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in
"Surface Treatments for Industrial Applications"

CHEMICAL AND ELECTROCHEMICAL TREATMENTS FOR ACCELERATING CAVITIES

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ACRONYM

EP – electrochemical polishing, electropolishing;

RRR – residual resistivity ratio;

LHC – Large Hadron Collider;

KEK – The High Energy Accelerator Research Organization (translated from Japanese);

SRF – superconductive radio frequency;

BCP – buffered chemical polishing;

SEM – scanning electron microscopy;

EDS (EDX) – energy-dispersive X-ray spectroscopy;

Cu – Copper;

Nb – Niobium;

INFN-LNL – Istituto Nazionale di Fisica Nucleare - Laboratori Nazionali di Legnaro;

HPR – high pressure water rinsing;

RMS – the root mean square.

ABSTRACT

During my master course I worked mainly in chemical laboratory to proceed chemical and electrochemical treatment protocols that involve several steps, and they vary from Niobium 6 GHz cavities to modeling square copper samples.

My main task was dedicated to the learning different techniques, that were applied to the problem of ARIES project, that makes the second part of this thesis. Here is the list of techniques: electropolishing, chemical polishing, cleaning processes and SEM, EDS, profilometer equipment.

To investigate the role of the substrate in the SRF performances, several surface treatments were applied to a certain amount of copper samples. Here is a list of the treatments involved: chemical polishing, electropolishing, combination of chemical and electrochemical treatment and to mechanical treatment (tumbling). The quality of the sample's surface were studied and evaluated by visual observation, under SEM, EDS, profilometer and by calculating average removal thickness.

The protocol optimization was done on flat samples in order to study the critical points of the processes and avoid wasting the real samples. In the nearest future, the quality of the work will be evaluated by comparing the performance of Nb thin film on different substrate preparation.

Part I

Theoretical part

INTRODUCTION

Industrial companies use several metallic surfaces in different areas of application. For that reason surface treatments are vital stage in any production line. Today there can be several reasons to modify the surface properties of metals. For example, surface treatments of metals are used for:

- Decoration and/or reflectivity.
- Improved hardness (e.g. for resistance to damage and wear).
- Prevention of corrosion.

Treatment of metal surfaces plays an enormous role in extending the life of metals, such as in automotive and construction materials.

The treatments can be classified in 3 main categories:

1) Surface modification without chemical reactions.

1.1) Mechanical processes.

1.2) Thermal processes.

2) Surface modification by chemical reactions.

2.1) Thermochemical diffusion processes.

2.2) Electrochemical processes.

2.3) Chemical conversion processes.

3) Surface modification by adding new material onto surface.

For the treatment of cavities, layer that is involved in RF is the most important, and it is vital to optimize fundamental parameters, prevent surface contamination and external oxidation. That should lead, for instance, to the maximum RRR (residual resistivity ratio) value.

$$RRR = \frac{R_{300K}}{R_{10K}},$$

where R_{300K} – is resistance of superconductor at 300 K, R_{10K} – is resistance of superconductor at 10K.

Applied work was focused on chemical and electrochemical treatment of Copper and Niobium. The aim of my researches was to optimize cleaning protocol to obtain shining surface with low roughness and minimum contaminations. Treatments were done based on square samples and real objects like 6 GHz cavities.

1 APPLICATION

Particle accelerators are fundamental engines of discovery, essential tools for understanding the universe and its properties. The 2013 Nobel Prize in Physics awarded to F. Englert and P. Higgs for the discovery of the Higgs mechanism, confirmed by the observations at CERN’s Large Hadron Collider (LHC), has been the peak of a major European endeavor and the latest of a long series of scientific discoveries stimulated by accelerators: as many as 25 out of the last 74 Nobel Prizes in Physics were connected to particle accelerators.

In addition to their use for fundamental research, a large number of particle accelerators across the globe are used as the core element of bright photon or neutron sources. They contribute to research fields as varied as life science, condensed matter, energy research, engineering materials and geosciences, environmental science, material science, cultural heritage, providing a wealth of data to science and a competitive advantage to their industrial users [1,2].

Superconductive radio-frequency (SRF) cavities are the central components of advanced linear colliders for particle physics, nuclear physics, medical science, and other implementations of accelerated charged particles [1,2]. Their distinct advantage over copper cavities is a much higher quality factor, by virtue of the very low surface resistance afforded by the superconducting state. The present technology is based on niobium, due to the favorable superconducting properties compared with other ductile superconducting materials at 2 K and frequencies in the order of GHz [1,2]. Niobium cavity has high purity, good formability, is amenable to electron beam welding, and typically takes on a shiny, smooth surface finish after electropolishing.

Surface treatments are founded to improve SRF performance. Electropolishing (EP) is a surface finishing process based on anodic dissolution of a metal or alloy in an appropriately chosen electrolyte. It is believed to be an effective technique to treat niobium cavity surfaces for reproducibly achieving high-performance SRF cavities. The EP process typically applied nowadays to cavities was inherited from Siemens Co. in the 1970s and was further developed by KEK in collaboration with Namura Plating [3,4,5].

Although accelerators for basic and applied science are the most visible and known elements of the accelerator landscape, they account for less than one percent of all particle accelerators in the world. The majority of the estimated 30,000 accelerators in operation worldwide are used for medicine or industry, of which the largest fields of application are cancer treatment and ion implantation [6,7].

1.1 ARIES project

ARIES brings together a consortium of 42 beneficiaries from 18 countries: accelerator laboratories, technology institutes, universities and industrial partners to jointly address common challenges for the benefit of a number of projects and infrastructures in high-energy physics, as well as in photon and neutron science.

By promoting complementary expertise, cross-disciplinary cooperation and a wider sharing of knowledge and technologies throughout academia and with industry, ARIES will significantly enhance the science and technology base for European accelerators.

The main goals of ARIES are linked to developing and demonstrating novel concepts and further improving existing accelerator technologies, providing European researchers and industry with access to top-class accelerator research and test infrastructures, enlarging and further integrating the accelerator community in Europe, and developing a joint strategy towards sustainable accelerator S&T.

ARIES comprises a strong industrial participation with 8 industrial partners, including three SMEs and one association. Innovation will be fostered by joint co-development programs with industry, by supporting innovative technologies with market potential, and by advancing concepts and designs for medical, industrial and environmental applications of accelerators for the wide benefit of European science and society.

The ARIES strategic goals are:

1. Ensure that Europe maintains the leadership in particle accelerators by developing novel concepts and technologies to improve the performance of the present generation, and to increase the performance, affordability, reliability, sustainability, and broader application of next-generation accelerators.
2. Provide European researchers and industry with access to top-class accelerator research infrastructures needed for the development of new technologies.
3. Enlarge and advance the integration of the European particle accelerator community through new crossborder and interdisciplinary connections between the operators of accelerator infrastructures, universities and industries.

4. Enhance innovation in the accelerator community by involving industry in the setting up of co-innovation programs and in the selection and promotion of innovative technologies, and by supporting the societal applications of accelerators.

