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in

"Surface Treatments for Industrial Applications"

TITLE

Study of the Electropolishing of 6GHz Niobium cavity in ionic liquids

Supervisor: *Prof. V. Palmieri*

Co-Supervisor: *Dott. V.Pastushenko*……

Student: *Dott. Malkova Olha Volodumurivna*

N.Matr.: 1064847

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Contents

Acronym

EP – Electrochemical Polishing,

ChChl - Choline Chloride,

SA - Sulfamic acid,

AS – Ammonium Sulfamate,

ADTA - Ethylenediaminetetraacetic acid,

BCP - Buffer Chemical Polishing,

BEP - Buffer Electrochemical Polishing,

IL – Ionic Liquid.

Abstract

INFN – LNL Laboratories have been already working for several years on the problem of removing fluoride ions from a solution for polishing of niobium. Ionic liquids are one of the possible solutions for this problem. The first results of niobium polishing have already been obtained in ionic liquid - Choline Chloride with Urea. During polishing in the ionic liquid was obtained smooth shiny surface with a roughness comparable as obtained after polishing in classic electrolyte. Various additives such as sulfamic acid, ammonium sulfamate, can improve the condition of the surface.

Our task is to apply this knowledge to polish RF cavities. In our work we try to create new ionic liquid and improve one that was previously obtained. In our laboratory we built new system for electropolishing 6 GHz cavities considering the experience of previous years.

1 Introduction

The goal of this work is to investigate the correct parameters the electropolishing of niobium RF cavity in ionic liquids. Almost all electrochemical industrial processes are generally based on aqueous solutions. The key advantages of using aqueous solutions are cost, non-flammability, high solubility of electrolytes, high conductivities resulting in low ohmic losses, high solubility of metal salts and high rates of mass transfer. However, despite these advantages, there are several limitations in using aqueous solutions such as limited potential windows, gas evolution processes that can result in hydrogen embrittlement, passivation of substrates, electrodes and deposits, and the necessity for hazardous complex agents causing environmental contamination. Ionic liquids have attracted considerable interest as potentially environmentally-benign reaction media due to their low vapor pressures and high thermal and chemical stability

A superconducting cavity is the device used to provide energy to the particles that are crucial to an accelerator. In the past, copper cavities were used for acceleration (e.g., at SLAC). However, superconducting niobium technology has proven itself over the last 20 years as a promising alternative, being used in machines such as HERA (Hamburg, Germany) and TJNAF (Newport News, VA) [1].

In our work we use 6 GHz niobium cavities. Obviously the most direct way to test RF properties of a superconductor would be the use real size cavities, but 1.5 GHz resonance structures would be too expensive for costs and long for time production. So the idea to build micro-cavities completely equal in shape to the real scale model brings a lot of opportunities. Considering that for polishing cavity usually use dangerous hydrofluoric acid, the idea of using miniature cavity become very attractive.

Surface finish dependence on duration of electropolishing, temperature and position of niobium cavity was also studied.

1.1 Properties of Niobium

Niobium is a chemical element with the symbol Nb and atomic number 41. It is a soft, grey, ductile transition metal, which is often found in the pyrochlore mineral, the main commercial source for niobium, and columbite. [2]

Niobium was discovered in 1801 by Charles Hatchett, and was originally named “columbium”, in the same time German chemist, Heinrich Rose, was recognized its metal and gave its name a “niobium”. “Niobium” was finally accepted in 1949. [3]

The metal takes on a bluish tinge when exposed to air at room temperature for extended periods. [4] Despite presenting a high melting point in elemental form (2,468 °C), it has a low density in comparison to other refractory metals. Furthermore, it is corrosion resistant, exhibits superconductivity properties, and forms dielectric oxide layers. [2]

The unique properties of niobium make its vital component in a diverse range of products and applications.

About 89 per cent of global niobium production is used to produce ferro-niobium, used in high strength low alloy steels, the remaining 11 per cent is used in manufacture of niobium alloys, niobium chemicals and carbides , high-purity ferro-niobium, and other niobium metal products.

Production of niobium in world, rapidly increased 20 000 tones in 1997 to over 100 000 tones in 2009. The increase in niobium production is linked to growing consumption of HSLA, used in manufacture of cars, buildings, ships and refinery equipment. Also niobium is used in mobile telephones, superconducting magnets, glass and camera lens coatings, superalloys and functional and structural ceramics [3]. And that's not all applications of niobium.

Niobium (Nb)	
Atomic number	41
Atomic weight	92.90638
Density at 293 K (g/cm^3)	8.581
Melting point °C	2468
Boiling point °C	4930
Vickers hardness MPa	1320
Electrical resistivity (nano ohm-meter)	152 at 0 °C
Crystal structure	Body centered cubic

Table 1.1. Some physical properties of Niobium

1.2 Application of Niobium as RF cavity

A radiofrequency (RF) cavity is a metallic chamber that contains an electromagnetic field. The RF cavity is molded to a specific size and shape so that electromagnetic waves become resonant and build up inside the cavity. Charged particles passing through the cavity feel the overall force and direction of the resulting electromagnetic field, which transfers energy to push those forwards along the accelerator. [5]

The many different materials are used to produce cavity. From pure metals the metals with coatings, alloys and inorganic compounds; Niobium is more and more applicable. There are several reasons. Its has the highest T_c of 9.25 K among the all available elements in the period table. This makes the requirement for cooling the cavities down to a temperature below T_c a relatively easy task. Furthermore, since E_{acc} is proportional to the peak electric field (E_{pk}) and peak magnetic field (H_{pk}) on the surface of a cavity, one has to be sure that the material that is used to make the cavity can sustain large surface fields before causing significant increase in surface resistance or a catastrophic breakdown of superconductivity (called quench). The ultimate limit to accelerating gradient is the theoretical RF critical magnetic field that is called the superheating field H_{sh}. Nb has the highest H_{sh} of 0.23 T among the all available metal elements.

Another advantage of Nb is that it is relatively easy to be shaped into different structures due to its outstanding ductility and the fact that it is relatively soft. Nb can be cold-worked to a degree more than 90% before annealing becomes necessary. This property is responsible for the recent new developments on fabricating seamless Nb SRF cavities by hydroforming and spinning.

Although there are other superconducting compounds that have higher T_c or higher H_{sh}, they either are not having the three mentioned characters in a superconductor or were discovered much later as superconductors than Nb. It is fair to say that so far Nb is the most investigated material for SRF applications and the major material used in particle accelerators based on SRF technology. Only limited research effort has been put on other superconductors such as NbN (T_c=16.2 K), NbTiN (T_c=17.5 K), Nb_3Sn (T_c=18.3 K), V_3Si (T_c=17 K), Mo_3Re (T_c=15 K), and MgB_2 (T_c=39 K).[6]

Between the different form and size, we stayed on the 6 GHz cavity. Because it is easier to handle like a sample, useful diagnostic way to accurately investigate local properties of a bulk superconductor, of the grown superconducting films and given surface treatments on them. For the produce one cavity is needed short time of fabrication, just half a day. For this reason with low research budget is possible to produce large amount cavities and make more tests.

Figure 1.1. 6 GHz cavities for the RF tests

2 Surface treatments of 6 GHz cavities

Fabrication of the 6 GHz cavities makes many internal imperfections. Such as surface defects, stress and dislocations. For achieving the necessary properties, surface of the cavity inside should be smooth and does not contain inclusions. Therefore to apply the following polishing processing: mechanical, chemical and electrochemical treatments.

2.1 Mechanical treatment

To achieve a high quality surface, the each step of process is important. For this reason before to start a chemical or electrochemical polishing, the surface is treated mechanically.

Tumbling - is a technique for smoothing and polishing a rough surface. Sample put together with liquid and abrasive materials inside a closed system. When system rotates the abrasive particles removes the material layer. The liquid provides a soft glide over the surface of the abrasive.

In previous years in LNL was used of small tumbling system for the polishing of 6 GHz cavity.

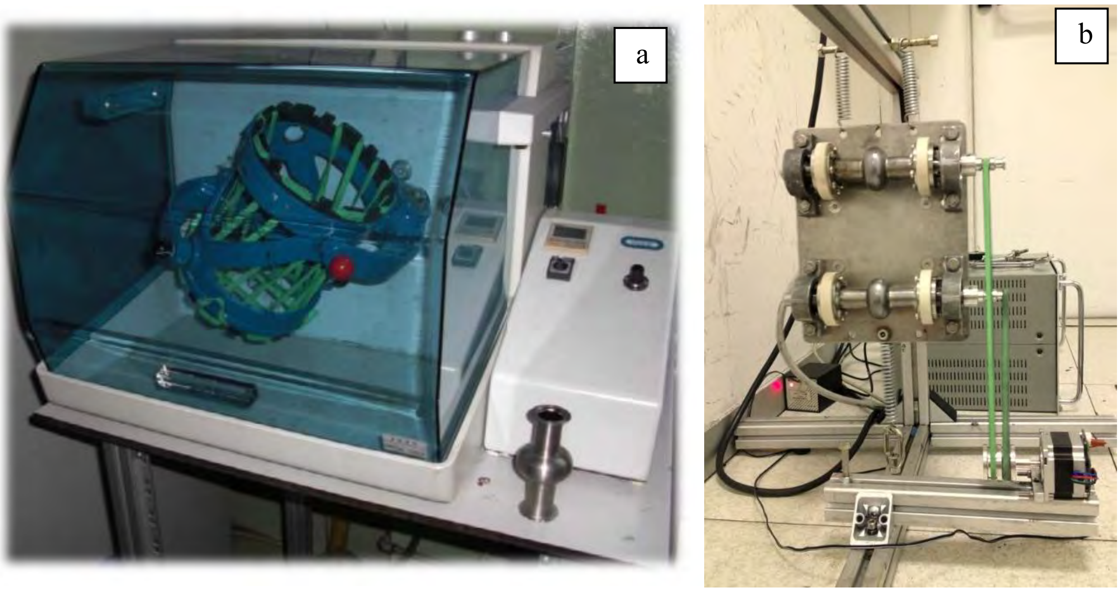

Figure 2.1. Systems for the tumbling. a- in previous years, b- new development.

It is possible to use the different materials for this mechanical polishing. Like example:

1) small SiC triangular shaped blocks - is a very hard material (it can be used for the first low level mechanical polishing)

2) 5 mm sphere of stabilized zirconium dioxide - is a high density material (the intermediate level)

3) flakes of Al_2O_3 and SiO_2 powders embedded in a polyester matrix – are soft (the final surface finishing)

In the last year in LNL our colleagues have developed new automatic system for the mechanical polishing of cavity. Advantages of this system are that we can implement the polishing more than one cavity in one time. We make polishing surface just inside and change parameters of system we can work with cavity of the different size.

2.2 Chemical Treatment

The Niobium chemical etchings, commonly called Buffer Chemical Polishing (BCP), are a mixture of Hydrofluoric, Nitric and Phosphoric acids, respectively in the ratio 1:1:1 or the ratio 1:1:2. Nitric acid plays the role of oxidant the Niobium surface. Hydrofluoric acid reduces the Niobium Pentaoxide into a salt that is soluble in water. Phosphoric acid acts as a moderator for the chemical reaction giving rises to a less turbulent and more controllable reaction. The main reaction happening at the Niobium surface is reported [7]:

1) $6\,Nb + 10\,HNO_3 = 3\,Nb_2O_5 + 10\,NO + 5H_2O$
2) $Nb_2O_5 + 10\,HF = 2\,NbF_5 + 5\,H_2O$
3) $3Nb + 5\,HNO_3 + 15\,HF = 3\,NbF_5 + 5\,NO + 10\,H_2O$

BCP etches the grains of different orientation and the grain boundaries at different rates and results in an uneven surface, but a surface free of any mechanical damage or residual stress.

2.3 Electropolishing

EP process involves material removal in an acid mixture under the flow of an electric current. A mixture of hydrofluoric (HF) and sulfuric (H_2SO_4) acids, with ratio 1 to 9, is used as the electrolyte. During the process solution is pumped throw the cavity from bottom part to top part for easier removing hydrogen from the cavity which is forming on cathode. After the half of process time cavity is swapped the position on 180 for flux substitution [1]. The cathode material is copper or aluminum. As the electric field is highest on the peaks of a rough surface, the peaks dissolve faster than the valleys, and therefore depending on the initial peak-to-valley value, EP can be a slow process. However, a very glossy surface can be obtained with EP [8].

