FLUORINE FREE IONIC LIQUID ELECTROPOLISHING OF NIOBIUM CAVITIES

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Abstract

Ionic liquids are an emerging breakthrough in green chemistry since the years 2000. In 2006, INFN-LNL was the first to apply a mixture of Choline Chloride and Urea to Niobium electropolishing. It was found that mirror-like surfaces could be obtained at temperature higher than 120°C, with high throwing power. Subsequently the process was successfully applied to the electropolishing of a 6 GHz monocell cavity with the addition of Sulphamic acid.

INTRODUCTION

A mixture of hydrofluoric (HF) and sulphuric (H_2SO_4) acids, with ratio 1 to 9, is used as the electrolyte for polishing Niobium (Nb). Due to the fact that hydrofluoric acid is very dangerous rise up problem of removing fluoride ions from a solution for polishing of niobium. Attempts to find the alternative recipe led us to such possible electrolytes as: solution based on fluosulphuric acid, the mixture of perchloric acid, ethylic acid, acetic anhydride, perchlorate salts diluted in methanol, the mixture of (NaCl-KCl-NbCln) and $AlCl_3$ melts at 710°C [1]. 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 electropolishing (EP) in Ionic Liquids (IL).

Ionic liquids contain organic cations and anions which melt at or close to room temperature. Their low vapour pressures allow chemical processes to be carried out with essentially zero emission of toxic organic solvents into the environment.

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.

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 [2]. All this characteristics give us opportunity successfully use IL in electropolishing the niobium.

EXPERIMENTAL PART

At first, the electropolishing of Niobium was provided on samples from the material that uses for production 6 GHz cavity. For all experiments we used the ionic liquids based on Choline chloride, carried out investigation of the possible variants of the original recipe: Choline Chloride (ChChl): Urea in molar ratio 1 to 4 with 30 g/l Sulphamic acid (SA) [3]. We studied the influence on Niobium surface roughness of several parameters such as:

- Other additives different than Sulphamic acid;
- The possible substitution of Urea;
- The current regime;
- Electrolyte temperature;
- Rotating horizontal electropolishing versus vertical electropolishing;
- Cathode shape and material.

Experiments were performed using a glass backer with immersed inside two-electrode system, where anode is a niobium sample. The molten salt was prepared by slowly heating of compounds, until the compositions became liquid. Cleaning of samples was done in the following order: washing in ultrasonic bath with soap, washing in ultrasonic bath in water, rinsing deionizer water, drying with alcohol or acetone using nitrogen blowing. Electric power was taken from power supply Alintel S4000 (0-100V, 0-40A).

When we found proper conditions for polishing niobium, we tried to apply them for the polishing of 6 GHz Niobium cavities. We create new system for polishing cavity in horizontal position (see Fig.1).

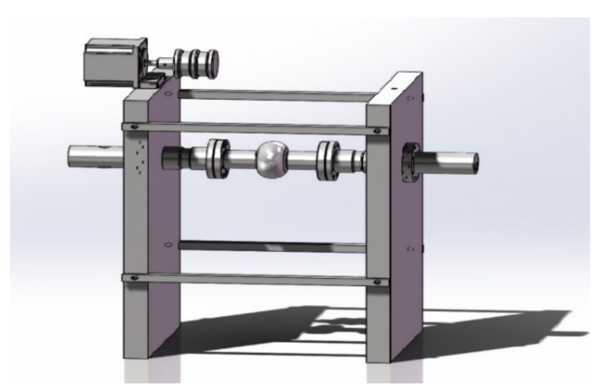

Figure 1: System for horizontal electropolishing.

Mechanical Treatment of 6 GHz Cavities

To achieve a high quality surface, the each step of the 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. It is possible to use the different materials for this mechanical polishing. Like example:

- small SiC triangular shaped blocks - is a very hard material (it can be used for the first low level mechanical polishing)
- 5 mm sphere of stabilized zirconium dioxide - is a high density material (the intermediate level)
- 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 has been developed new automatic system for the mechanical polishing of cavity [4]. 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.

Mechanical treatment of cavities was done by new vibrating system (see Figure 2).

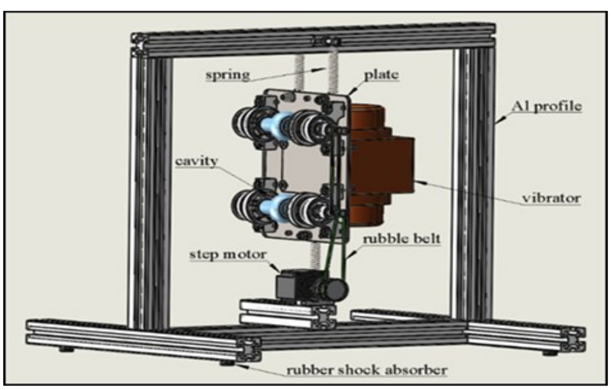

Figure 2: Schematic drawing of the vibrating system.