5. Ensure the long term sustainability of particle accelerator research by defining scenarios and strategic roadmaps for the future integration of accelerator facilities and by setting a framework for the scientific and technical training of young European researchers, which is vital for the development of new ideas.

In ARIES there are several widest programs (WP). LNL participate in the WP “Thin films for superconducting cavities” with the main objective of “Develop and test new coatings and techniques for superconducting RF cavities” This subproject with internal number WP15 federates a large number of laboratories and universities for a breakthrough in thin film coating technology of superconducting accelerating cavities. Conventional bulk Niobium technology is very close to its theoretical peak performance; this activity will test and improve different coatings (Nb_3Sn, Nb on Cu) to achieve quality factor and surface resistance equal or higher than bulk Niobium and 20% increase of RF critical field. The participating teams have an expertise in different fields (thin film deposition, surface analysis, superconductivity, RF, etc.) and joining them together is expected to provide the critical mass for breakthrough achievements.

During this work I have participated to the task 15.2 Substrate surface preparation (CERN, INFN, STFC, USIEGEN).

This task is focused on defining an optimum cleaning and polishing procedure which dictates the optimum RF properties of the films and on providing the partners with the sample substrates prepared exactly in the same surface chemical state and mechanical topographical finish, in order to minimize the substrate effect on the final film properties. The samples prepared at INFN will be used for deposition at other partner’s laboratories. This task will include an intense coordination and exchange of information between partners. The results will be compared to the ones obtained with in-house prepared substrates. This task will provide samples or optimum cleaning and polishing procedure for sample preparation for Task 15.3.

Objectives are declared below:

- Coordinate and approve among all laboratories surface preparation for all samples to be exactly the same.

- Execute the surface treatment (mechanical, chemical and electrochemical) of the substrate used for thin film deposition in Task 15.3 and the subsequent measurements of surface resistance in Task 15.4.
- Define optimum cleaning and polishing procedure.
- Identify possible causes of delamination, loose thermal contact, etc.

2 WAYS OF TREATMENT

To achieve necessary quality of surface, samples should be treated with several different techniques, that vary from “what you need?” to “what material do you have?”. In this part of thesis, it will be presented the most common treatments I were connected or directly involved in.

A list of most known surface treatments:

Table 2.1 List of possible well-known treatments

Surface Treatment Type	**Principle, short explanation**
Chemical Process (Chemical Coating)	Creating or modifying surface by chemical reaction. Usually it can be observed for metallic colorization, corrosion protection, pretreatment before main treatment.
Electroplating	This is mainly an electrochemical procedure, during which the material is immersed into electrolyte solution and connected as a cathode. The film is formed due to the sub-reduction reaction.
Anodic oxidation	Usually it is applied for light metals such as aluminum and titanium to grow oxide films.
Hot Dipping	Products are dipped in dissolved Tin, Lead, Zinc, Aluminum, and solder to form surface metallic films.
Electrochemical polishing	This is an electrochemical process that removes material from a metallic workpiece. It is used to polish, passivate, and deburr metal parts. It is often described as the reverse of electroplating. Mainly used to decrease surface roughness, and to make it smoother.
Vacuum plating	Gasified or ionized metals, oxides, and nitrides in vacuum chambers are vapor deposited. Some methods are vacuum vapor deposition, sputtering, ion plating, ion nitrating, and ion implantation.

Continuation of table 2.1

Surface Treatment Type	**Principle, short explanation**
Painting	Electrostatic painting, electrodeposition painting, electro-conductive painting, non-adhesive painting.
Surface hardening	The process of hardening is made by increasing the amount of carbon, nitride. It is a quite known technique for carburizing, nitrating and induction hardening of steel. The result is improved fatigue strength and anti-wear properties.

2.1 Mechanical treatments

For microscopic examination, a sample should be smoothed in such a way that the surface becomes highly reflective, free of scratches and deformations. Mechanical grinding and polishing methods are the most common. They are usually accomplished by abrasive removal, using a manual technique on fixed abrasives, vibrating platens, rotating wheels, or continuous belts. During such treatment, the surface is removed by the abrasive in the form of shavings or chips [8].

During polishing and grinding the abrasive particle size decreases from one step to the next.

2.1.1 Production

Strip and sheet, extruded and rolled sections, castings, stamped, drilled and cut parts, components and assemblies are examples of metal products that cannot be used in the condition in which they are received. The surfaces may be contaminated with lubricating oils, greases and waxes, drawing compounds, as well as metal particles, scale, casting sand, or other foundry materials. General soil from the workplace and handling compounds is the problem. In addition, there may be burrs, laps, flash, and other surface defects present. A variety of surface preparation techniques are used based upon what is to be accomplished [9].

2.1.2 Polishing

Polishing is an intermediate step used to improve the surface finish from the grinding step, such as found on a common treatment of stainless steel that is shining, but not mirror-like. Polishing uses abrasives firmly attached to a flexible backing, such as a wheel, belt or orbital motion tool. Mechanical polishing is performed in steps with progressively finer abrasives until a desired smoothness is achieved. The precision polishing process removes material and plastically deforms the surface while it alters the macroscopic and microscopic surface texture [9, 10]. The polishing media remains often embedded in the workpiece surface, but this is unacceptable for cavity surface.

Polishing with abrasive tape.

Polishing with abrasive tape (see fig. 2.1) is a type of grinding. The working surface of the tape on which the polishing paste is applied is characterized by the dimensions of the abrasive grains of the paste and the number of them per surface unit. It is used for machining large parts with a complex profile.

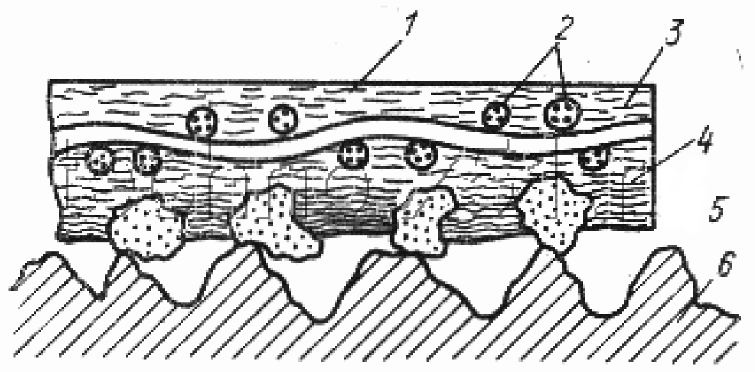


Figure 2.1 – Schematic view of the polishing process with abrasive tape.

1- tape-base; 2 - the yarn of the thread; 3 - apparatus; 4 - ligament; 5 - abrasive grains; 6 - machined surface

Abrasive tape is normally forbidden for cavities, because of abrasive embedding. That’s why it is often used scotch-brite as abrasive media.

Mechanical polishing and buffing cannot be viewed as an adequate substitute for electropolishing in most applications due to the embedded abrasives and compounds, exposed grain structure of the metal, and the lack of the non-particulating, non-contaminating, and non-outgassing characteristics of an electropolished surface [11].