2.3.1 Fundamentals of electropolishing

Electropolishing is a surface finishing process by which a metal surface is made smooth and bright by making it an anode in an appropriate electrolytic solution [9, 10]. There are many applications of electropolishing, for example in surgical tubing, medical cutting instruments, food processing blades, hard disk drives and automotive parts [11]. The earliest explanations of electropolishing were given by Jacquet and Elmore. Jacquet attributed electropolishing to the formation of a viscous layer on the work piece [9]. The non-uniform thickness of the viscous layer over the material surface results in a different ohmic resistance from the cathode to the anode. This cause greater dissolution of the protruded parts compared to the depressed part, thus creating a uniform surface profile. The value of the diffusion layer thickness, δ over the protrusion is smaller than the value over the valley. Therefore, the value of the limiting current, would be larger over the protrusion compared to that over the , resulting in the metal surface being leveled out as electropolishing proceeds. This is the generally accepted mechanism for electropolishing and mass transport control has been established as the reason behind electropolishing.

Electropolishing of many metals was studied henceforth and it was found a particular voltage range in the I-V characteristics (Figure 2.2.) of the metal in the electrolytic system is necessary to get the best surface finish. This voltage range is associated with mass transport control and is characterized by a constant current density independent of the voltage applied.

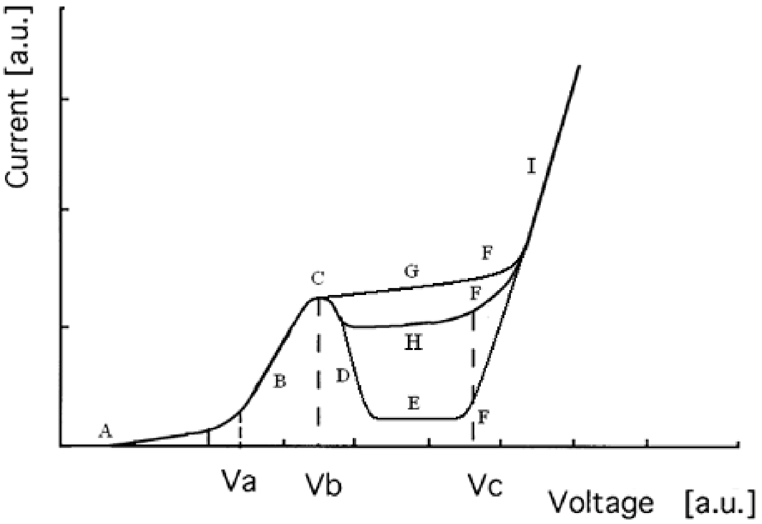

Figure 2.2. Schematic diagram of anodic polarization.

In the Nernst diffusion layer model, it is assumed that a concentration gradient exists at the interface which varies linearly initially and then has a curvature and merges with the final constant bulk concentration of the species under consideration [12]. It is a mathematical construct that separates the electrolyte region near the surface in which transport is by diffusion from rest of the electrolyte.

The mechanism of electropolishing is related to the current distribution on the surface of the sample. The current distribution has been classified as primary, secondary, tertiary or quaternary depending on the factors influencing it [13]. The primary current distribution is affected by the ohmic resistance and its role in electropolishing is dependent on geometrical factors like anode-cathode distance and initial geometrical profile of the surface to be polished. The secondary current distribution includes the effect of charge transfer overpotential along with the geometrical factors. Concentration overpotential along with the above factors constitutes the tertiary current distribution and is a necessary condition to obtain a smooth surface by electropolishing. Hydrodynamic effects also contribute to the current distribution. Hydrodynamics has been found to be an important consideration for defects generated during electropolishing [14].

2.3.2 New recipes for the Electrochemical polishing

In the new recipes Buffer Electrochemical Polishing (BEP) uses the acid mixture of hydrofluoric, sulfuric, and lactic acids as the electrolyte at a volume ratio of 4:5:11. Here lactic acid acts as a buffer in a similar way as what H_3PO_4 does in BCP. By replacing the majority of H_2SO_4 in the electrolyte of the conventional EP by lactic acid, BEP treatment reduces the aggressiveness of the electrolyte significantly. It has been demonstrated that BEP can produce the smoothest [15 -1 8] Nb surface ever reported in the literature. Smoother inner surface of a Nb SRF cavity is known to have positive effects on its RF performance. Experiments also show [15, 19] that Nb removal rate can be as high as 4.67μm/min. This is more than 10 times faster than 0.38 μm/min of EP. Faster Nb removal rate can contribute significantly to the reduction of the capital costs of the surface treatments. Other benefits of BEP as compared with EP include:

a) Acid mixture is much safer to handle,

b) The life of the acid mixture is longer,

c) Acid mixture is cheaper,

d) Less or any sulfur precipitation.

Figure 2.3 shows a quantitative comparison on the surface smoothness for Nb treated by BEP, EP, and BCP as measured by a precision 3-D profilometer [20]. The scans are plotted with the same parameters for comparison.

Following the reasons not to use HF, as an extremely dangerous, it is possible to use the next electrolytes for the polishing of niobium:

1. Electrolyte base on Fluosulphuric acid. But this acid is strongly suspected to be cancerogenic.

2. The mixture of Perchloric acid, Ethylic acid, Acetic anhydride is an universal electropolishing mixture for the electropolishing of transition metals. But ethyl-perchlorate is as dangerous as nitroglycerin.

3. Perchlorate Salts were successfully used for electropolishing niobium samples. The recipe consists of $Mg(ClO_4)$ in 0.05 M/l diluted in methanol.

4. It can also successfully electropolished by sulphuric acid in methanol. But methanol is very flammable, harmful if inhaled or absorbed through skin.

5. Electro-dissolution of niobium is possible in 1 M KOH solution at 70°C, with stirring.

6. The mixture of ($NaCl$-KCl-$NbCl_n$) and $AlCl_3$ melts at 710°C. But anhydrous $AlCl_3$ can give rise to unpleasant exothermic reactions [21].

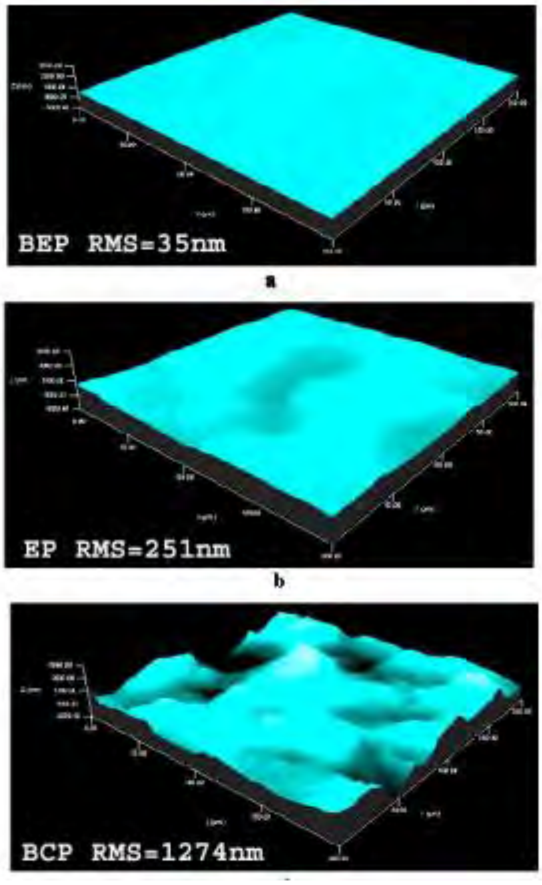

Figure 2.3. Typical high resolution 3D profilometry scans on the surfaces of: (a) buffered electropolished Nb, (b) electropolished Nb, and (c) buffered chemical polished Nb.

Many of these recipes are even more toxic or dangerous than HF. Only in the last decade has opened the possibility electropolishing of the niobium by method that is simple and safe. This method is EP in Ionic Liquids (we will talk about it more in the next chapters).

2.4 Other new technologies to remove Niobium

Plasma etching on Nb is a R&D project through the collaboration [22] between University of Old Dominion and JLab. The idea here is to use some reactive gas species such as, for instance, Ar/Cl_2 or BF_3 to chemically react with Nb under the discharge from a DC or RF source. This will generate some volatile Nb compounds that can be pumped away. It was demonstrated [23] that an etching rate of 1.5 μm/min can be reached when Cl_2 was used as the reactive agent. The surface finish produced by plasma etching appears to be comparable to that by BCP at the present stage of development. This technique is attractive since it does not employ HF and it can produce be done with a decent etching rate.

3 Ionic liquids

The early history of ionic liquids began in 1914 when the first report of a room temperature molten salt was reported by Walden. He reported the physical properties of ethylammonium nitrate, which has a melting point of 12 ˚C, formed by the reaction of ethylamine with concentrated nitric acid. The major interest in ionic liquids was first connected with their potential for the development of new electrolytes to be used in the electrical batteries and electroplating of aluminum. One such kind of room-temperature molten salt system was reported in the late 1940s by Hurley and Wier. They stated that a room temperature ionic liquid could be prepared by mixing and warming 1-ethylpyridinium chloride with aluminum chloride. In the 1970s and „80s, Osteryoung and Hussey et al [24, 25], carried out extensive research on organic chloride-aluminum chloride ambient temperature ionic liquids and the first major review of room temperature ionic liquids was written by Hussey [26, 27].

Figure 3.1. Ionic liquid that have used in this work: from the left – Choline Chloride; from the right – Urea; in the center combination both components were heated to about 100°C.

Ionic liquids are molten salts with melting points below 100 ˚C and they consist solely of cations and anions. The charge on these ions is delocalized or shielded by side groups, which is one reason why the melting points of ionic liquids are remarkably low. There are a wide range of different ionic liquids, binary and ternary mixtures with versatile properties [28]. In contrast to conventional molecular solvents, ionic liquids are usually non-volatile, non-flammable, less toxic, good solvents for both organics and inorganics and can be used over a wide range of temperatures [29]. Most ionic liquids have at or near room temperature vapor pressures of 10^{-11}-10^{-10} mbar [30] allowing experiments to be done at temperatures up to 400 ˚C. The very small vapor pressure of ionic liquids also allows their use in vacuum experiments even at elevated temperatures. The most important advantage of ionic liquids which is of significant relevance to this study, is their large electrochemical windows (> 5V) which gives access to elements that cannot be electrodeposited from aqueous or organic solutions such as for example, Al, Mg, Ti and Ta, at moderate temperatures [31, 28]. A series of transition and main group-metal containing ionic liquids have been formulated and electrodeposition of these metals have been achieved. It is important to review the principle factors that make ionic liquids differ from aqueous solutions. Some of these principle factors are conductivity, viscosity and potential window. All of these factors will affect the rate at which metal ions diffuse to the electrode surface and the thermodynamics and kinetics of the metal reduction process. These in turn control the nucleation and growth mechanisms and affect the material morphology and it is the fundamental mechanism of material growth that needs to be understood. It must be stressed however, that while the deposition of a wide range of metals has been demonstrated from a number of ionic liquids, the practical aspects of controlling deposit morphology have not been significantly addressed in literature due to the complex nature of the process parameters that still need to be understood. Furthermore, there are still a lack of reliable models to describe mass transport and material growth in ionic liquids1. The degree and type of substitution determines the salts low melting point, largely by reducing cation-anion Coulombic interactions and disrupting ion-ion packing. This results in low melting salts with reduced lattice energy and a marked tendency to form glasses on cooling, rather than crystalline solids. Common anions that yield useful ionic liquids include hexafluorophosphate $[PF_6]^-$, tetrafluoroborate $[BF_4]^-$, bis(trifyl)imide, $[NTf_2]^-$ and chloride, $[Cl]^-$ [32]. Although high symmetry, pseudo-spherical, non-coordinated anions are commonly regarded as optimal for formation of ionic liquids, the existence of low melting ionic liquids containing anions such as methylsulfate, dicynamide, and bis(trifyl)imide, show that shape and ion-interaction factors are more complex than predicted. Generally, the cation controls the physical properties of the salt such as its structure and morphology and the anion affects the stability and chemical reactivity [33]. Moreover, the anion affects coordination geometry around the metal ion which effects reduction potential, reduction current and nucleation. Both the anion and cation affect the conductivity and viscosity. The anions, in particular, have been substituted by increasingly stable alternatives.

3.1 Properties of ionic liquids

Properties such as dissolving ability from metal salts, polarity, viscosity and density can be tuned by an appropriate choice of the anion and the action. Overall, ionic liquids are inevitably advanced, technological solvents that can be designed to fit a particular application. One of the fundamental properties of an ionic liquid is ion conductivity. Ionic liquids have reasonably good ionic conductivities, between 10^{-3} and 10^{-2} Ω^{-1} cm^{-1}, compared with those of organic solvents/electrolyte systems [27, 34]. These conductivities make ionic liquids interesting solvents for low-temperature electrodeposition studies. At elevated temperatures of e.g. 200°C, a conductivity of 0.1 Ω^{-1} cm^{-1} can be achieved for some systems. However, at room temperature their conductivities are usually lower than those of concentrated aqueous electrolytes. Aqueous electrolytes typically have conductivities in the region of 100-500 mS cm^{-1} because they are mostly high strength aqueous acids. The reason for significantly lower conductivities at room temperatures is the large constituent ions of ionic liquids which reduce the ion mobility which, in turn, leads to lower conductivities [27].