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. Measure range – middle was 65000nm. Analyses were done using average roughness Ra and root of the mean square deviation of the depth of the rough less profile Rq. For every samples were measured 5 times, after were calculated medium value roughness for the each samples.

Inspection Tests

The cavity has a complex profile design, to compare the surface before and after the electrochemical treatment, we use a miniature camera (see Figure 3).

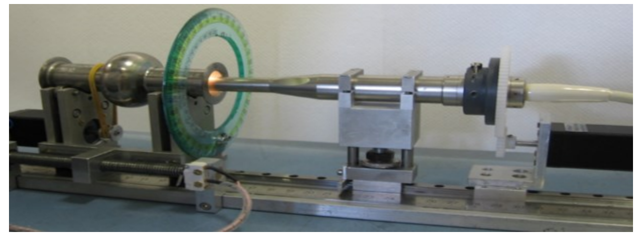

Figure 3: Miniature camera.

We do pictures before and after and compare results. 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.

RESULTS AND DISCUSSION

In the previous investigations in Superconductivity Laboratory at LNL INFN, it was found that the adding of surface-active substance (SAS) such as Sulphamic acid to the ionic liquid could successfully electropolished niobium. However, these electrolytes have their disadvantages.

In our work, we have gone further and tried to polish niobium in ionic liquids of different composition and with various additives, to improve the results obtained earlier. Table 1 shows the attempts to get new combination of Ionic Liquids based on Choline chloride.

Table 1: Composition of New Ionic Liquids Based on Choline Chloride

Components	Observation
ChChl : Sulphamic Acid (1:1)	Not create IL
ChChl : Ammonium persulfate (1:1)	Not create IL
ChChl : Malic Acid (1:1)	No polishing
ChChl :Tin(II) Chloride (1:2)	No polishing
ChChl : Ethylene glycol (1:2)	Pitting

Figure 4 shows appearance of Niobium surface treated in Ionic Liquids based on Choline Chloride.

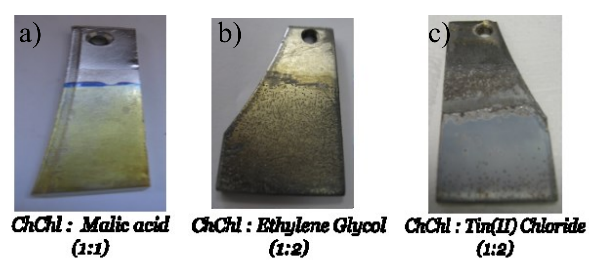

Figure 4: Samples treated in new Ionic liquids: a) 1 ChChl: 1 Malic acid; b) 1 ChChl: 2 Ethylene Glycol; c) 1 ChChl: 2 Tin (II) Chloride.

Nevertheless, collected data shows us that better solution for polishing Niobium is Choline Chloride with Urea.

Thereby we continued our investigations with this recipe and tried to find new possible SAS for smooth and shine polishing (see Table 2).

Table 2: List of Surfactants Added to Ionic Liquid Base on Choline Chloride and Urea

Surfactants	Observation
Polyethylene glycol	Not polished, pitting
Sulphamic acid + Polyethylene glycol	Not polished, lot a foam
Malic acid	Passivated
Tiron	Partially Passivated
Ammonium acetate	Partially Passivated
Sulfamate ammonium	Good
Sulphamic acid	Good

Figure 5 shows appearance of Niobium samples treated in Choline Chloride with Urea and different additives.

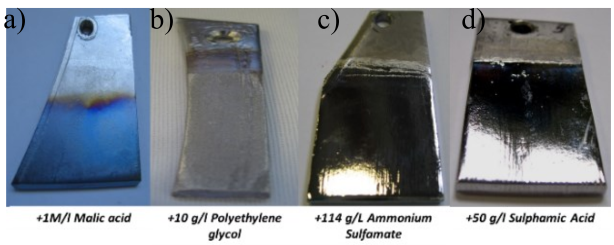

Figure 5: Samples treated in Choline Chloride and Urea (ratio 1:4) with: a) 1M/l Malic Acid; b) 10 g/l Polyethylene glycol; c) 1 M/l Ammonium Sulfamate; d) 50g/l Sulphamic Acid.

As we can see the best results were obtained with addition of Sulphamic acid and Sulfamate ammonium. Thus, we start to study proper quantity of these additives (see Figure 6).

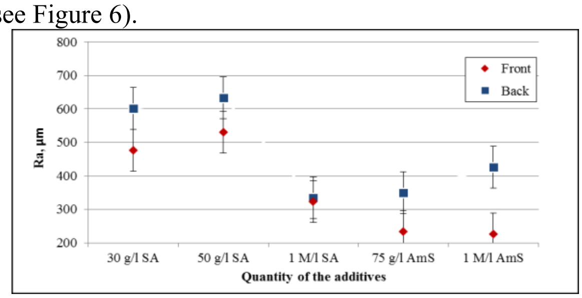

Figure 6**:** The dependence of surface roughness on the additives concentration.

In addition, we studied such parameters of electropolishing as cathode material, carried out experiments with Titanium; Niobium and Aluminium cathodes (see Table 3).