Polishing with the circles (polishers)

Polishing with circles is carried out on polishing machines with a polishing compound (paste) or suspensions, polishing wheels made of felt or round brushes.

For mechanical polishing using mixtures or suspensions, a large number of different grinding wheels exist. Products of simple shape - flat or square, can be processed on a universal machine with a polishing wheel of a straight profile. For rough processing, hard wheels are used, and for thin processing, they are soft. The hard circle intensively polishes, but is quickly greased, especially when processing soft colored and precious metals and alloys. Soft elastic circle is ineffective in preliminary operations and, in addition, when pressed hard it can deform [11].

Tumble finishing, also known as tumbling or rumbling. There is a similar process called barreling, or barrel finishing.

Tumbling is a technological process of machining, cleaning and preliminary surface treatment of parts from various materials: metals, ferrous, non-ferrous and precious alloys, polymers, glass, ceramics, minerals, wood and others [9].

The process of tumbling is carried out on various equipment such as: drums of tumbling and tumbling vibrators of various types.

To perform the tumbling process, a filler (medium) is required in which the parts are machined and which provides the required quality of the machined workpiece surface.

Figure 2.2 – Photo of tumbling barrel.

In several fields of activity filler (medium) is also called: tumbling bodies, abrasive granules (in engineering), chips (in the jewelry industry), abrasive. The most appropriate names are tumbling bodies or abrasive granules when it needs to be clarified that the tumbling bodies contain an abrasive. The filler and parts are moved relative to each other in the working capacity of the machine (drum). Machines for tumbling are divided into a large number of types, for example, mechanical and electromagnetic. In turn, mechanical are divided by the type of motion into: rotating drums and drums with a vibrating drive.

Tumbling is divided into dry and wet. Dry tumbling uses dry tumbling bodies. In wet tumbling, a buffer solution or working fluid is added to the tumbler drum. For example, when processing metal parts a wet tumbling is effective while working with wooden parts, the dry tumbling is [9, 11].

Tumbling bodies are divided into ceramic, porcelain, plastic. They usually have the form of a tetrahedron (pyramid), a cone, a parallelepiped, a cylinder or sphere/lenses. Furthermore, as tumbling bodies, materials without a bundle can be used: corundum, a crumb of a walnut shell, wood and other materials.

2.2 Chemical treatments

2.2.1 Degreasing

Any process of manufacturing parts is associated with surface contamination, whether it is punching, cutting or polishing. Items made of steel contaminated with animal and vegetable fats are well cleaned in alkaline solutions with a high pH. However, in most cases, solutions with a lower pH value of the order of 10.5-12 are used to prepare the surface for plating. Since vegetable and animal grease are often combined with mineral greases, pre-degreasing is practiced in organic solvents with subsequent purification in alkaline solutions.

In the degreasing of non-ferrous metals - copper, zinc, tin, aluminum, lead and their alloys - inhibitors are added to alkaline solutions, which cover the surface with a very thin film, which prevents its etching and tarnishing. When degreasing steel parts, the main components are caustic soda of non-ferrous metals - alkali metal salts and a small amount of emulsifier.

The mechanism of removing fats of vegetable and animal origin in alkaline solutions is reduced to their saponification and emulsification.

The process of saponification can be illustrated by the example of the interaction of stearin (the main part of fat) with caustic soda

$$(C_{17}H_{35}COO)3C_3H_5 + 3NaOH = 3C_{17}H_{35}COOH + C_3H_5(OH)_3.$$

The resulting sodium salt of stearic acid, sodium stearate or soap, forms a colloidal solution with water.

The emulsifier introduced into the degreasing solution is adsorbed on the surface of two phases (fatty film-solution) and lowers the surface tension, facilitating the detachment of fat droplets from the surface of the metal and their transition to the state of emulsion. As emulsifier, sodium silicate Na_2SiO_3 is more often used [12].

There is also a very effective and simple method called ultrasonic cleaning. It is cleaning of the surface of almost any complexity and material by excitation of ultrasonic frequency in the washing solution. A dedicated bath is used for this process. Such cleaning has many advantages compared to other cleaning methods.

The most important advantage is that ultrasonic cleaning does not require the use of manual labor. The ultrasonic bath is designed so that the parts are cleaned by means of cavitation bubbles that penetrate the impurity film, thereby destroying it and peeling off the contaminants from the surface of the part or object being cleaned. In addition, in such baths it is possible to clean hard-to-reach areas of products without the use of organic solvents, which is impossible with other methods of purification.

To increase the efficiency and reduce time of cleaning industrial soaps can be used in combination with temperature.

2.2.2 Chemical etching, activation, polishing

Solutions for activation to prepare surface for further treatments (plating, polishing, oxidation etc.) are widely used to remove thin layer of oxide. These solutions are usually used before plating process.

As well, there is a very similar process, which is called etching. The main purpose of the procedure is to remove layer of metal, oxides, salts. All chemical treatments are required for almost every purpose, especially those which require minimum contaminations.

Typical agents for etching are acids or bases, less often – salts or desoxidation agents.

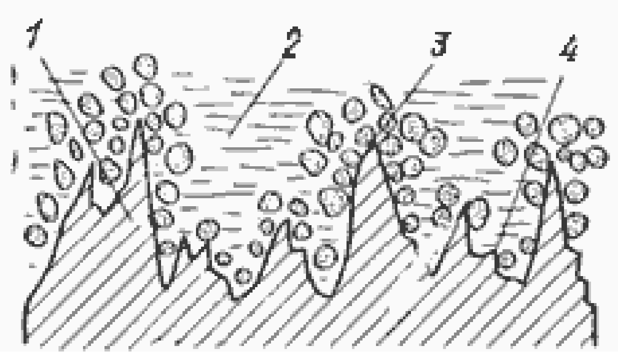


Figure 2.3 – Schematic view of surface under chemical polishing
1 – workpiece surface; 2 – electrochemical solution; 3 – peak; 4 – valley.

When the process of etching is controlled and moderated by agents, the process became chemical polishing. Chemical polishing consists in immersing the workpiece for some time in a vessel with a chemically active solution, where the metal dissolves as a result of the arising chemical and local electrochemical processes. The surface roughness is reduced or completely eliminated, while the treated surface acquires a luster. All the processes of chemical polishing are accompanied by a rapid release of gases and vapors of acids or alkalis [13].

In the polishing process, it is recommended to mix the solution or shake the parts in the container. This makes possible to eliminate the accumulation of gas bubbles in individual parts of the workpiece, since gas bubbles reduce the quality of polishing. One of the main advantages of chemical polishing is its simplicity. To obtain the desired result, it is sufficient to submerge the workpiece for several minutes into the appropriate solution, without applying an electric current, without mechanical action. The method does not require too complex equipment.

The disadvantages of such polishing include the complexity of correction (maintaining the exact proportions of all elements in the solution by adding the consumed element), solutions and their short life. The gloss of the surface is less than in electrochemical polishing [9].

Electrochemical polishing is the main competitor of chemical polishing, however the latter one is less controllable.