One of the main differences between ionic liquids and aqueous solutions is the comparatively high viscosity of the former [35]. Viscosities are typically in the range 10-500 cap (0.01-0.5 Pa s) [27] and this has a direct effect upon the diffusion coefficients not only of the metal species to the electrode but also the counter ions and complex ants away from the diffusion layer. The viscosity of room temperature ionic liquids is several orders of magnitude higher than high temperatures molten salts due partially to the difference in size of the ions, but also due to the increased void volume. At elevated temperatures, however, the viscosity decreases by more than one order of magnitude. Hence, increasing the temperature increases conductivity and lowers viscosity. Generally, ionic liquids are also denser than water with values ranging from 1 to 1.6 g/cm^{-3} and their densities decrease with increase in the length of the alkyl chain in the action [27]. The density of ionic liquids is also affected by the identity of anions, as different anions have different densities.

Another fundamental property of ionic liquids is that they have a wide liquid range and thermal stability [33, 34]. Thus these liquids can be used at wider temperature ranges and still have great thermal control of electrochemical processes, unlike when using conventional molecular solvent/electrolyte systems. Moreover, due to their extremely low vapor pressures, ionic liquids can be thermally stable up to temperatures of 400 ˚C. Studies have shown though, that high temperatures are only tolerated by most liquids for a short time and that long time exposure to high temperatures leads to decomposition [27]. The decomposition temperature of ionic liquids depends on the component ion structure, similarly to other thermal properties

Ionic liquids are differentiated from typical inorganic salts by their low melting point (T_m). Typical inorganic salts have a high T_m; around 1000 ˚C reflecting high lattice energies, i.e., the high T_m is attributable to a strong electrostatic attractive force between the ions. Since the ionic liquids are organic compounds, van deer Waals interaction, hydrogen bonding, and π-π interaction are additionally present among the component ions and affect the T_m of ionic liquids. Accordingly, the structural design of component ions to weaken the electrostatic interaction as well as other interactions is directly effective in lowering the T_m of the salts. When ions have equivalent charges, the electrostatic interaction decreases with increasing ion radius since the surface charge density decreases with increasing ion radius and the separation between the ions also increases. As a result, the electrostatic interaction of larger ions is then weaker and accordingly the salts show lower T_m. In general, organic salts have lower T_m than inorganic salts because of their larger ion size. Symmetry is another factor to affect T_m. The salts with symmetric ions generally show higher Tm than those with asymmetric ones [36].

The electrochemical window of ionic liquids is an important property and plays a key role in using ionic liquids in the electrodeposition of metals [27, 33]. The electrochemical window is the electrochemical potential range over which the electrolyte is stable and neither reduced nor oxidized at an electrode, which in turn determines the electrochemical stability of solvents. The potential window is influenced not only by the chemical structure of the materials used but also by the electrode materials, sweep rate of the potential, temperature, atmosphere, solvent and impurity. In addition, the use of various reference electrodes for the determination of cathodic and anodic limits of ionic liquids makes the situation even more complicated.

Generally, cathodic and anodic limits of pure ionic liquids are attributed to the oxidative decomposition of the anion and the reductive decomposition of the cation, respectively. Impurities, especially water and halide anions, must be removed carefully, otherwise these drastically narrow the potential window. The electrodeposition of elements and compounds in water is limited by its low electrochemical window of only about 1.2 V. The following two reactions: $2H_2O \rightarrow O_2 + 4e + 4H^+$ and $2H^+ + 2e \rightarrow H_2$, limit the potential window in water hence materials with a redox potential outside of the window, such as refractory metals, will be thermodynamically unstable. On the other hand, ionic liquids have significantly larger electrochemical windows and can go up to 6 V [32]. As a result, the wide electrochemical windows of ionic liquids have given access to the electropolishing of metals and semiconductors at room temperature, which were formerly obtained only from high temperature molten salts [37]. However, ionic liquids can have a significant impact on the potential limits and the corresponding electrochemical window. In addition, residual water in ionic liquids can be reduced and oxidized within the electrochemical window of many ionic liquids. Consequently, contamination of an ionic liquid with significant amounts of water can decrease the overall effective electrochemical window. Furthermore, water can react with anions in the ionic liquid to produce products that are electroactive in the electrochemical potential window [38].

Due to their multitude of useful properties and abilities, ionic liquids have become alternatives for many industrial applications such as synthesis and extraction processes, electrochemistry, electrodeposition, photochemistry, liquid crystals, CO_2 capture, desulfurization of fuel, enzymatic synthesis, lubrication, rocket propulsion and thermal storage devices, to name just a few. One of the main reasons in using ionic liquids is because electroplating a range of metals: Al, Ti, Ta and Nb are impossible in aqueous solutions due to hydrolysis [36]. Moreover, the ability to deposit or polish these metals in ionic liquids will bring forth opportunities in various industries because of these metals‟ heat corrosion resistance, abrasion resistance and high or low density.

3.2 The advantages of using Ionic Liquid

From the environmental perspective ionic liquids are environmentally cleaner than other media. When used in electroplating processes, strongly aqueous electrolytes create quantities of metal-laden, corrosive effluent solution, whereas in ionic liquid electrolytes the metals will precipitate and be readily separated and recycled. Most of the ionic liquids are non-toxic and non- flammable. In addition, their very low vapor pressures allows them to be used in open galvanic baths at variable temperatures without releasing harmful vapors, which, in turn, reduces the amount of volatile organic compounds released into the atmosphere [30].

Although the cost of ionic liquids will be greater than aqueous electrolytes, high conductivity and better efficiency will provide significant energy savings compared with water. Furthermore, ionic liquids have been considered to be possible environmentally friendly, recyclable media for synthetic organic chemistry, separation sciences and other chemical sciences and engineering. Ionic liquids contain organic cations and anions which melt at or close to room temperature. Their low vapor pressures allow chemical processes to be carried out with essentially zero emission of toxic organic solvents into the environment.

Therefore, such systems are becoming increasingly technologically important. However, due to considerable lack of appreciation and basic research, the use of ionic liquids in chemical industry and other disciplines has not yet become widespread [39].

3.3 Previous success Electropolishing of Niobium in Ionic Liquids

In the work [40], have obtained successful dates, with using of an ionic liquid prepared from (2-hydroxyethyl-trimethylammonium) chloride (CC) (Across Organics 99%), ethylene glycol (EG) (Sigma-Aldrich 99.8%), urea (UA) (Aldrich > 99%), and ammonium fluoride (AF) (Aldrich). With the ratio of components 2CC:2AU:2EG:1AF. All trials were performed at 70°C with chronoamperometric tests set to 900s. The electrochemical polishing reduces the surface roughness to less than 22 nm of niobium.

In previous years at INFN – LNL Laboratories it was done the first Electropolishing of Niobium by a harmless mixture of Choline Chloride and Urea heated around 150°C. Different additives have been tried, such as Ammonium Sulfate, Ammonium Persulfat, Sulfamic Acid and e.t.c.

One from the best result consists of choline chloride and urea at a ratio of 4:1 plus sulphamic acid in a concentration of 30 g/l. The other is a mixture of urea and Choline chloride at a ratio of 3:1 plus ammonium chloride in a concentration of 10 g/l. Polishing has to take place at 120 °C and 190 °C respectively [41, 42]. The highest Nb removal rate can be 12 times quicker than that of the conventional EP. In the fig. 3.2 is shown of the surface before and after electropolishing in a mixture of Choline Chloride, Urea and ammonium chloride at 80°C [43].

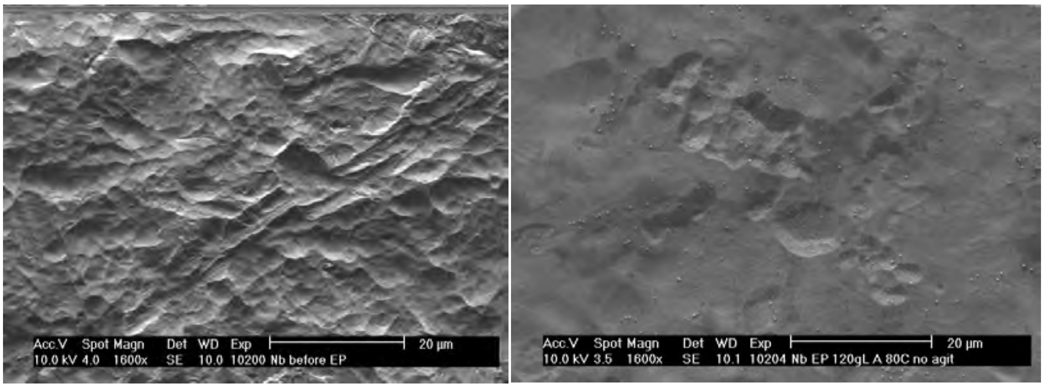

Figure 3.2: Surface of Niobium sample of: a) before treatment;

b) after treatment by ionic liquid.

The electropolishing by Ionic liquids can be comparison with classical solution for the electropolishing. Speed of the process more 10 times faster, work with this solution more care. In the fig. 3.3 [1] we can see 3D surface of the classical polishing and polishing by Ionic liquid (30g/l Sulfamic acid in 1:4 choline chloride – urea).

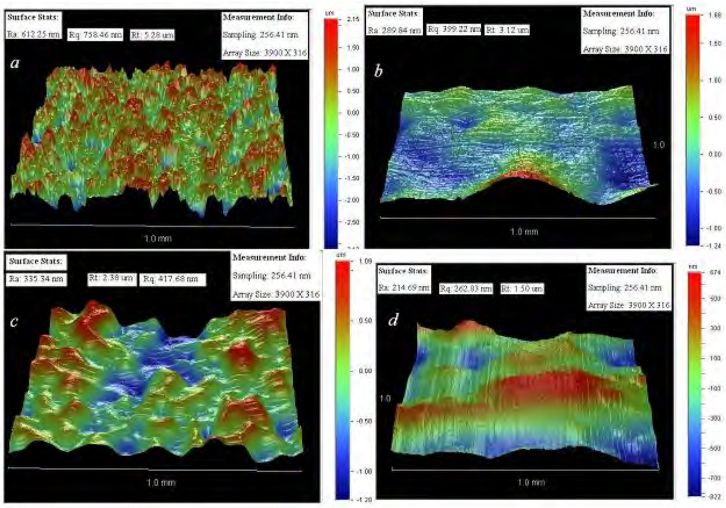

Figure 3.3 : 3D surface maps of different treatments of Niobium.

a – without treatment; b – 10 min classical EP; c – 10 min IL; e – 60 min IL.

4 Experimental part

4.1 Apparatus and procedure

4.1.1 Samples and solutions preparing

Samples were made from the material what uses for production 6 GHz cavity. Size of the sample is 5cm length and 2,5cm width. Samples were immersed on 3 cm inside the solution. Cleaning of the samples was in the next order:

1) washing in ultrasound bath with soap
2) washing in ultrasound bath in clean water
3) rinsing of demonized water
4) drying with alcohol or acetone using nitrogen blowing.

We have prepared the different amount of solution. ChChl and other additives (calculated quantity of weight), put together in baker and were heated slowly in the water bath. When components were melted we removed baker with the water and continue heating on the heater till 120°C. For the evaporation of residual water we continue heating about 1,5 hours.

In cause when we use mix ChChl and Urea, we pass some quantity of electricity before the process, use system with niobium cathode and anode. Concentration of Nb in solution is 2-4 g/l. And after we put in solution different additives, heat again till 120°C. After all this preparations we use electrolyte for polishing of the samples.

4.1.2 Two electrode system

Experiments were done in a backer with quantity of electrolyte ranging from 400 to 600 ml. The solution temperature was increased using heater. The electrolyte is always stirred (Figure 4.1). Electric power was taken from power supply AUNTEL S4000 (40A, 100V).

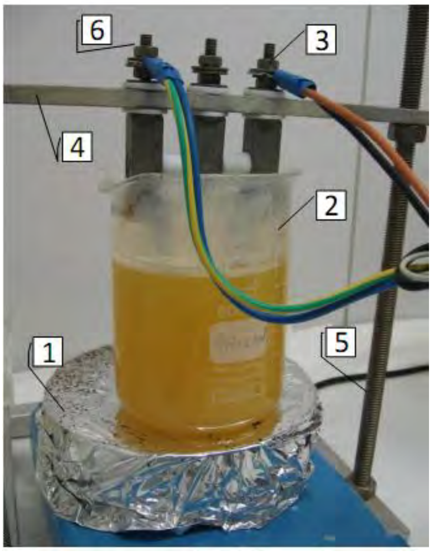

Figure 4.1: Investigation samples system

1 – heater; 2 – beaker; 3 – anode; 4 - sample holder; 5 – support;

6 – cathode.

