

NIBIUM ELECTROPOLISHING BY IONIC LIQUIDS: WHAT ARE THE NAKED FACTS?

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Abstract

Among possible Surface Treatments, Electropolishing (EP) occupies a key role, because is the cleanest way for removing hundreds of microns of material. The standard recipe for Niobium EP foresees the utilization of a mixture of H_2SO_4 and HF. Literature results with this standard mixture are excellent, however the EP of thousands of cavities could become an industrial nightmare from the point of view of security at work. HF is not like other highly corrosive acids: if by accident it gets in contact with skin, pain is not felt, but F^- ions begin to pass through, searching for the bone calcium. Up to little time ago, it was common opinion that Niobium EP without HF was impossible, unless of explosive mixtures based on perchloric acid. The paper will show that this statement is not true anymore. Since a few years a green chemistry based on ionic liquids has come to the fore, and our group was the first to EP Niobium by a harmless mixture of Choline Chloride and Urea heated around $150^\circ C$. If compared to the HF based recipe, ionic liquids provide an extremely high etching rate and a definitely low surface roughness. In this talk, the application attempt to 6 GHz cavity EP is reported. Exceptionally good results have been obtained by the addition of Sulphamic acid to the Urea-Choline Chloride mixture. This recipe has been tested on 6 GHz monocell cavities showing at 4,2 K Q versus E_{acc} curves comparable with those obtained by the standard HF Electropolishing.

INTRODUCTION

Niobium Electropolishing for superconducting cavity applications has been traditionally done in a Hydrofluoric and Sulphuric acid mixture normally in a ratio 1:9. Alternative recipes foresee the addition of Lactic acid to Hydrofluoric and Sulphuric acid in a ratio 18 lactic: 21 HF: 61 H_2SO_4 .

Although this latter reaction is more controllable, lactic acid is suspected to make this mixture explosive, whenever used in large quantities or stocked in not proper conditions.

In both cases however HF is present. HF is a terribly dangerous chemical product, since it can silently promote human body necrosis in case of accidents. Moreover a plethora of devastating histories in refineries using Hydrofluoric acid is reported in literature:

In particular on contact, HF passes through skin and tissue. Contact with HF does not cause immediate pain, so systemic poisoning begins before the person is aware. Because its action can be delayed for many hours, it can distribute throughout the body, causing the erosion of bone. F^- ions bind to Ca^{++} and Mg^{++} ions to form insoluble salts, CaF_2 and MgF_2 salts forming natural gemstones.

In the body, Ca and Mg ions are used to mediate a variety of physiological processes, such as muscle movement. Cardiac arrests have been reported from concentrated acid burns to as little as 2.5% of exposed body surface area. All that means the following: for cavity mass production, large quantities of hydrofluoric acid are required. The risk assessment related to the HF handling and use can be manageable, but it would be strongly advisable to avoid it. HF-free electrolytes for electropolishing Niobium would be then required. A research and development activity then would solve this problem would be simplify technology, reduce costs and would be of great impact for the feasibility of cavity mass production.

The problem however is not new. HF-free electrolytes already exist and many solutions exist. The problem is in substitution of Hydrofluoric acid, chemicals even more dangerous than HF have been proposed. For completeness they are listed in the following:

1. The first possibility to electropolish Niobium without HF consists in using Fluosulphuric acid [1]. The process has been investigated by K. Saito. Technical results are good, moreover the risk of mixing Hydrofluoric with Sulphuric acid is suppressed, but Fluosulphuric acid is strongly suspected to be cancerousgenic.
2. The mixture of Perchloric acid, Ethylic acid, Acetic anhydride is an almost universal electropolishing mixture that is frequently used with success for the electropolishing of Transition metals, but its use is heavily discouraged by the author since some technical literature claim that ethyl-perchlorate is as dangerous as Nitroglycerin.
3. Perchlorate Salts were successfully used for electropolishing niobium samples by Schober and Sorajic, extrapolating what proposed by Epelboin [3]. The recipe consists of $Mg(ClO_4)_2$ in 0.05 mole/lit diluted in methanol. The electropolishing voltage is in the range 50-70 V, at a temperature of