2.2.3 Chemical deposition

Chemical deposition has several advantages, like uniformity or an easier way to deposit, and even deposition on non or semi conductive materials. Let’s divide this topic into 2 groups.

2.2.3.1 Chemical oxidation

This method is applicable only for metal, as it requires substrate material to oxidize and grow oxide or salt layer. It’s widely used for decorative purpose, but also could be applied for special cases. Oxidizing could be used to make material adsorb more energy, because of black oxide color, or to protect from corrosion.

Chemical oxidation is carried out by processing the product in solutions of oxidants (chromates, nitrates, persulfates etc.). With this method, the surface of the product is passivated or applied to protective and decorative layers. For ferrous metals, chemical oxidation is carried out at a temperature of 30 to 100 ° C in alkaline or acidic formulations. For acid oxidation, a mixture of several acids is used, for example, nitric (or orthophosphoric) and hydrochloric acids with some additives ($Ca(NO_3)_2$, Mn compounds). Alkaline oxidation is carried out at temperatures slightly higher, about 30-180 °C. Oxides are added to the formulation. After the oxide layer is applied, the metal products are well washed and dried.

Protective layers obtained with the use of chemical oxidation have less protective properties than films obtained by anodizing [14,15].

2.2.3.2 Chemical reduction of metals

In recent decades, the chemical coating method has been used to metallize dielectrics, giving the surface electrical conductivity. In particular, metallized plastics possess chemical resistance, wear resistance, heat resistance and mechanical strength, have a decorative appearance and are resistant to light. Due to these properties, metallized plastic is widely used in automotive and instrument making. Decorative-metallized plastics make furniture fittings, jewelry, toys and other household products. There are several ways of chemical deposition of metal coatings from aqueous solutions: 1) contact; 2) contact-chemical; 3) method of chemical reduction [16].

- The contact method is based on the displacement of metal ions from the solution by the more active metal.
- The contact-chemical method of metal deposition creates a galvanic pair between the base metal and the more active metal.
- The method of chemical reduction (chemical metallization) consists in obtaining metal coatings as a result of the reduction of metal ions from aqueous solutions containing a reducing agent.

Solutions for the production of chemical coatings, in the simplest case contain a metal salt and a reducing agent. However, such solutions are unstable, and metal ions are reduced to form a metal precipitate in the entire volume of the solution. At the initial time, the reaction between the metal ions and the reducing agent is non-catalytic, but as soon as the metal particles form, the reaction takes on a catalytic character, and its rate increases with the surface of the precipitate.

To stabilize the solution, the following are introduced: 1) complexing agents (ligands), which ensure the formation of strong complexes with metal ions. With increasing strength of the complex, the reaction rate of the interaction of the metal ions with the reducing agent decreases; 2) substances that produce a certain pH (alkalis or acids, buffering additives); 3) stabilizers - special substances, which in small concentrations (1-100 mg/l) significantly increase the stability of the solution.

2.2.4 Chemical passivation

Passivators are substances by which a metal surface is transferred into a passive state. Most often, passivators are inorganic substances that have oxidative properties (chromates, molybdates, nitrates).

When the metal surface interacts with certain substances, protective layers (films) form on it. These substances shift the corrosion potential in a positive direction, thereby reducing the rate of corrosion.

Chemical passivation is carried out by immersion or direct application of reagents to the surface itself without the use of an electric current. Depending on the substances used, chemical passivation can be carried out at room temperature or heating the electrolyte.

2.3 Electrochemical treatment

To begin with, electrochemical process is the process in which two sub processes occur, called cathodic & anodic or oxidation & reduction reactions. The real cause of the electrochemical reaction is the current, which flows from cathode through conductive electrolyte solution to anode. Oxidant and reducing agent, which participate in partial reaction of electrochemical process are usually called like participants.

In electrochemical processes, the transition from one participant, in the reaction, to the other must be done along a rather long path. The production of energy is always associated with the passage of an electric current, that is a stream of electrons, which are moving along the same path. Therefore, for an electrochemical process that can be separated, the reducing agents must be separated, and the electrons must be transferred from the reducing agent to the oxidizer along one common pathway. To this end, direct contact between the participants is necessary, which can be achieved for each other with two metal plates, connected together by some metallic conductor. In order for the electron flow to be continuous, it is necessary to ensure the passage of electric current through the reaction space, which is usually performed by the participants in the electrochemical reaction (if they are present in the form of ions) and special added compounds with high ionic conductivity.

Thus, for the implementation of electrochemical treatment, a certain system is needed - the electrochemical chain. Essential elements of such a system are:

1) two electrodes, consisting of electron-conducting materials (metal, graphite, etc.), in contact with ionic conductors (electrolytes). They use the exchange of electrons with the participants in the reaction;
2) a metallic conductor (conductor of the first kind), connecting the electrodes and providing the passage of an electric current between them. It is an external circuit;
3) electrolyte solution, its melt or solid electrolyte (conductors of the second type). This part of the system is an internal chain.

Electrochemical process could be controlled by several ways in addition to chemical one. And this is the main advantage of most electrochemical reactions. Additional variable parameters could be presented as: voltage (Volts) and current (Amperes), in general “difference in potential”.

In principle we can divide any electrochemical processes into 2 main groups: cathodic and anodic, those correspond to the main reaction of the system. The above described degreasing procedure (see chapter 2.2.1) sometimes performed also electrochemical way. In principle, solutions are the same, but could be different anodic and cathodic reactions. On electrodes 2 main reactions occur:

$$C: 2H_2O + 4e^- = H_2 + 2OH^-$$

$$A: 4OH^- = O_2 + 2H_2O + 4e^-$$

According to the balance, it is clearly seen that with the same amount of charge, cathodic reactions is more efficient, due to the amount of gas evolution. But, at the same time, cathodic part is more dangerous, because hydrogen could interact with the surface, integrate inside the coating, thus causing hydrogen embrittlement and other mechanical properties decrease even up to the cathode destruction.

2.3.1 Cathodic electrochemical process

Mostly, this kind of process corresponds to plating. The process used in electroplating is called electrodeposition. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. A power supply supplies a direct current to the anode, oxidizing the metal atoms that it comprises and allowing them to dissolve in the solution. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they "plate out" onto the cathode. The rate at which the anode is dissolved is equal to the rate at which the cathode is plated, according to the current through the circuit. In this way, the ions in the electrolyte bath are continuously replenished by the anode.

The most known plating is copper electrodeposition, which is widely used as the sub-layer to increase adhesive properties of the surface.

2.3.2 Anodic electrochemical reaction

The fundamental idea of any anodic process is the oxidation process. It means that on the anode part, the reaction that will consume electrons occurs to provide increasing positive charge of the atoms/ions. In general, any metal constructed as a anode will be dissolved in the solution as an ion Me^{z+}, where z is the charge. This kind of process can be considered as corrosion of metal and at the same time as dissolving metallic layer.