4.1.3 Stylus profilometry

Profilometry is a method used to measure the profile of a surface, in order to quantify its roughness. The stylus detects small variations in vertical displacement as a function of lateral position. A typical profilometer is sensitive to vertical height variations ranging from 10 nm to 1 mm. Scan speed, contact force, and stylus radius all affect the lateral resolution. A typical stylus radius ranges from 5 to 25 µm. The profilometer used in this work was Veeco Dektat 32.

The scan length was 1000 µm. Scan duration was 13,0 sec. The contact force was 10 mg. The stylus radius was about 5 µm. Measure range – middle was 65000nm. Analyses were done using average roughness R_a and root of the mean square deviation of the depth of the roughness profile R_q.

For every samples were measured 5 times, after were calculated medium value roughness for the each samples.

4.1.4 Systems for the electropolishing of cavity

6GHz cavities electropolishing was done in different ways:

- Open system horizontal
- Open system vertical
- Closed system vertical
- Closed system horizontal

In horizontal variants (closed and open), we have tried to polish all cavity and half of cavity, with rotation and without, with flow of nitrogen and without.

4.1.5 The miniature camera

The cavity has a complex profile design, to compare the surface before and after the electrochemical treatment, we use a miniature camera (see Figure 4.2). We do pictures before and after and compare results.

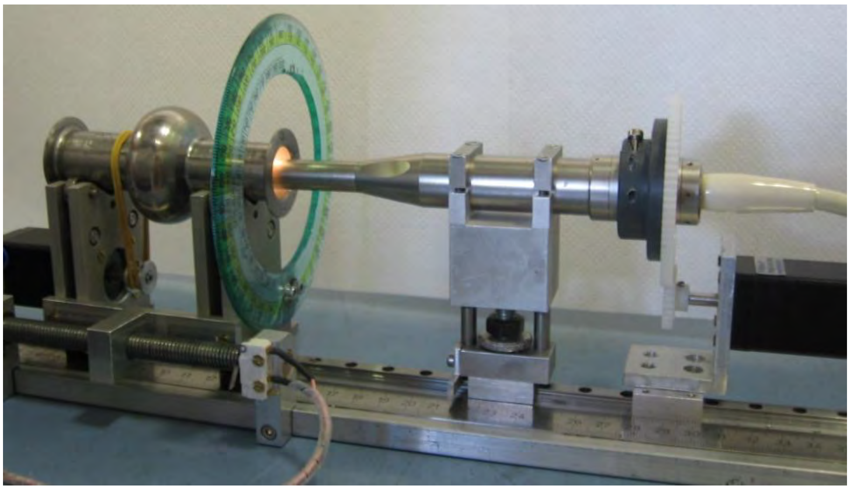

Figure 4.2. Miniature camera.

The miniature camera tool can be moved forward, backward, up and down inside the cavity. The tool displacement along the cavity axis can be easily measured with the ruler fixed on the system basis.

4.2.1 Electropolishing in Choline Chloride based solution

We tried to create ionic liquids with Choline chloride and different components. We prepared solution by dissolving compounds together at temperature higher than 100°C. We immersed the Niobium sample inside solution with niobium cathode and supplied current.

The results represented in the next three tables. Ionic liquids which create oxide films on Nb surface, compounds what together do not create ionic liquids and ionic liquids which dissolve Nb but can not create the mirror like surface (Table 4.1, 4.2, 4.3 respectively).

Table 4.1. Solutions that creates oxide films on Nionium.

Solution	Over voltage, V	Temperature, °C	Observation
1 ChChl : 1 Malic acid	30	80	Passivation (color blue)
	60	80	Passivation (color yellow)
1 ChChl : 2 Tin(II) Chloride	40	90	Passivation (color white)

We can't represent current or time, because passivation of the surface happened immediately when we applied current.

Table 4.2. Solutions that does not create ionic liquid.

Solution	Observation
1 ChChl : 1 Sulfamic Acid	Does not melt
1 ChChl : 1 Ammonium Persulfate	A brown foam, which rises, is formed by heating

Table 4.3. Solutions that creates ionic liquids but does not polish surface.

Solution	Over voltage, V	Temperature, °C
1 ChChl : 2 Ethylene glycol	30	80
1 ChChl : 2 Ethylene glycol + 30 g/l SA	30	80
	50	100
1 ChChl : 2 Ethylene glycol + 100 g/l SA	50	70
1 ChChl : 2 Ethylene glycol + 180 g/l AS	50	85

In the Figure 5.1 showed samples at we have obtained in new ionic liquids. Parameters for these processes you can see in Tables 4.1 and 4.3.

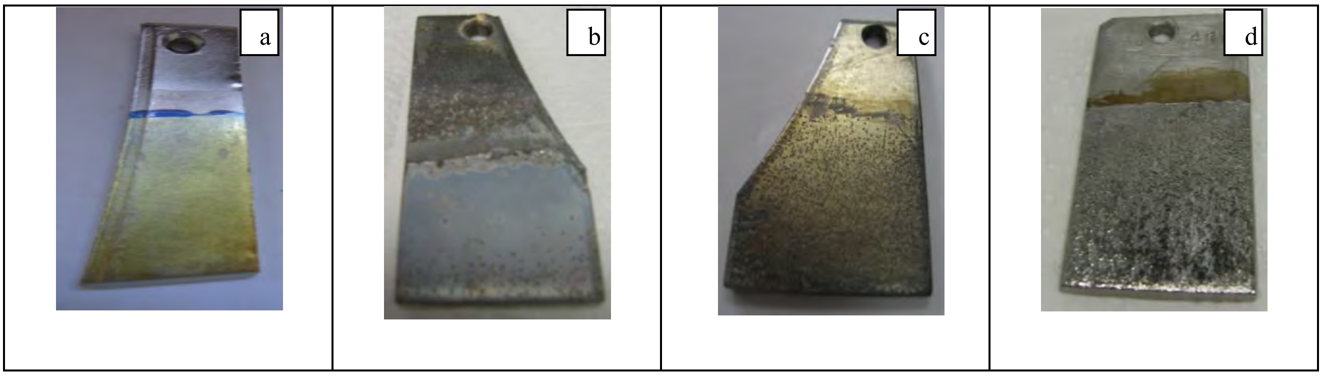

Figure 4.1. Samples treated in new Ionic liquids: a - 1 ChChl : 1 Malic acid; b – 1 ChChl : 2 Tin(II) Chloride; c – 1 ChChl : 2 Ethylene Glycol; d - 1 ChChl : 2 Ethylene Glycol +180 g/l AS.

The try to creation new ionic liquids on base ChChl and different additives did not give success.

4.2.2 Electropolishing in Choline Chloride and Urea basic solution, with additives

Like a basis of ionic liquid, we have taken ChChl and urea, which has already shown good results in previous researches in LNL.

First we tried to put small amount additives. Results are presented in the Table 4.4, the surface that was obtained in Figure 4.2.

Table 4.4. Solutions base on Choline Chloride and Urea with small amount different additives

Solution ChChl : Urea (ratio)+ additive	Over voltage, V	Temperature, °C	Observation
1 : 2 + 1% Tiron	50	80	Partially passivated
1 : 2 + 1% Ammonium Acetate	40	80	Partially passivated
1 : 2 + 5 g/l EDTA	50	90	Passivated, pitting
1 : 2 + 30 g/l EDTA	50	95	Passivated, pitting
1 : 4 + 1-2 g/l Acetylthiourea	50	85	The surface is polished but not smooth

Continue experiment we did set of experiments with Choline Chloride and Urea (ratio 1 : 4) and additive Sodium Sulphite. In the Table 4.5. shown parameters of the processes, in the Figure 4.3. photos of the samples.

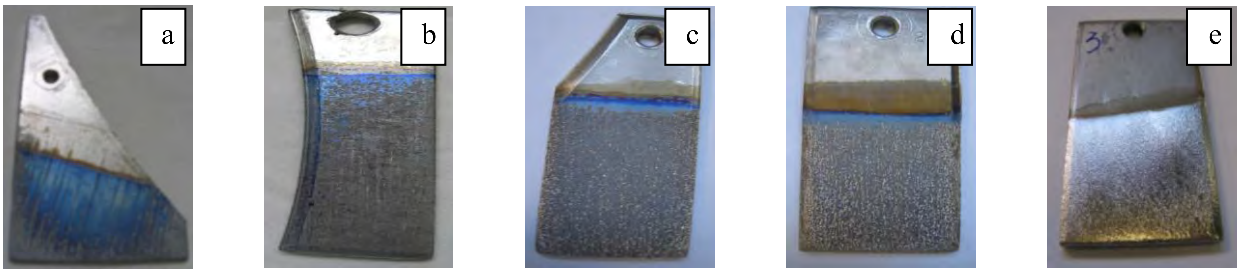

Figure 4.2. Samples Choline Chloride and Urea with small amount different additives. a – 1 ChChl : 2 Urea + 1% Tiron; b – 1 ChChl : 2 Urea + 1% Ammonium Acetate; c - 1 ChChl : 2 Urea+5 g/l EDTA; d – 1 ChChl : 2 Urea+30 g/l EDTA; e – 1 ChChl : 4 Urea + 1-2 g/l Acetylthiourea.

Table 4.5. Solutions Choline Chloride and Urea (ratio 1 : 4) with Sodium Sulphite

Solution Choline Chloride and Urea (ratio 1 : 4)	Over voltage, V	Temperature, °C	Voltage, V	Current, A
+ 5 g/l Sodium Sulphite	40	110	20	4,5
+ 10 g/l Sodium Sulphite	50	100	20	4,5
+ 30 g/l Sodium Sulphite	50	105	23	4,5
+ 50 g/l Sodium Sulphite	50	115	23	4,5

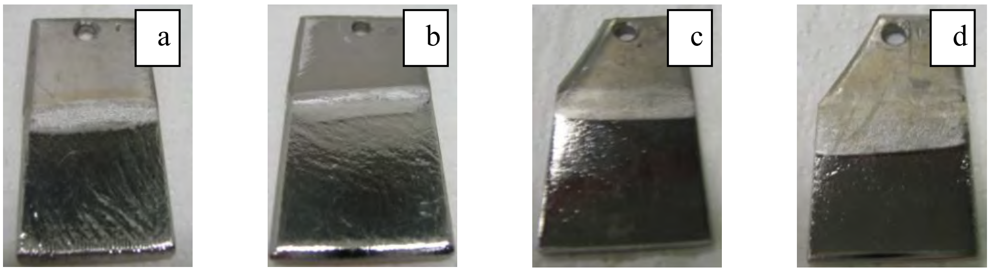

Figure 4.3. Samples treated in Choline Chloride and Urea (ratio 1 : 4) with Sodium Sulphite. Concentration of Sodium Sulphite: a – 5 g/l Sodium Sulphite; b - 10 g/l Sodium Sulphite; c - 30g/l Sodium Sulphite; d - 50 g/l Sodium Sulphite

Check the influence of Polyethylene glycol and Sulfamic acid as additives in the solution Choline Chloride and Urea in ratio 1 to 4 (Table 4.6).

The parameters of the set experiments with Sodium Hydroxide and Sulfamic acid you can see in the Table 4.7.

Pictures of the samples for both Tables represented on the Figure 4.4.

Table 4.6. Solutions Choline Chloride and Urea (ratio 1 : 4) with Polyethylene glycol and Sulfamic acid

Solution Choline Chloride and Urea (ratio 1 : 4)	Over voltage, V	Temperature, °C	Observation
+ 1 g/l Polyethylene glycol	30	80	Pitting
+ 2 g/l Polyethylene glycol	30	80	
+ 10 g/l Polyethylene glycol	30	80	
+ 1 g/l Polyethylene glycol + 30 g/l SA	40	70	A lot of foam, pitting
+ 2 g/l Polyethylene glycol + 30 g/l SA	40	70	

Soluble compounds of the Niobium are formed in pH more then 6. We try to use this fact and apply to our system and move pH in alkaline side, using sodium hydroxide.

