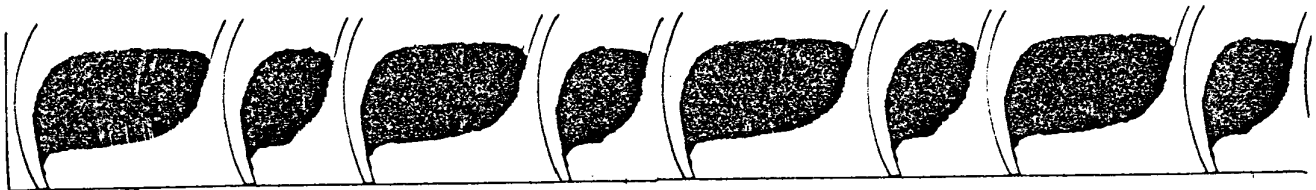


Fig. 13. "Pockets" at pauses of 45 sec.

"Pockets" in fig.12 correspond to $0.01 \mu\text{m}$ of metal removal per "pocket" (pause between "pockets" is 5 min).

"Pockets" in fig. 13 have pauses of 45 sec.

Advantages of this method :

1. There are actually no defects caused by development of pitting, which saves some amount of expensive Niobium.

2. Elimination of pittings and smoothing the microroughness on the working surface of SC cavities reduce the effect of field emission.

3. Since the boundaries of the existence of oscillations described by the strange attractor are stable, it is possible to automatize the process using a fairly simple scheme.

COMPARISON OF EXPERIMENTAL RESULTS.

1. All laboratories working on SC cavities arrived at the conclusion that it necessary to remove by hard EP or CP 60-100 μm from the working surface of a cavity. This is actually the layer thickness deteriorated by mechanical treatment or rolling.

2. The techniques of hard EP of SC cavities were developed at KEK, WU, IHEP. Among them are:

- horizontal rotation electrochemical polishing with current density control;
- electrochemical polishing with potential control method;
- alternating current electrochemical polishing.

They are all continuous EP methods used for preliminary treatment of the working surface.

3. In addition, KEK and IHEP have developed the techniques of the final EP of SC cavities:

- horizontal rotation electrochemical polishing with current density control;
- electrochemical polishing with current oscillation "pockets", described by strange attractor (IHEP).

4. All classical methods, i.e.,

- electrochemical polishing under current oscillations control
- horizontal rotation electrochemical polishing with current density control,
- electrochemical polishing with potential control method,

when compared, make it possible to obtain the height of microroughnesses within a range of 0.15-0.2 μm . The results obtained by different methods are summarized in table 1.

Method	height of microroughnesses, μm
HR-ER	0.15-0.20
EP-PC	0.20-0.25
CE-AC	0.10-0.08
EP-CPSA	0.04-0.05

Some words about the EP method with the control of oscillations "pockets" shape.

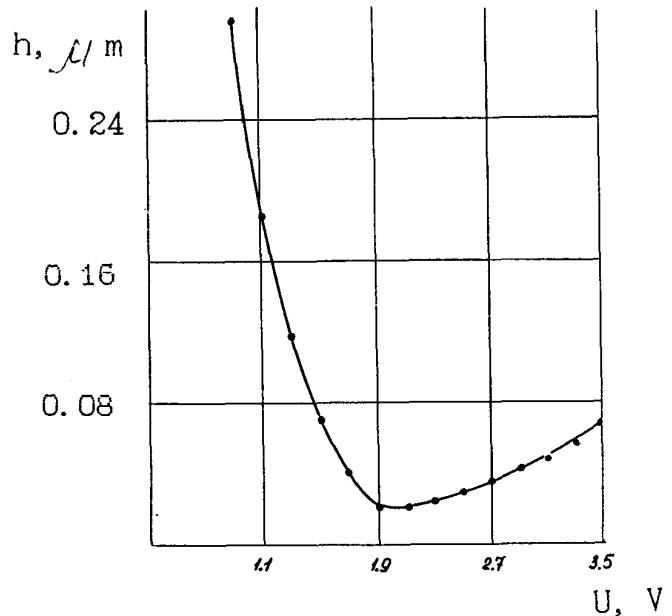


Fig. 14. The height of microroughnesses versus the voltage.

Figure 14 shows the height of microroughnesses on the niobium surface versus the EP voltage.

The minimum of this dependence coincides with the region of formation of oscillations "pockets", shown in figs. 12 and 13. This means that the control of EP polishing according to the form of current oscillations "pockets" ensures the most efficient smoothing of the working surface in the 0.04-0.05 μm range.

5. Process rate.

A very important factor during large-scale production of SC cavities is the reduction rate, especially when it is necessary to remove 50-100 μm from the working surface of a cavity.

The most productive methods are:

- horizontal rotation electropolishing with current density control;

- electropolishing with potential control method;

- method of continuous EP with alternating current control.

Since it is expedient to obtain the best results during the final EP, one should sacrifice some time for treatment as in this case only 6-20 μm of the working surface are removed.

The safest method for personnel and equipment is alternating-current EP developed by IHEP. The ratio of the solution used in this process is $\text{HF}:\text{H}_2\text{SO}_4 = 1 : 25$ or even less.

5. C O N C L U S I O N.

So, the EP technique is presently getting more popular among the people working on SC cavities. The results obtained in different laboratories testify to the promising nature of this technique for the technology of SC cavities. These results allow us to hope that we can improve the working surface of cavities and, using the EP technique, raise the gradients of SC RF structures.

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