Electrochemical processing replaces labor-intensive mechanical methods and does not lead to undesirable structural changes in the surface layer of products. The cracked surface in many cases has a higher corrosion resistance and improved mechanical properties. Electrochemical polishing is the treatment of the surfaces of parts immersed in an electrolyte, which is a solution, usually containing acids. During a process at a constant voltage of 2-20 V, the product is connected to the positive pole (anode) of the power source.

When electrochemical polishing occurs, the process of smoothing the micro-roughness at the surface submicro-relief level is associated with the presence of a passivation film on the metal. The degree of reduction in roughness is determined by the magnitude of the electric charge that has passed through the electrolyte. In the course of electrolysis, along with a decrease in the height of the microprotrusions, their peaks are rounded and the wave-like microroughness of the surface is formed. These processes are caused by the uneven distribution of electric current over the microrelief of the surface and the concentration changes in the electrolyte in the pre-anode layer. The quality of electrochemical treatment depends on the composition of the metal or alloy, the degree of residual deformation and the thickness of the workpiece.

The basis of industrial electrolytes for electrochemical polishing is orthophosphoric or perchloric acid. In chloric acid electrolytes, aluminum, zinc, lead, and titanium are processed. In three-component phosphoric-sulfuric-chromate acid electrolytes, steels of various grades are treated, and in phosphoric-sulfuric acid - stainless steels of austenitic class.

Despite the rather wide range of applications, the electrochemical method has significant drawbacks, such as [9]:

1. High energy consumption
2. Toxicity, fire hazard and explosion hazard
3. Technological complexity
4. Restriction of the nomenclature of the processed metals
5. Corrosion of equipment

Another common used process very similar to EP, but with other properties of the final surface, is called oxidation process.

Electrochemical oxidation (anodizing) is the process of depositing an oxide film on the surface of metals, alloys, and semiconductors. The film protects the product from corrosion, has electrical insulating properties, it serves as a good basis for paint coatings and it is used for decorative purposes. The oxide film can be grown on various metals (for example, aluminum, niobium, tantalum, titanium, zirconium, etc.), for each of them there are special conditions for the process. The thickness and properties of the film depend on the particular metal. Aluminum is unique in its kind, because in addition to the thin oxide layer, its alloys in certain acid electrolytes form thick oxide films having a highly porous structure.

2.3.3 Mechanism of electrochemical polishing

In order to understand better the electrochemical process, the mechanism of this procedure is described below.

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 [18]. The non-uniform thickness of the viscous layer over the material surface results in a different ohmic resistance between the cathode and the anode. It causes 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. This is the generally accepted mechanism for electropolishing and mass transport control has been established as the reason behind electropolishing.

According to Elmore, instead, the cause of the surface levelling is related to the diffusion of anodic dissolution products from the anode through the film. The dissolution rate is higher from protrusions than from wells. Elmore’s model was criticized by Edwards, which predicted that electropolishing processes are controlled by the diffusion of anionic acceptors such as $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} to the anode surface.

Electropolishing of many metals was studied so far and it was found that a particular voltage range in the I-V characteristics (see fig. 2.4.) 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.

Before Va point – there is no sufficient speed of metal dissolving. Starting from Va to Vb, we can observe linear increment of the dissolution speed. In this region is strongly recommended not to perform electropolishing due to formation of oxygen bubbles that cause local pitings. Point C corresponds to the maximum velocity of the dissolution. Along D slope the passivation of the metal in form of oxides or hydroxides starts. Due to different behavior of metal to their oxides, hydroxides, salts and the pH media, the anodic curve could be represented in 3 sub curves (G, H, E).

Polishing effect is observed between Vb and Vc. However, the best result is obtained close to F point. On the plateau there is a minimum of oxygen bubbles evolution. Moving to the top, these bubbles can easily make traces on the surface. One of the ways to fight this problem is to use agitation and other ways of increasing the mass-exchange process.

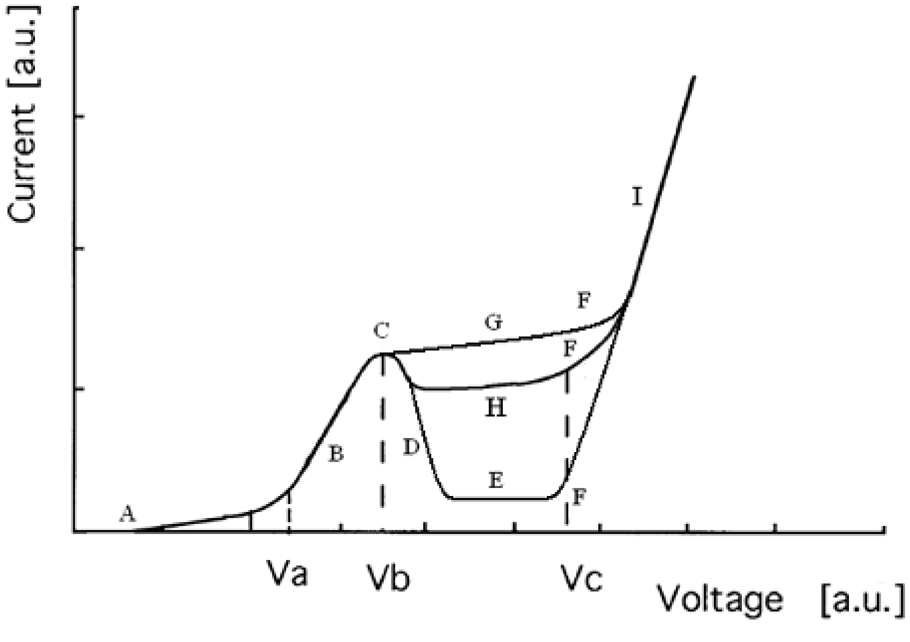


Figure 2.4 – Schematic diagram of anodic polarization of metals

After Vc voltage, gas evolution increases its rate, and so pittings takes place even more corroding the surface. However, moving far above after Vc voltage, it is possible to carry out the EP, since the oxygen bubbles could have time to stick on surface. Based on this information, it's possible to provide shock polishing, for final polishing. With this technique, the voltage is increased by approximately 50%, the solution is agitated at a high rate, and the time is very short (1/4 to 1/2 s).

Summarizing all possible reactions that take place during EP in general overview [17]:

Cathodic reactions – are the reactions where the reduction process takes place. During this reaction there is always "consuming of electrons". Examples:

1) Oxygen reduction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \text{ (pH<7)}$$

$$O_2 + 4H+ 4e^- \rightarrow 2H_2O \text{ (pH>7)}$$

2) Hydrogen evolution:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \text{ (pH>7)}$$

$$2H^+ + 2e^- \rightarrow H_2 \text{ (pH<7)}$$

3) Reduction of the metal (if possible, example Cu)

$$Me^{z+} + ze^- \rightarrow Me$$

4) Reduction of ions (ex. ferric ions):

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

Anodic reactions are the reactions that release electrons and generally oxidizing occurs. Behavior in electrolytic polishing depends mainly on the nature of the dissolving metal, the electrolyte composition, the temperature, the current density and the degree of agitation.