Table 4.7. Solutions Choline Chloride and Urea (ratio 1 : 4) with Sodium Hydroxide and Sulfamic acid

Solution Choline Chloride and Urea (ratio 1 : 4)	Over voltage, V	Temperature, °C	Time, min	Current, A
+ 2 g/l Sodium Hydroxide	50	115	30	4,5
+ 5 g/l Sodium Hydroxide	50	115	30	4,5
+ 10 g/l Sodium Hydroxide + 30 g/l SA	50	110	30	4,5
+ 20 g/l Sodium Hydroxide + 30 g/l SA	50	100	30	4,5

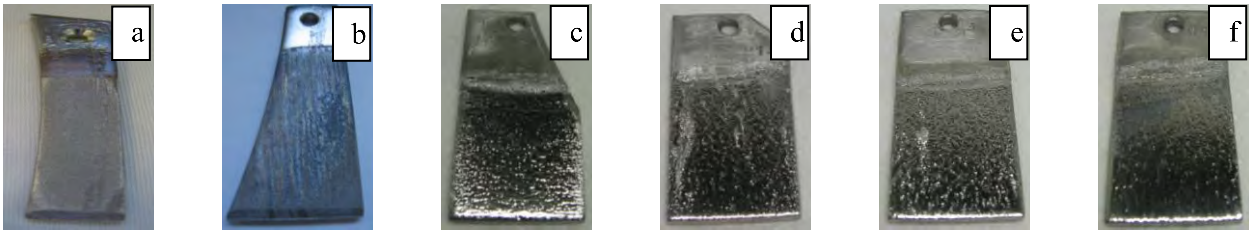

Figure 4.4. Samples treated Choline Chloride and Urea (ratio 1 : 4) with: a - 10 g/l Polyethylene glycol; b - 2 g/l Polyethylene glycol + 30 g/l SA; c - 2 g/l Sodium Hydroxide; d - 5 g/l Sodium Hydroxide; e - + 10 g/l Sodium Hydroxide + 30 g/l SA; f - 20 g/l Sodium Hydroxide + 30 g/l SA.

Displacement the pH of the solution in the alkaline direction gives a positive effect in presence of sulfamic acid. But addition of NaOH alone in the solution Choline Chloride: Urea (1:4) gives a negative effect. But Sodium can penetrate into the surface of niobium and impairs its RF properties.

In the next step we tried to polish in the same ratio of ChChl and Urea 1 to 4, but had added Sucrose. Parameters of the process are represented in Table 4.8. Photos of the samples shown in Figure 4.5.

Table 4.8. Solutions Choline Chloride and Urea (1 : 4) with Sucrose

Solution Choline Chloride and Urea (ratio 1 : 4)	Over voltage, V	Temperature, °C	Voltage, V	Current, A
+ 5 g/l Sucrose	40	90	27	4,5
+ 10 g/l Sucrose	50	90	22	3,0
+ 20 g/l Sucrose	50	90	18,5	2,3
+ 30 g/l Sucrose	50	90	18	2,3

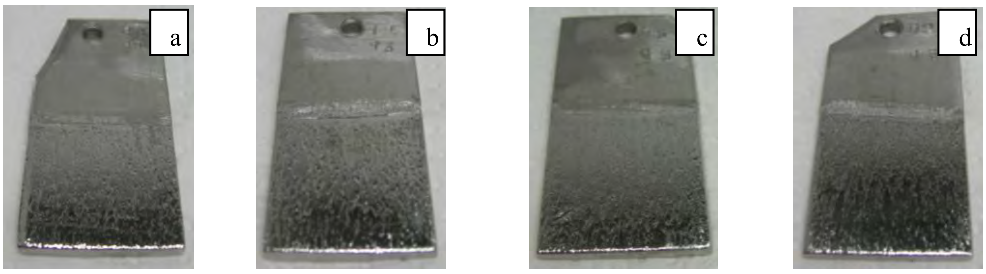

Figure 4.5. Samples treated Choline Chloride and Urea (ratio 1 : 4) with: a – 5 g/l Sucrose; b - 10 g/l Sucrose; c - 20 g/l Sucrose; d - 30 g/l Sucrose

Sucrose does not help to create of smooth and shiny surface as we expected. Sucrose is decomposing during the process, it impossible to use such compounds.

We have tried to create new ionic liquids on the basic of ChChl and Urea with additive Malic acids (Table 4.9 and Figure 4.6).

Table 4.9. Solutions Choline Chloride and Urea with Malic or Oxalic acids (in ratio)

Solution (ratio)	Over voltage, V	Temperature, °C	Observation
1ChChl : 1Urea : 1Malic acid	30	80	Blue oxide
1ChChl : 1Urea : 1Malic acid	50	80	Yellow-blue oxide

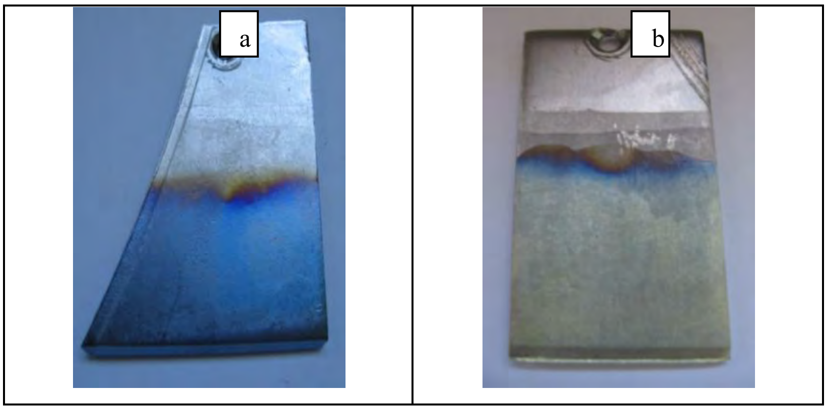

Figure 4.6. Solutions Choline Chloride and Urea with Malic acids in ratio (with over voltage):a - 1ChChl : 1Urea : 1Malic acid (30V);
b - 1ChChl : 1Urea : 1Malic acid (50V).

Added Malic acid passivated of Nb.

We had putted amount of Sulfamic acid (Table 4.10 and Figure 4.7).

Table 4.10 Solutions Choline Chloride and Urea (1:4) with SA.

Solution 1 ChChl : 4 Urea + additives	Over voltage, V	Temperature, °C	Voltage, V	Current, A
+ 30 g/l SA	40	85	28	5,0
+ 50 g/l SA	50	90	33	4,5

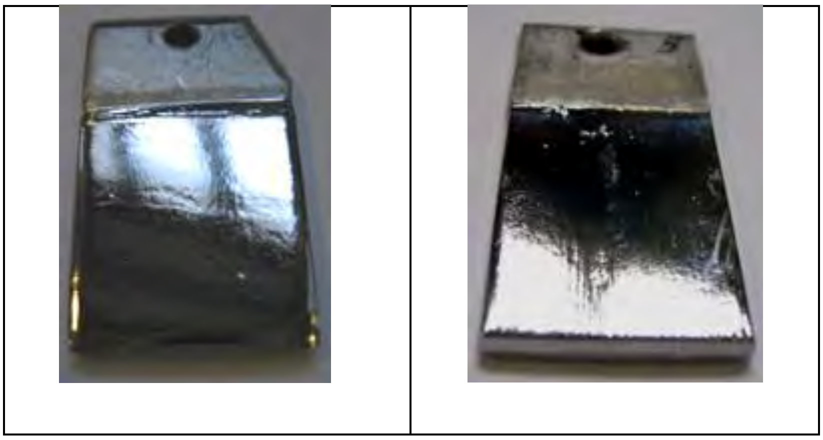

Figure 4.7. Solutions Choline Chloride and Urea (1:4) with SA: a – 30 g/l SA; b - 50 g/l SA.

The best result was obtained with a concentration of Sulfamic acid is 30 g/L, as in previous years in LNL. The other one additive that has given a good result was Ammonium Sulfamate.

We wanted to check what will be if we increase concentration of Ammonium Sulfamate, how it will influence for the polishing. In the Table 4.10 are represented parameters of the electropolishing, on the Figure 4.8 are results.

Table 4.10. Solutions Choline Chloride and Urea (1:4) with Ammonium Sulfamate.

Solution 1 ChChl : 4 Urea + additive	Over voltage, V	Temperature, °C	Voltage, V	Current, A
+ 75 g/l AmS	50	105	25	4,5
+ 114 g/L AmS	50	85	25	4,5

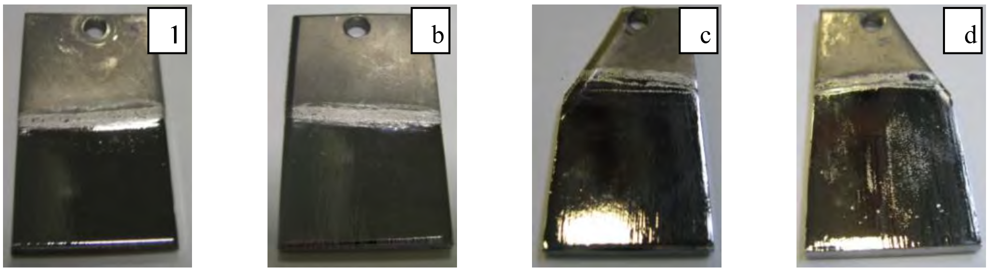

Figure 4.8. Solutions Choline Chloride and Urea (1:4) with Ammonium Sulfamate: a, b - 75 g/l AmS (front and back); c, d - 114 g/L AmS (front and back).

Electropolishing with addition of Sulfamate ammonium has given good result. Surface is very shiny. But it has high resistance, electrolyte heats up quickly.

Studying the influence of concentration Urea in the solution, we took two solutions: ChChl - Urea (1 to 2) and ChChl - Urea (1 to 4). With additive 1 mol per liter of Sulfamic acid (Figure 4.9).

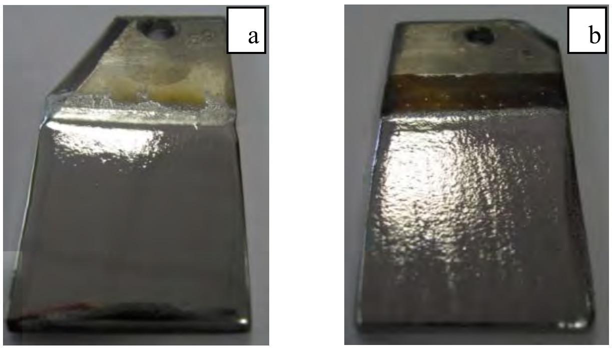

Figure 4.9. Studying the influence concentration of Urea: a - 1ChChl : 4 Urea + 1 M/l SA; b - 1ChChl : 4 Urea + 1 M/l SA.

The good results was obtained with SA and AmS. How we can see solution 1 ChChl : 4 Urea with 1 M/l SA give us the most smooth and shiny surface, in this reason we will use its in future investigations.

4.2.3 Electropolishing in Choline Chloride and Urea with Sulfamic acid, influence of process parameters

In EP process all parameters have important role for the obtain successful results. We did some sets of experiments for the studying: cathode material, temperature, time, current density and type of power supply.

4.2.3.1 Cathode material

We have used solution ChChl and Urea (ratio 1: 4) with 30 g/l Sulfamic Acid. Applied the same parameters: Time – 30 min, Over Voltage – 50 V, Current – 4,5 A, Temperature – 115°C, Stirring – 4. And used three materials for cathode: Aluminum, Titanium Platinized and Niobium. Results you see on Figure 4.10.

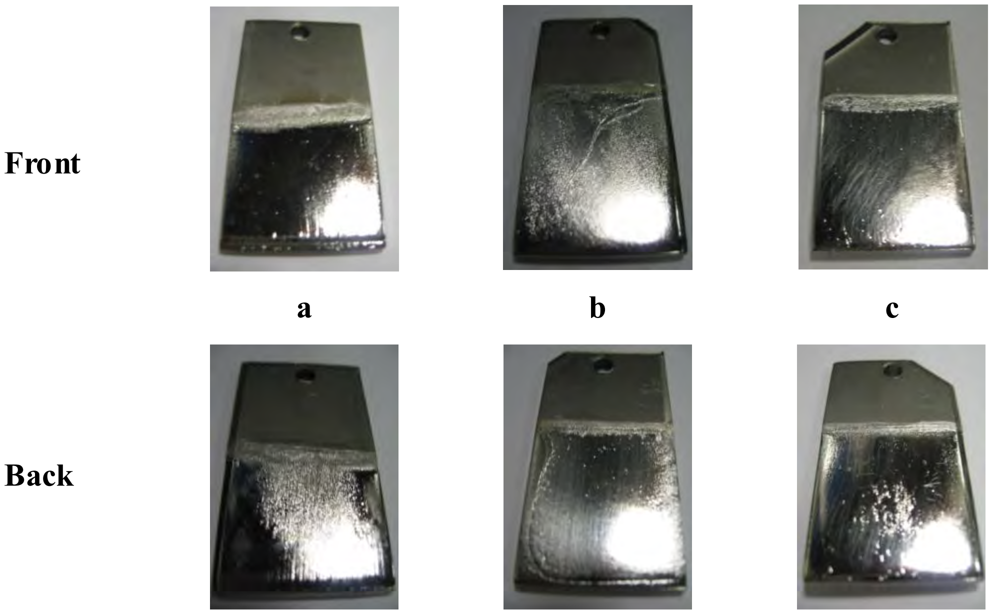

Figure 4.10. Influence of the cathode material: a – Aluminum, b - Titanium Platinized (net), c – Niobium.