-5°C. Risks of using a perchlorate salt are sensibly lower than using a mixture of perchloric acid and ethylic alcohol. However the storage of large quantity of those salts is a problem that must not be neglected

4. Niobium can also successfully electropolished by sulphuric acid in methanol [4,5], but methanol may be fatal or cause blindness if swallowed; it is harmful if inhaled or absorbed through skin; it affects central nervous system, reproductive apparatus and liver with irreversible consequences up to death. Moreover Methanol is very flammable. The pure liquid catches fire easily and aqueous solutions containing a significant amount of methanol can also catch fire. The flame above burning methanol is virtually invisible, so it is not always easy to tell whether a methanol flame is still alight. The explosion limits for methanol are unusually wide.
5. Niobium electro-dissolution is possible in 1 molar KOH solution at 70°C with stirring. A potential of 1.3 Volts and a resulting etching rate of 15 micron/min [6].
6. Anodic dissolution of Niobium is also possible in molten salts. The mixture of (NaCl-KCl-NbCl_n) and AlCl₃ melts at 710°C, but anhydrous AlCl₃ can give rise to unpleasant exothermic reactions.

NIOBIUM ELECTROPOLISHING IN IONIC LIQUID SOLUTION

A revolutionary possibility to electropolish niobium is the use of Ionic liquid solutions. "Ionic liquids" are fully ionized molten salts that solely consist of cations and anions, with a melting point less than 100 °C. Started as academic research in the end of nineties, Ionic liquids are penetrating the industry contest because of their biodegradability and fully ecological properties; because they permit to electropolish, and also to electroplate, metals unapproachable with the standard solutions; because of a high throwing power of the electrochemical reaction. Especially for their application to the industry of stainless steel and also that of non-ferrous materials, such as titanium and aluminium, a new road, called by the specialists of the field the road to green chemistry, has been opened.

In this respect, a breakthrough has been certainly signed by the proposal by Abbot of Choline Chloride and urea eutectic for electropolishing steel [7]. With a Choline cation and a Chloride anion, Choline Chloride is a quaternary ammonium salt which molecular formula is C₅H₁₄ClNO; it has a Molar Mass of 139.6 g mol⁻¹ and decomposes at 302° C. It has a white appearance of deliquescent crystals and it has a high solubility in water.

Choline Chloride enhances and accelerates growth in animals during times of rapid development. It is especially effective at doing so in poultry, and so it is a common poultry feed additive. Choline is particularly

important for fetal development and for children. Human milk contains high amounts of Choline. Choline is important for cell membrane structure, for synthesizing folic acid and vitamin B12, and for protecting the liver from accumulating fat. Choline Chloride supplements can be taken in order to protect the liver from damage, to lower cholesterol, to improve memory, to preserve prostate and to enhance mood. On the other side urea, ((NH₂)₂C=O), that in the reaction acts as a hydrogen bond 'donor' is a common fertiliser. Urea mixed with Choline chloride in a 2:1 ratio produces a colourless liquid that freezes at ca 12°C, which is remarkable, given the melting points of the constituents. The lowest melting point of these mixtures occurs when the ratio of salt to hydrogen bond donor is 1:2. The depression of freezing point and the eutectic composition changes with the nature of the molecule providing the hydrogen bonds, e.g. oxalic acid (HOCCOOH): Choline chloride has a eutectic composition of 1:1 and a freezing point depression of 212°C.

Therefore looking to the success of Choline Chloride for the electropolishing of steel reported in literature, some of the authors of the present paper have explored the possibility to modify the Abbot recipe. They were the first to succeed in reaching the goal, by discovering a new electrolyte for electropolishing Niobium [6]. Originally it was observed that the addition of Ammonium Chloride to the Urea-Choline Chloride eutectic could successfully electropolish Niobium, providing a final surface roughness comparable, when not even lower, than the one obtainable by the standard HF-H₂SO₄ electrolyte. The 1/1; 2/1; 3/1; 4/1 Molar ratios of the Urea and Choline Chloride were explored, as well as the temperature effect at 70 °C, 130 °C, 190°C and the addition of NH₄Cl at 2.5 g/L, 5g/L and 10g/L concentration.