The following reactions may take place:

1) Dissolution of the metal inside the solution

$$Me = Me^{z+} + ze$$

2) Formation of oxide layers:

$$Me + 2OH^- \rightarrow MeO + H_2O + 2e^-$$

$$Me + H_2O \rightarrow MeO + 2H^{+} + 2e^{-}$$

4) Depassivation of the surface (example for double charged metals):

$$MeO + 2OH^{-} \rightarrow Me^{2+} + H_2O$$

$$MeO + 2H^{+} \rightarrow Me^{2+} + H_2O$$

4) Evolution of oxygen:

$$4OH^{-} \rightarrow O_2 + 2H_2O + 4e$$

$$2H_2O \rightarrow O_2 + 4H^{+} + 4e$$

5) Oxidation of various components of the solution.

According to what was mentioned above, scientists believe and represent the reaction of dissolution of metal (for example Cu) [19]:

$$Cu + {}_{sA}\cdot A^{m-} \rightarrow (CuA_{sA})^{\,2-s}A^{m} + 2e$$

2.4 Cleaning process

The last treatment process, but not the least by the importance is cleaning procedure. This kind of operation is determined by the cleanliness of the surface. The term "clean" by itself is indefinite in meaning and has different meanings in different contexts. "Clean" in terms of bacteria is not necessarily the same as "clean" in terms of chemical or particulate matter. Cleanliness is related to the product considered; it is not an absolute measure. If a mechanism or system must be free of contamination to function reliably, measures of contamination control must be taken. The purpose of any such effort is to reduce or manage - contamination at the desired level.

It is widely known that superconducting cavity devices are quite sensitive objects to deal with. Their characteristics like Q-value, break-down field and electron loading behavior is not always reproducible. There is good evidence that contamination is the key to that behavior; contamination can enter in the form of contamination of the bulk or contamination of the surface [20].

Contamination may be classified in 4 general categories:

1) Particulates - dust, chips, fibers
2) Chemical contamination - gases, liquids, inorganic compounds, organic compounds
3) Biological contamination - bacteria, viruses, fungi, spores
4) Radioactive contamination

Each of these contaminants can be present in gases (particularly air), liquids (particularly water) or at surfaces.

Contaminants in liquids are:

- Nonvolatile residues like skin oils, solder fluxes, cutting fluids, cleaning solvents, plasticizers, lubricants;
- other liquids in suspension or solution;
- absorbed gases;
- particulate matter;
- viable and non-viable microbiological matter.

In gases we can find:

- hydrocarbons residues from cleaning agents, lubricants;
- water;
- absorbed or mixed-in gases;
- particulates - corrosion, rust, flakes from wear.;
- microbial matter.

Superconducting RF cavities in their final stage of surface treatment are nowadays treated with:

1) Acids;
2) Water;
3) Solvents.

In the assembly stage they are in contact with gases or air. In all these stages, contamination takes place if not avoided or managed at a certain level. To minimize the risk of contamination, it's mandatory to use distilled water, as much as possible pure solvents and other chemicals during the process of cleaning.

There is not an ideal way to eliminate contaminations, the only thing we can do is to reduce the level of probability to contaminate at every level [9]. By

1) using distilled water with almost no inorganic salts, organic solvents, microorganism and dissolved gases.
2) using only cleanliness compounds during treatment,
3) minimizing the exposure of samples/surfaces to the air;
4) cleaning all surfaces with alcohol and drying with high pressure N_2.

5) exposing to ultrasound, to remove adhered molecules from surface by cavitation effects.

It is often even necessary to clean the sample several times within one preparation sequence. This is done by rinsing the sample under running water and additional wiping with cotton or by ultrasonic cleaning.

Ultrasonic cleaning is the most powerful cleaning technique. Residual polishing compounds can be completely remove, even from very fine cracks, pores of porous or fractured samples, or at the interfaces between the specimen and the mounting material. Ultrasonic cleaning removes even very persistent dirt residues.

To dry the specimen surface, the samples are rinsed with water either alcohol. With the low boiling point, drying process appears to be very quick and does not stain when using a hot air dryer. Any remaining liquids in cracks and pores have to be evaporated.

A clean surface, free of grease or oil, is a prerequisite for chemical or electrolytic treatment especially for etching, since any traces can badly affect the overall result.

In ultrasonic cleaning, high frequency sound waves are applied to a liquid cleaning solution. These sound waves generate zones of high and low pressure throughout the liquid. In the zones of negative pressure, the boiling point decreases and microscopic vacuum bubbles are formed. As the sound waves move, this same zone becomes one of positive pressure, thereby causing the bubbles to implode. This is called cavitation and is the basis for ultrasonic cleaning. Cavitation exerts enormous pressures (approximately 700 bar) and temperatures (approximately 1000 °C on a microscopic scale). These pressures and temperatures loosen contaminants and perform the actual scrubbing of the ultrasonic cleaning process [21, 22].

Part II

Experimental part

3 SURFACE TREATMENTS FOR ACCELERATING CAVITIES

3.1 Why 6 GHz cavities?

The R.F. characterization of samples is a useful diagnostic tool to accurately investigate local properties of superconducting materials. However, the biggest problem of implementing this characterization is scaling for industrial sizes. It is easier and more accurate to use smaller objects, like 6 GHz cavities.

Testing 1.3/1.5 GHz resonant cavities is obviously the most direct and right way, but it can take big expenses of production and cry maintains. Instead, smaller cavities, that are fully equal in shape to the real scale resonators would be the best and most right way for measuring R.F. properties of the material.

Using the spinning technique, it becomes feasible to produce small scale resonators in little time, negligible cost and in large quantity. At INFN-LNL a large number of 6 GHz cavities made of niobium, copper, lead and even iron (see fig. 3.3) have been produced by spinning technique to study the effectiveness of innovative surface treatments, new thin film deposition techniques, new superconducting materials for RF applications and also chemical behaviour of different treatments [24].

6 GHz cavities are made from the remaining material of the larger cavities production. They don’t require welding (even for flanges) and successfully, they can be directly measured inside a liquid helium Dewar. With 6 GHz cavities it is possible to perform more than one RF test per day, while 1.3/1.5 GHz cavities need no less than 1-week time preparation for the RF test. As well, for chemistry aspect, economy of chemicals could play significant role in saving money for experiments.

Figure 3.1 – 6 GHz cavities made of different materials: Nb, Nb, Cu, Fe, Pb

With a technology like this it is possible to study traditional and innovative surface treatments and to perform RF tests on a large amount of cavities with a research budget much lower than the one necessary to treat and test real cavities. It is also possible to study new thin film superconducting materials grown for example by sputtering or thermal diffusion [25].

Summarily, the spinning seamless technology has several advantages in comparison with welding one:

- no welding required;
- short production time;
- equipment could be adapted for any size of the cavity, and any quantity of cells;
- comparably low fabrication costs;
- no intermediate annealing;
- almost no scraps.

3.2 Production of the 6 GHz Cavitiy

Well-known spinning technology was adapted at the National Institute of Nuclear Physics in Legnaro (INFN-LNL) to form a fully seamless resonator without electron beam welding. In this way, starting from a disk or a seamless tube, it is possible to build seamless cavities with no intermediate annealing, more rapidly, simply, and with a uniform thickness. Both elliptical niobium and copper cavities can be easily manufactured with high reproducibility and significant savings in manufacture costs.