Aluminum, Niobium and Titanium Platinized as cathode materials give good results. Stirring has a significant impact on the quality of the surface. Because if we stirring electrolyte the gas that was formed on the cathode damage surface of the anode. The surface that was obtained with using of the Ti (Pt) cathode is the worst. And other two samples have the scratches. All as a cathode material does not satisfy us, because Chlorine ions that are present in our Ionic Liquid dissolve its. The best variant for us is using the Nb cathode.

4.2.3.2 The Temperature and Time

Since we work with ionic liquids which viscosity is high, the temperature play a key role. We carry out two different series of experiments for the processing time at different temperatures (Table 4.12). In solution of ChChl : Urea (1:4) with 1 M/l SA. Other parameters were the same (Cathode – Nb, Over Voltage – 50 V, Current – 4,5 A).

Table 4.12. Parameters process for the researching influence Temperature and Time.

Time, min	Temperature of the Process (initial - in the end),°C		
	Sample 1	Sample 2	Sample 3
5	90 - 120	110-135	120-135
20	90 - 125	110 - 150	120-150

We measured the roughness of the samples. Dependence roughness of the samples from the temperature and time can be seen on Figure 4.11.

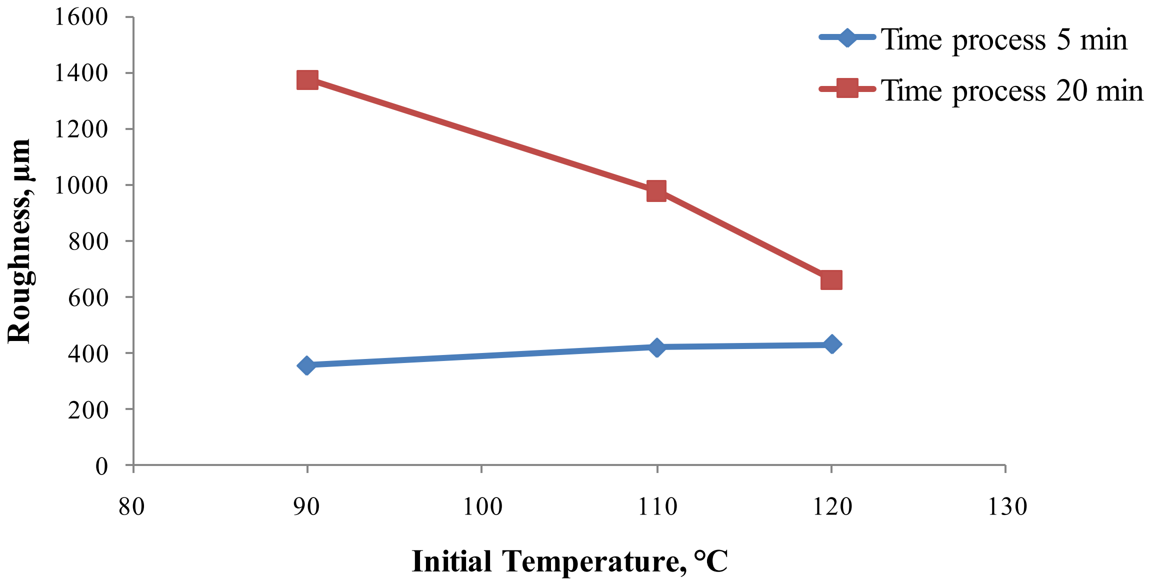

Figure 4.11. Graph dependence roughness of the samples from the temperature and time.

We observed a linear dependence, for the processing time 5 minutes its increases with increasing temperature, for 20 minutes of processing time its decreases with increasing temperature. It can be assumed that at some point the two lines will intersect, that is mean, that at certain time affect for the roughness will not influent any more.

4.2.3.3 The Influence of Current density and the type of power supply

We applied to the system of two power supply. The one is PC with direct current, the other is Rectifier. We have choosen two main parameters - current and time. Current - 1,5A was supplied during 60 minutes, current - 4.5A for 20 minutes. Thus, the amount of electricity what had gone to the dissolution of niobium for each sample is the same. Current density was different. For each experiments were used the same process parameters: solution - 1 ChChl : 4 Urea + 1M/L Sulfamic acid; Cathode – Nb; U =40V (30 sec); avarege temperature - 110°C. Work area of sample is 15 cm², it means that we have two current density – 0.1 and 0.3 A/cm^2.

To the check what the current density and power supply are more effective, we measured the roughness before and after electropolishing, calculated the difference between these values and plotted graph of the dependence (Figure 4.12).

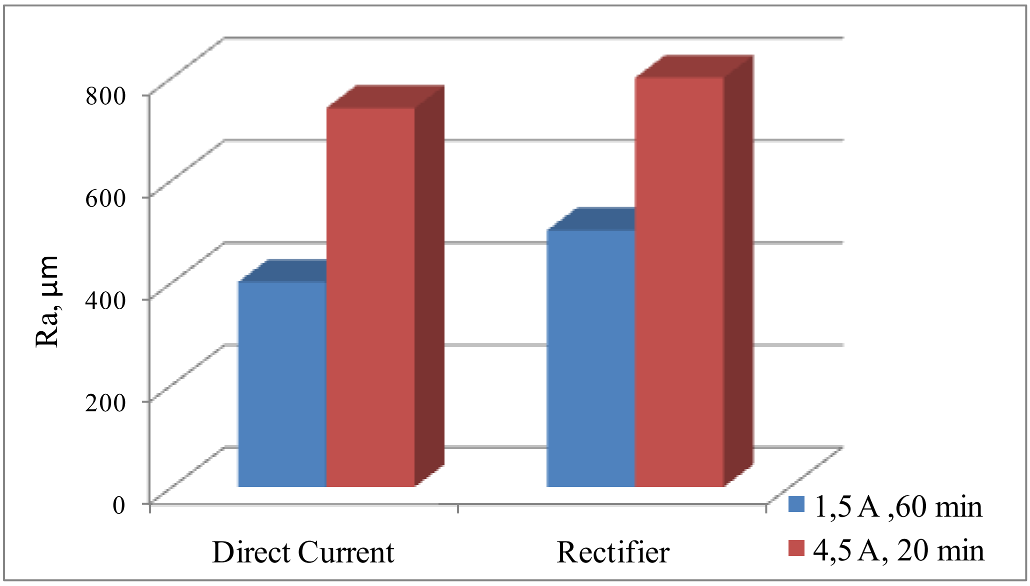

Figure 4.12. Graph of the dependence current density and the type of power supply.

It is not the big difference between using of the Direct current or Rectifier. But between current density, difference is exist. How we can see with the density 0,3 A/cm^2, we can achieve more smooth surface.

In conclusion we can say that the best parameters for polishing Nb samples are following:

Choline Chloride - Urea	1-4
Sulfamic acid, g/l	97
Material cathode	Nb
T,°C	Higer then 120
Current density, A/cm^2	0,3
Time, min	20

5 Electropolishing of the 6 GHz cavity

To work with planar samples is more easy. For the electropolishing of the cavity, which has complex profile, we have to take in accent: orientation of the cavity (horizontal or vertical); the way to supply of electrolyte (open system, closed space system, cavity from one side); quantity of solution according to cavity (filled all or half); stationary regime or rotation; shape of the cathode; without or with supply Nitrogen. For each variant electropolishing we carried out set of experiments. Was used electrolyte - ChChl : Urea (1:4) with 1 M/l SA.

5.1 Vertical Electropolishing

5.1.1 Vertical Electropolishing in open system

We tried vertical electropolishing of the cavity in open system. Cavity was putted in solution vertically, and fixed by Niobium wire to the holder (figure 5.1). Parameters of the process are in the Table 5.1. As cathode was used cylinder 6 mm diameter from Ti(Pt) net.

Parameter	Value
Cathode	Ti(Pt)
Time, min	20
Over Voltage, V	40
Voltage, V	23-18
Current, A	20
Temperature, °C	100-130

Table 5.1. Parameters of the vertical Electropolishing cavity in open system.

Figure 5.1. Open system for the vertical Electropolishing cavity.

In the Figure 5.2, we can see photos of surface inside the cavity after polishing.

Figure 5.2. Cell after vertical Electropolishing in open system

We tried to investigate the behavior of surface the cut-off and cell separately. Parameters of both processes are presented in the Table 5.2 photos on Figure 5.3. The cathode was rod with disk 15 mm in the middle.

Table 5.2. Process parameters for the vertical electropolishing in the open system cut-off and cell.

Parameter	For the cut-off	For the cell
Cathode	stainless steel	stainless steel
Time, min	15	15
Over Voltage, V	25	30
Voltage, V	20-15	25-15
Current, A	6,5	15
Temperature, °C	115-150	95-150

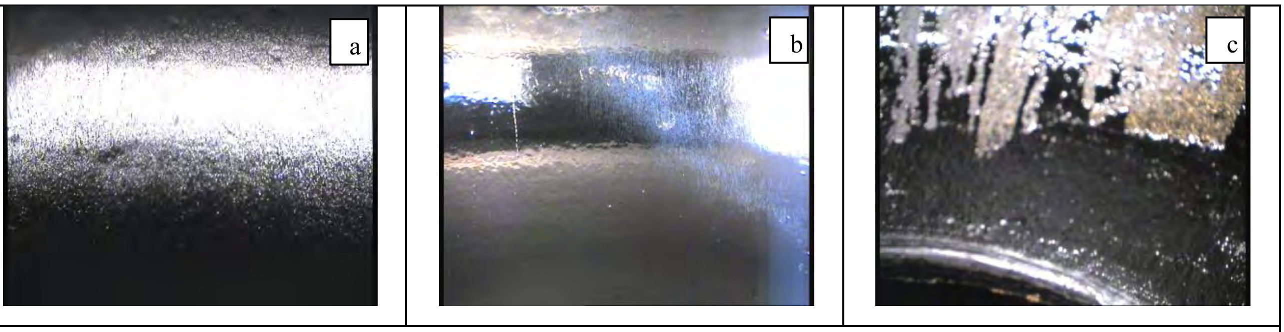

Figure 5.3. Photos after Electrochemical polishing in vertical open system (Electropolished separately): a, b – cut-off; c – cell.

Surface in the cut-off is smooth and shine, but on the cell polishing wasn‟t uniform. It happens because, the form of cavity isn‟t planar, the foam collects in the cell and in this position surface wasn‟t polished. We try to supply electrolyte to create flow of the solution inside cavity.

5.1.2 Vertical Electropolishing in open system with supply Electrolyte from one side

We immersed a cavity in the solution and insert tube in the bottom of cavity, the electrolyte supplies from downwards. You can see parameters of the process, photo of the system and photos surface after electropolishing, in the Table 5.3, on figure 5.4 and 5.5, respectively. The stainless steel rod was used as cathode.

Parameter	Value
Cathode	stainless steel
Time, min	15
Over Voltage, V	40
Voltage, V	40-27
Current, A	20
Temperature, °C	105-125

Table 5.3. Parameters of the vertical Electropolishing cavity in the open system with supply electrolyte from one side.

Figure 5.5. Open system for the vertical Electropolishing cavity with supply electrolyte from one side.

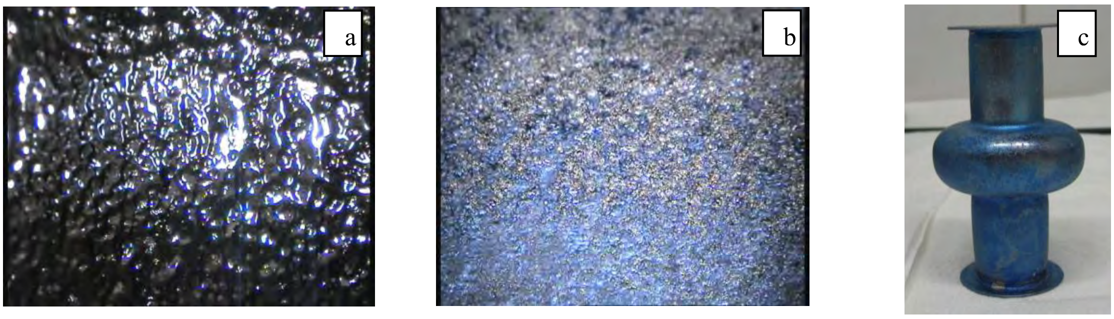

Figure 5.5. Photos after Electrochemical polishing in vertical open system with with supply electrolyte from one side: a– cut-off; b – cell; c – outside surface of the cavity.

Surface from outside under the influence of oxygen, solution and under voltage - oxidized (blue film you can see in figure 5.5).

5.1.3 Vertical Electropolishing in closed system

We have used system that was created in previous years in LNL. The electrolyte is feed from the bottom and goes out from the top (Figure 5.6). Parameters that were used for this system described in Table 5.4. Cathode – sphere from Aluminum.

Parameter	Value
Cathode	Al
Time, min	15
Over Voltage, V	60
Voltage, V	22
Current, A	25
Temperature, °C	100-110

Table 5.4. Parameters of the vertical Electropolishing cavity in closed system.