Mirror-like finishing and surface roughness values more than 30% lower than the one obtained by standard HF based procedure were obtainable on niobium planar samples with the following recipe:

Urea:Choline Chloride in ratio 3:1 plus Ammonium Chloride 10g/l at 190°C with a current density of 200 mA/cm².

Further works have explored a large number of different mixtures obtained by mainly shifting from the eutectic point and by substituting Ammonium Chloride with many other possible candidates [8-10].

Nevertheless the above mentioned process was with difficulty applicable to the cavity electropolishing both for the non planar shaper of a cavity and for the huge amount of bubbles produced during the process both at the anode and at cathode. An oxygen bubble for instance enhances the etching in the contact point with the metal surface, giving often rise to micro-craters with an incredibly flat surface at the centre of the well for a microscopical observer, but a terrible pitting on the surface for a macroscopical observer, that travel

according the wave length proper of a radiofrequency wave.

After a long research, but luckily full of intermediate successful steps, the authors have found a magic component that added to the Choline Chloride and Urea mixture extraordinarily works on three-dimensional surfaces, giving rise to mirror like surfaces. This magic component is the Sulphamic acid. The reason for which it was selected in our research lays in the presence of the NH_2 group that has good solubility in Urea's melts.

The final recipe proposed to the interested scientific community hence is the following:

Choline chloride: Urea ratio 4:1 plus Sulphamic acid in the 30 g/l concentration at a temperature of 120°C, a current density of 0,33 A/cm³, an over-voltage from 20 to 60 volts and moderate stirring. It is important to notice that the etching rate in this exotic way approach is about 12 times higher than the etching rate obtainable by the standard $\text{HF-H}_2\text{SO}_4$ electrolyte.

The new original recipe has been rf-tested at 4,2 K onto a 6 GHz monocell resonator. Being the theoretical Q-factor predicted by the BCS theory or the order of $3e+07$, the displayed results of fig. 1 show that, even if heterodoxal, this new way of electropolishing cavities is definitely promising.

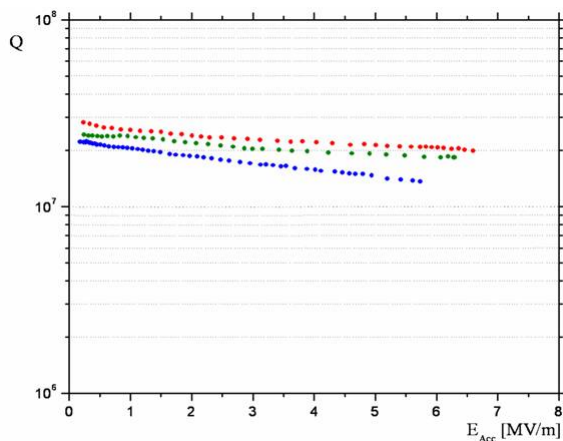


Figure 1: Q-factor versus accelerating field at 4,2 K for a 6 GHz cavity electropolished by means of the standard HF recipe (intermediate curve signed by the green dots) and by the Choline Chloride base recipe containing Sulphamic acid (lower and higher curve signed respectively by the blue and red dots).

CONCLUSIONS

Choline Chloride - Urea Based Ionic liquids are a possible alternative to the hazardous standard electropolishing electrolyte based on hydrofluoric acid.

The addition of Sulphamic acid solves the problem of application to three-dimensional shapes of the electropolishing process.

The solution has been applied to the polishing of a 6GHz cavity that has been tested at 4,2 K, proofing results comparable to the standard approach. A

measure at 1,8K must be foreseen for having higher sensibility. Technological problems could also occur whenever one would think to apply the ionic liquid electropolishing to the fabrication of niobium cavities for particle accelerators. One for example is related to the high current density employed for the electropolishing. Besides that It must be reported however that this work, although still preliminary, proofs that other approaches are however possible and that with further work on the search of the best recipe, the road to substitute a dangerous and hazardous process with an ecological one is opened and by sure full of pleasant surprises.

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