Spinning of a seamless mono-cell resonator from a circular blank is depicted on Figure 3.2 the process is mainly divided in four steps [23]:

A. a circular disk is first to be preformed onto a custom shaped mandrel,

B. then the first half-cell is formed and a cylindrical shape is given to the remaining part of the piece, by means of a second pre-mandrel.

C. the third step consists in spinning the obtained manufacture onto a collapsible mandrel that has exactly the same shape of the cavity interior, up to when the roller overcomes the equator and fixes the piece to spin onto the mandrel.

D. the last step consists in inserting a further frustum shaped collapsible mandrel in order to guide the material when spinning the second half-cell. Both collapsible mandrels are then removed.

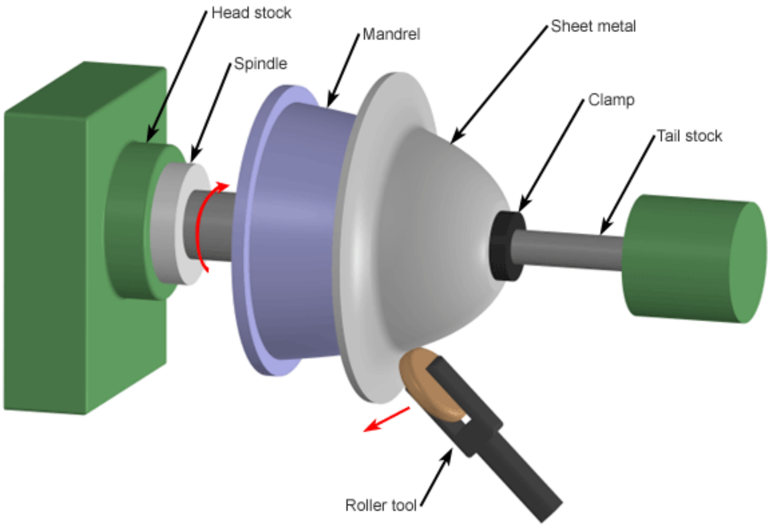


Figure 3.2 – Schematic representation of a spinning process for an elliptical single cell cavity from a single sheet of copper [26]

In order to have mirror like flanges and avoid leaks during the RF test, a lapping of the flanges with 4 different grades abrasive paper is needed. The process has been done at LNL.

Figure 3.3 – Process of flange lapping – a; resulting quality of the surface after lapping – b

3.3 Technological process of Cu cavity treatment

In this part of the thesis the technological process that is applied to cavities is described starting from production to aluminium packaging before Nb sputtering.

1. Fabrication of the copper cavity by spinning (only for new cavity);
2. Grinding, lapping of the flanges;
3. Degreasing in ultrasound, 40 °C, 1 hour with GP 1740 soap.
4. Initial etching of the surface (if needed) with $(NH_4)_2S_2O_8$ (20-50 g/l);
5. Cleaning protocol (Water cannon→ Ultrasound→ Alcohol→ high pressure N_2);
6. EP in (H_3PO_4 : Butanol in the ration 3:2 v.r.%);
7. Cleaning protocol (Water cannon→ Ultrasound→ Alcohol→ high pressure N_2);
8. SUBU treatment (Sulfamic acid 5g/l, Ammonium citrate 1g/l, H_2O_2 50 ml/l, Butanol 50 ml/l);
9. Passivating in sulfamic acid (5-20 g/l; med – 10 g/l);
10. Cleaning protocol (Water cannon→ Ultrasound→ Alcohol→high pressure N_2);
11. High pressure rinsing(100 atm) - Alcohol→ N_2 drying;
12. Packaging.

3.3.1 Initial etching of the surface in ammonium persulfate solution

For its powerful oxidizing property, it is used to etch copper on printed circuit boards from 1970s. But today continuous regeneration systems and a cyclic system based on ammonium persulfate are no longer used. Persulfates, as well as electrolysis of Copper and metallization, are widely used to create an oxide film in the inner layers during micro-etching. Persulfate solutions are compatible with all major types of resistors of printed circuit boards, including solders, Tin, Tin-Nickel alloy, protective paints and photosensitive films [26].

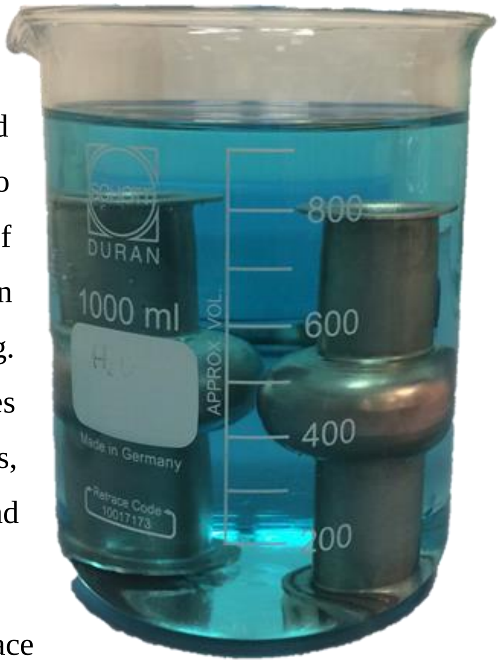


Figure 3.4 – Process of Cu cavity etching

Initial etching is a rough way to remove surface layers of oxides, salts and other compounds. Main task is to remove upper layers, without any sufficient controlling or moderating that can cause shining effect (as in EP method).

Chemical composition.

Ammonium, potassium and persulfates are stable salts of persulfuric acid ($H_2S_2O_8$). Dissolving in water, these salts form the persulfate ion ($S_2O_8^{2-}$). This is the most powerful oxidizer from currently used peroxide compounds. During copper etching, persulfate oxidizes metallic copper to form a cupric ion.

During the hydrolysis of solutions of persulphuric acid, a peroxy monosulfate ion (HSO_4^{1-}) is formed, followed by hydrogen peroxide and oxygen. The catalyst for hydrolysis is acid, which causes instability of acid pickling solutions of persulfuric acid [27].

$$\text{I } H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4$$

$$\text{II } H_2SO_5 + H_2O <=> H_2SO_4 + H_2O_2$$

$$\sum H_2S_2O_8 + 2\ H_2O = H_2O_2 + 2\ H_2SO_4$$

- Copper Oxidation:

$$Cu + S_2O_8^{2-} = Cu^{2+} + 2SO_4^{2-}$$

- Formation of copper sulphate:

$$Cu^{2+} + 2SO_4^{2-} = CuSO_4 + SO_4^{2-}$$

- Completed reaction:

$$(NH_4)_2S_2O_8 + Cu = CuSO_4 + (NH_4)_2SO_4$$

A solution of ammonium persulfate is acidic. Hydrolysis and etching reactions reduce the pH from 4 to 2. The concentration of persulfate falls and ammonium sulfate is formed with hydrated bivalent copper $CuSO4 \cdot (NH_4)\ 2SO4 \cdot 6H_2O$. This precipitate can interfere with the etching process [28].