Figure 5.6. Closed system for the vertical Electropolishing cavity.

Photos of the surface inside the cavity are represented on the Figure 5.7.

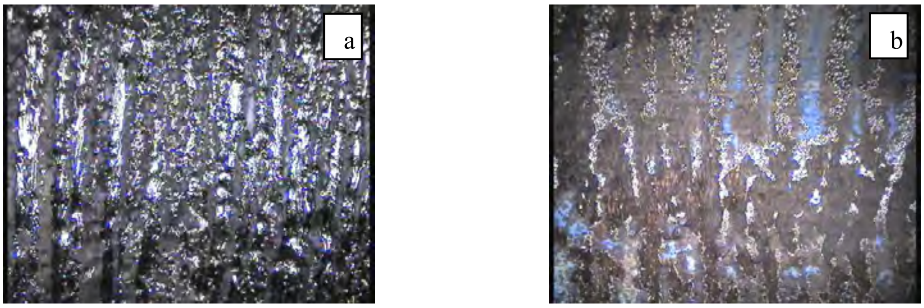

Figure 5.7. Surface inside cavity after Electropolishing in vertical closed system: a – cut-off; b – cell.

In a closed system, the quality of polishing is not satisfactory as in two previous variants (vertical polishing in open system and vertical polishing with supply electrolyte from one side). Because when the electrolyte passes inside cavity with pressure it creates turbulent regime with a lot of bubbles. The best result from these three systems is Vertical open system, in this cause the solution inside almost does not move, and we have shiny surface of the cut-off. But cell in these three systems was not polished. This is connecting with low current distribution, and with creating foam and bubbles, what hinder surface wetting and as result surface does not polish.

5.2 Horizontal Electropolishing

5.2.1 Horizontal Electropolishing in open system

We immersed whole cavity inside the solution horizontally, and fixed by Niobium wire to the holder (figure 5.7). Parameters of the process - Table 5.4. Cathode was sphere of Aluminum.

Parameter	Value
Cathode	Al
Time, min	60
Over Voltage, V	without
Voltage, V	20,8
Current, A	5
Temperature, °C	150-159

Table 5.5. Parameters for the horizontal electropolishing in open system.

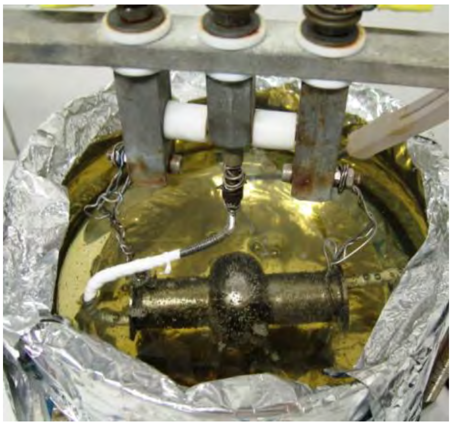

Figure 5.8. Open system for the horizontal electropolishing.

We have obtained next results (Figure 5.9).

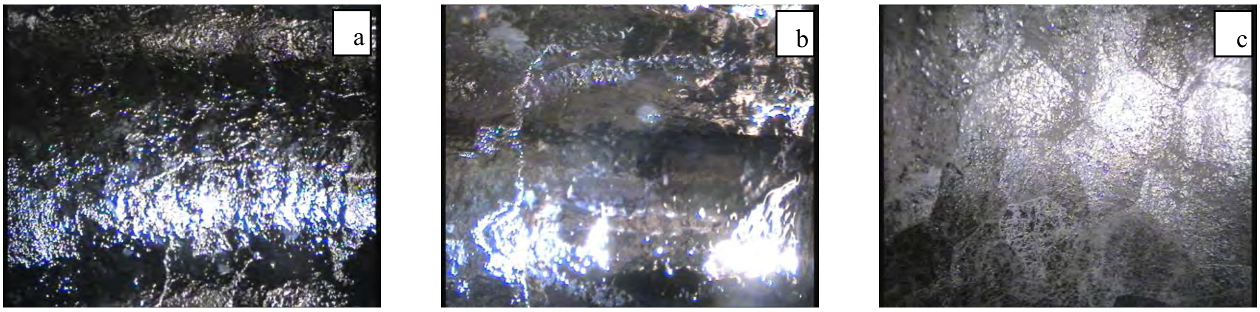

Figure 5.9. Cell after electropolishing in horizontal open system: a – down part, b – side, c – Top part.

We obtained quite good results: part of the cell at interface gas/solution ; down part is polished but not so good, it can be connect with that solution sticks to the surface; top part is passivated, because gas that was created during the electrochemical process collected in this part.

To avoid that electrolyte stick to the surface, we tried to move it by feeding from one side. We tried to create half of level solution for prevention that foam damage surface.

5.2.2 Horizontal Electropolishing in open system with supply Electrolyte from one side

We fixed cavity on the support over solution. Solution fed from one side by pump. Cathode was stainless steel disk 15 mm diameter. Table 5.6 and Figure 5.10 show parameters of the process. Photos of the cell after electropolishing are represented on the Figure 5.11. The cathode was metal strip made from stainless steel, bent in shape of the cell.

Parameter	Value
Cathode	stainless steel
Time, min	30
Over Voltage, V	30
Voltage, V	20-40
Current, A	3
Temperature, °C	110-50

Table 5.6. Parameters process of the horizontal electropolishing in open system with supply electrolyte from one side

Figure 5.10. The process of the electropolishing cavity by horizontal open system with supply electrolyte from one side.

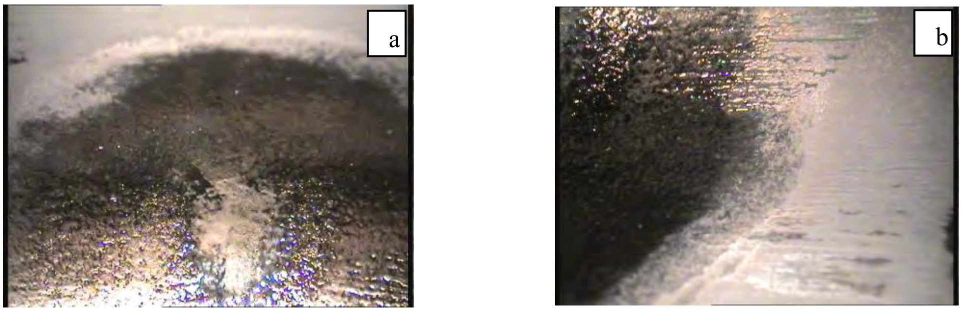

Figure 5.11. Down part of the cell, after electropolishing in horizontal open system with supply electrolyte from one side.

We obtained the following results:

1. Polish only the surface what is closest to the working surface of the cathode
2. The rest of the surface is passivated

Imperfection of the system: the electrolyte flows impulse motion. Therefore, the input of cavity is completely filled by solution. We cannot create half – level.

After all experiments that were done, we have next parameters for the electropolishing cavity:

1. Horizontal orientation – foam won‟t collected in the cell;

2. Half – level of the solution – foam wont damage surface;
3. Supply of the Nitrogen – for the creation half of level and delete vapor products of the electrolyte from up part of the cell;
4. Shape of the cathode repeats the form of the cell – it increases current distribution;
5. Material of the cathode is Niobium, it is chemical stable and does not contaminate the solution.
6. Rotation of the cavity – it give us possibility polishing the half of cavity uniformity.
7. Moves of the electrolyte must be slow – in this cause it won't damage surface by bubbles, and will stir solution in down part of cell.

We created system that should satisfy all the necessary parameters (Figure 5.12).

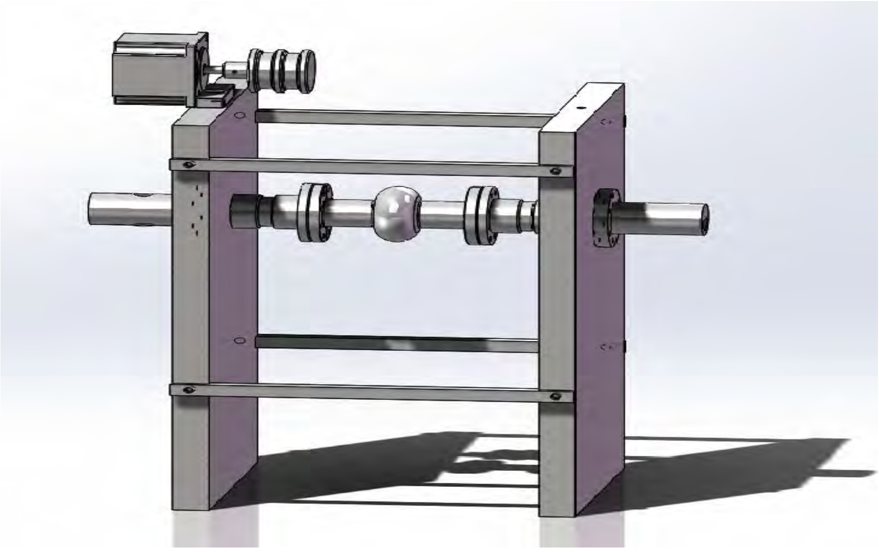

Figure 5.12. System for the closed electrochemical polishing of cavity.

5.2.3 Horizontal Electropolishing in closed system

Figure 5.13, shows the new system. Feed electrolyte (by a pump) and of nitrogen implements from one side, removal electrolyte from opposite. Electrolyte flows into a container where it heated and again re-enters in the system. Thus hot electrolyte circulates in the system. With the motor we rotate cavity with the reference frequency. In the Table 5.7 are represented parameters of the process.

On the figure 5.14, you can see surface inside cavity after electrochemical polishing, obtained by new system. We can see not polished and passivated surface. Its possibly connect with following:

- we could not create half – level of solution, pump feeds electrolyte by impulse motion and the input part of cavity is filled by solution;

- moves of the electrolyte were turbulent, and solution mixed with the foam and gases that were evaluating during the process;
- we could not flow the Nitrogen, because solution was filling tube for the supply of gas.

Parameter	Value
Cathode	
Time, min	
Over Voltage, V	
Voltage, V	
Current, A	
Temperature, °C	

Table 5.7. Parameters process for the Horizontal Electropolishing in closed system.

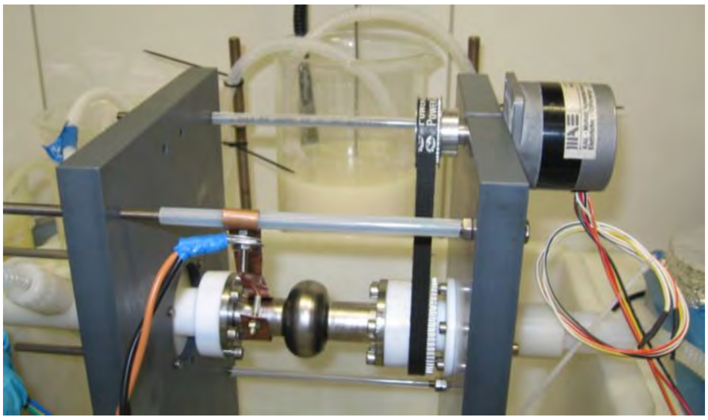

Figure 5.13. System for the closed electrochemical polishing half of cavity, in the work.

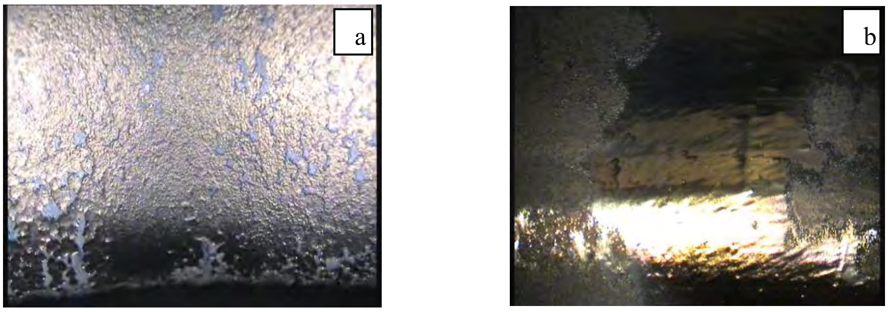

Figure 5.14. Surface inside cavity after electrochemical polishing in system for the closed horizontal electropolishing.

We tried to use expander to create laminar regime of the solution, but in this cause temperature of the solution decrease very fast and we cannot achieve required temperature for the electropolishing.

We will try to polish cavity just immersed in the solution, in open system in this cause we will try to have temperature that is necessary for uniform remove of Niobium. To avoid damaging of the top cavity by the foam, we immerse only half of it inside solution.

5.3 Horizontal Electropolishing half of cavity

5.3.1 Horizontal Electropolishing whole cavity half immersed in the solution

We immersed half of cavity into the solution. It was fixed by Niobium wire to the holder (Figure 5.15). Cathode was sphere of Aluminum. Parameters of the process wrote in the Table 5.8.