We provided series of experiments with different current sources (DC/AC), temperature of working electrolyte.

Table 3: The roughness of samples depending on the cathode materials

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

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

- Choline Chloride: Urea – molar ratio 1 to 4;
- Sulphamic acid – 1M/l;
- Cathode material – Niobium;
- Working temperature – from 120˚C to 170 ˚C;
- Current density – 0, 3 A/cm².

According to this data, we started the electropolishing of 6 GHz cavities.

Electropolishing of 6 GHz Cavities

To work with planar samples is easier. For the electropolishing of the cavity, which has complex profile, we have to take in account: orientation of the cavity (horizontal or vertical); the way to supply of electrolyte; stationary regime or rotation; shape of the cathode; without or with flow of Nitrogen.

Vertical Electropolishing

We tried the vertical electropolishing of the cavity with different supply of electrolyte. In this mode, we had certain problems with gas evolution, what during the process formed a large quantity of foam, causing surface damages and partially passivated the Niobium (see Fig.7).

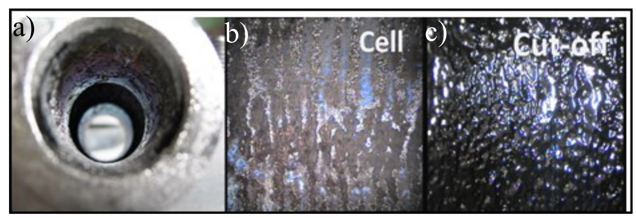

Figure 7: Vertical electropolishing of cavity: a) top part; b) cell; c) cut-off.

Thus to avoid this we immersed cavity inside the solution horizontally.

Horizontal Electropolishing

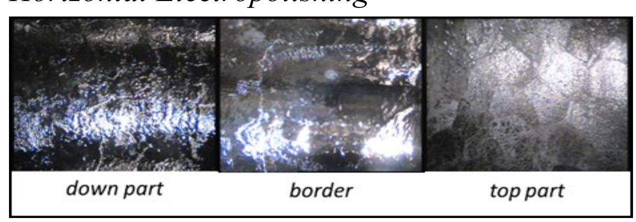

Figure 8: Horizontal electropolishing of 6 GHz cavity, half immersed inside solution.

Obtained results were equate good on the part of the cell at interface gas/solution; down part is polished but not so good, possibly, because solution sticks to the surface; top part is passivated, because gas collected in this part (see Figure 8).

To avoid that electrolyte stick to the surface, we tried to move it by pumping solution from one side. We tried to create half of level solution for prevention that foam damage surface. Also in this mode, we obtained oxide layer on internal surface of cavity.

For the better studying the influence electrochemical process on surface inside cavity, we cut cavity to the half, and electropolished it in the solution (see Figure 9).

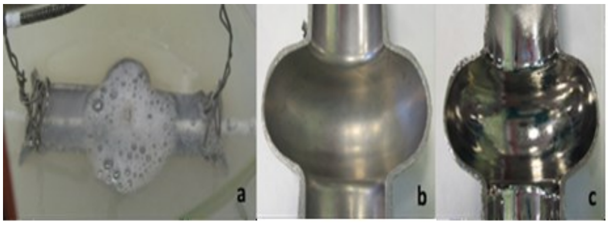

Figure 9: Horizontal electropolishing of half cavity: a) during the process; b) before treatment; c) after treatment.

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

- Supply of the Nitrogen – for the creation half of level and delete vapour products of the electrolyte from up 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 does not contaminate the solution.
- Rotation of the cavity – it give us possibility polishing the half of cavity uniformity.
- Moves of the electrolyte must be slow – in this case, it will not damage surface by bubbles, and will stir solution in down part of cell.

We constructed new system for horizontal electropolishing of cavity. However, in this system, we had problems with temperature, and we again had to modify it (see Fig. 10).

Figure 10: The new system for the electropolishing half of cavity.

We made it open and create half level, inject flow of Nitrogen in top half of cavity, and rotate by motor. Figure 11 shows the cell before (a) and after (b, c) electropolishing in Ionic liquids in horizontal mode.

We see that surface is shiny and smooth. We removed just thin layer of Niobium (near 60µm). This system already gave us good result and we will continue work with it.

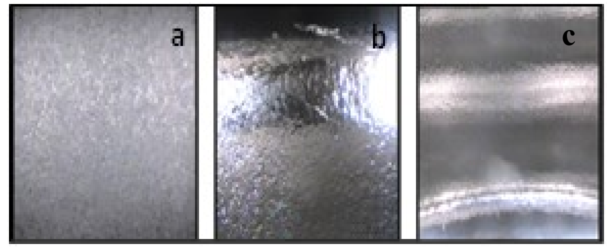

Figure 11: Cell before and after Electrochemical polishing in New system: a) before, b) and c) after.

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 Sulphamic acid.

All parameters of the process are very important for the Electropolishing Niobium, but temperature is the main parameter. In addition, 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 achieving good results.

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

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