Parameter	Value
Cathode	Al
Time, min	10
Over Voltage, V	without
Voltage, V	18-22
Current, A	4,5
Temperature, °C	130-125

Table 5.8. Parameters for the process horizontal electropolishing whole cavity immersed on the half in solution.

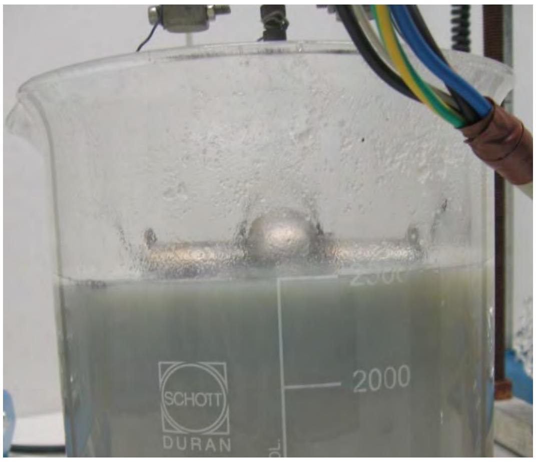

Figure 5.15. System for the horizontal electropolishing whole cavity half immersed in the solution.

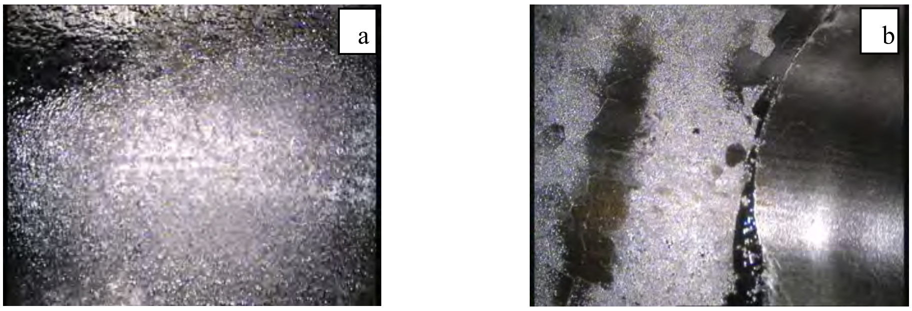

Figure 5.16.The Cell after electropolishing in the system of horizontal electropolishing whole cavity half immersed half in the solution.

After electropolishing we have obtained the next results: down part of the cell does not polished; border air – solution has oxidized film, produced by foam; top of the cavity has initial surface; the side surface that was immersed in the solution is a very shine and smooth, because in this part of the cavity solution can easily retreat from the surface.

5.3.2 Horizontal Electropolishing of the cavity cut to the half

For the better studying the influence electrochemical process on surface inside cavity, we cut cavity to the half, and electropolished it in the solution. Gas evaluation that was creating during the process we can see on the Figure 5.17. We choose the parameters as in previous case, but increase the time, for the more visible results (Table 5.9).

Parameter	Value
Cathode	Al
Time, min	30
Over Voltage, V	30
Voltage, V	19
Current, A	4,5
Temperature, °C	130-150

Table 5.9. Parameters for the electropolishing the half cavity.

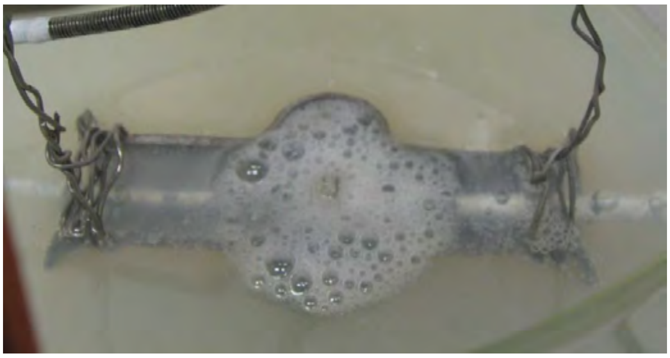

Figure 5.17. System for the electropolishing the half cavity.

On the Figure 5.18 represented photo of the half cavity before treatment and after.

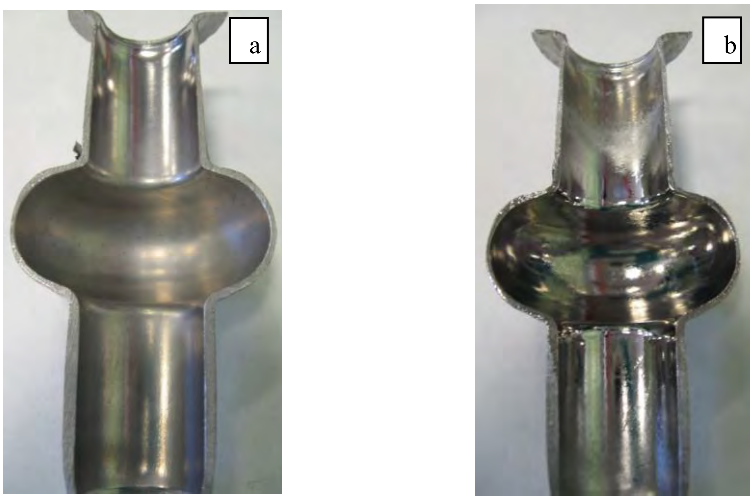

Figure 5.18. The half cavity before and after treatment:

a – before; b – after.

We obtained good results in open system with the half cavity. Surface is smooth and shiny, we don‟t have pitting or dots, just one imperfection is down part of the cell. The solution degrades and sticks to the surface. The rotation can eliminate this effect.

We modify previous system, make it open and create half level. We will flow Nitrogen in top half of cavity, and rotate by motor.

5.3.3 Electropolishing half of cavity in New system.

We immerse cavity on the half in the solution, Nitrogen flows across the top part cavity. Shape of the cathode repeats the form of the cell. Parameters of the process wrote in the Table 5.10. Figure 5.19, shows the new system.

Parameter	Value
Cathode	Nb
Time, min	30
Over Voltage, V	without
Voltage, V	19 -27
Current, A	6,5
Temperature, °C	150 - 120

Table 5.10. Parameters for the electropolishing half of cavity in new system.

Figure 5.19. The new system for the electropolishing half of cavity.

On the figure 5.20, you can see surface inside cavity after electrochemical polishing, obtained by new system.

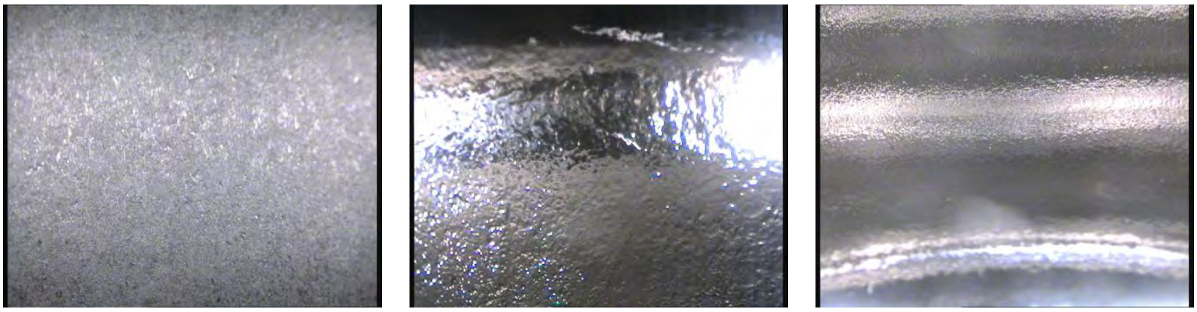

Figure 5.20. Cell before and after Electrochemical polishing in New system:

a – before, b,c – after.

We see that surface is shiny and smooth. We deleted just thin layer of Nb. This system already gave us good result and we will continue work with it.

6 Results

We tried to find new Ionic Liquid for our process, that could be not consist Urea. But results show us that solution consists of Choline Chloride and Urea creates the best conditions for electropolishing Niobium.

We carried out researches in suitable ratio of ChChl and Urea in solution, influence of additives. And have identified that most effective solutions for the Electropolishing of Niobium are ChChl : Urea (1:4) with Sulfamic acid or Ammonium Sulfamate (Figure 5.21).

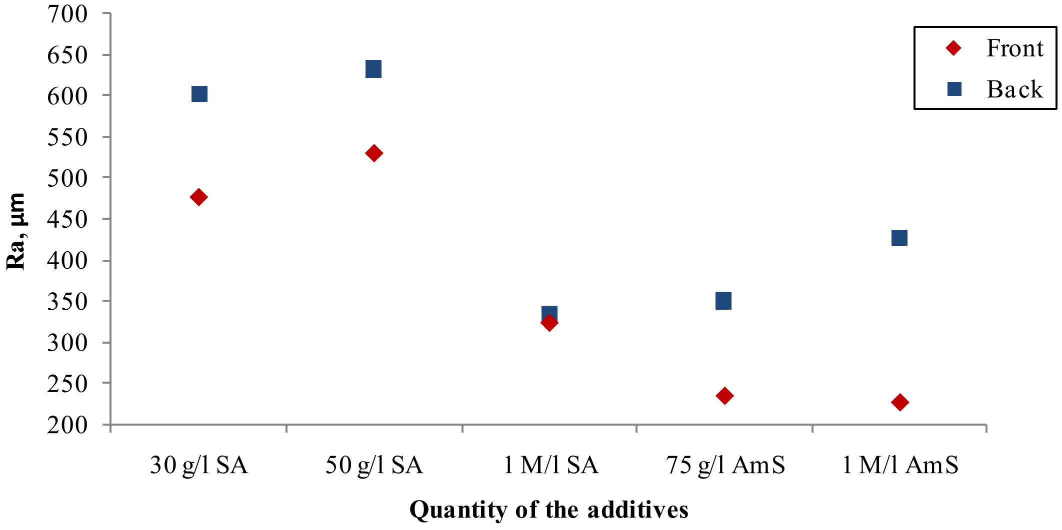

Figure 5.21. Roughness of the samples that were electropolished in solution ChChl : Urea (1:4) with additives.

The low roughness we have obtained with additive 1 M/l Sulfamic acid, also competitive results we have with additive 75 g/l or 1 M/l Ammonium Sulfamate. Order to the conductivity of solution with SA is higher, and it depredates at more high temperature, what is very important for the process. Between these components we choose Sulfamic acid.

From the different materials of cathode, we select the Niobium, because it is inert metal that doesn‟t contaminate solution, and give us shiny surface (Table 5.11).

Material of Cathode	Front Ra, µm	Back Ra, µm
Niobium	266,80	388,72
Aluminum	447,78	481,98
Titanium Platinized (net)	1658,8	518,61

Table 5.11. The roughness of samples that were obtained with different cathode materials.

With temperature higher then 120°C we achieved better results and this parameter is crucial in this process. Using the different Power supply doesn‟t change so much quality of surface, more important is current density, the best for our process is 0,3 A/cm^2.

After all experiments that were done for the 6 GHz cavity, in the different system with the different parameters, we found the system where we achieved the required quality of surface. These parameters are following:

- ✓ Horizontal orientation – foam won‟t collect in the cell;
- ✓ Half – level of the solution – for avoidance the damaging surface by foam;
- ✓ Supply of the Nitrogen – for the creation half of level and delete vapor products of the electrolyte from upper part of the cell;
- ✓ Shape of the cathode repeats the form of the cell – it increases current distribution;
- ✓ Material of the cathode is Niobium, it is chemical stable and doesn‟t contaminate the solution;
- ✓ Rotation of the cavity – it give us possibility to polish the cavity uniformly;
- ✓ Flow of the electrolyte has to be slow – in this cause it won‟t damage surface by bubbles, and will stir solution in down part of cell.

We have built this system and already have good results.

7 Conclusions

The best solution that we found for Electropolishing of Niobium is Choline Chloride with Urea in ratio 1 to 4 with 1 M/l Sulfamic acid.

All parameters of the process are very important for the Electropolishing Niobium, but temperature is the main parameter. Also we need to take in account the following:

- cathode should be made from inert material, and has form of the cell;
- current density have to be proper and don"t damage the surface by gas that evaluate during the process;
- time – enough to delete layer of Nb that necessary for the achieve required roughness;
- flow of electrolyte, supply of Nitrogen and rotation of cavity - parameters what help to avoid passivation of the surface and allow to achieve good results.

The electropolishing in new system give us shiny surface without pitting and damages.

8 Future developments

We already have good results in new system for the electropolishing 6 GHz cavity. And we will be continued the work with this system and solution. For further work we need to improve some parts of the system and parameters of process:

- to choose regime of rotation, flow the Nitrogen and current density that will be optimal;
- to find a way keep temperature of the solution stable;
- to change all metallic parts of system on inert material that resist to high temperature;
- to investigate what compounds we obtained during the process.

List of Figures

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