Table 3.1 Solution and condition for deoxidizing copper

Solution	Concentration	Time	Temperature
$(NH_4)_2S_2O_8$ *ammonium persulfate*	20-50 g/l	20-60 min	room

3.3.2 Electrochemical polishing of Cu SRF cavities

As it was described earlier (see chapter 2.3) the classical mechanism of electropolishing is based on viscous anodic layer that is formed during EP on the surface of cavity. In practice, for almost every electrochemical process mixing the solution, pumping and other ways of increasing mass-exchange process are highly recommended. That’s why, to reach maximum result (minimum roughness and contaminations) it was used pumping system for vertical EP of 6 GHz cavities. Principle scheme is shown below (see fig. 3.5), where 1 is membrane pump, 2 - box with electrolyte, 3 – cavity (anode), 4 - power supply, 5 – PC to control and observe the process. The cathode is done in that way to copy the cavity shape, and placed inside sealed construction, through which will be conducting a flow of electrolyte during EP.

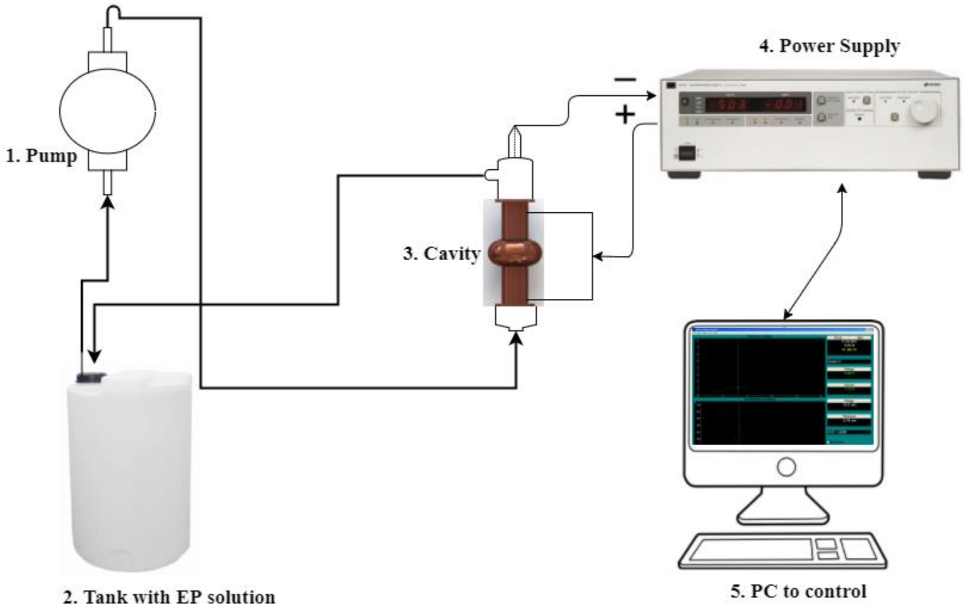
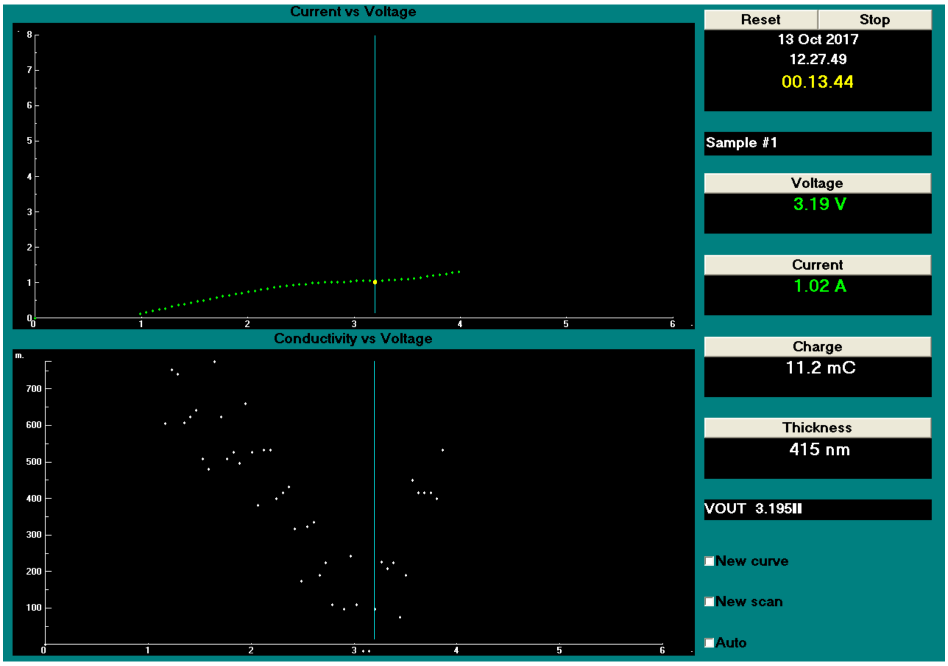


Figure 3.5 – Principal scheme of EP system build in LNL-INFN for EP of 6 GHz cavities

For electropolishing of Cu it was used an electrolyte which is prepared in volume ratio 60:40 respectively H_3PO_4(85%) : n-Butanol in volume ratios. New solution is transparent and during the EP it becomes blue due to saturating of Cu^{2+} ions.



13 Oct 2017
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Sample #1

Voltage
3.19 V

Current
1.02 A

Charge
11.2 mC

Thickness
415 nm

VOUT 3.195II

Figure 3.6 – Typical I-V and dI/dV curve of 6 GHz cavity EP

As power supply an HP were used with such parameters 60 Volts and 50 Amperes and was controlled via PC in voltage control regime. To minimize parasitic effects (such as pitting, vertical traces due to gas formation) EP is done in the point of minimum differential conductance that is given by I-V characteristic. This point corresponds to the maximum resistance of viscous layer. This point is shown on fig. 3.6

As observed earlier, the polishing effect is not equal between top and bottom part of cavity. The cause is geometrical, and one possible way to eliminate this effect is to perform EP in two steps, rotating the cavity by 180° after first step.

EP process is done usually for 1,5 hours. Due to electrochemical process, mass-transport phenomena the point of EP is usually chosen by changing its value throw several polishing and as well in time during each EP. Usually it is observed that this EP point, described earlier, is decreasing in voltage value since start of EP for ~15-20 minutes, and then stabilize on certain value for whole EP. But, since polishing is done for several cavities, the solution started to saturate and decreased EP voltage and solution conductivity. That's of course affects on current, which is strongly correlate to etching rate.

To control the quality of the internal cavity surface we are doing visual analyzing, performing internal studying with small camera to find imperfectness of the surface and determine whether the problem is due to initial mechanical treatment or to EP process. To understand the approximate amount of Cu we removed, we are weighting cavity during all procedures of treatment. Usually, new solution is removing around 3 grams of Cu for 1,5 hours of EP.

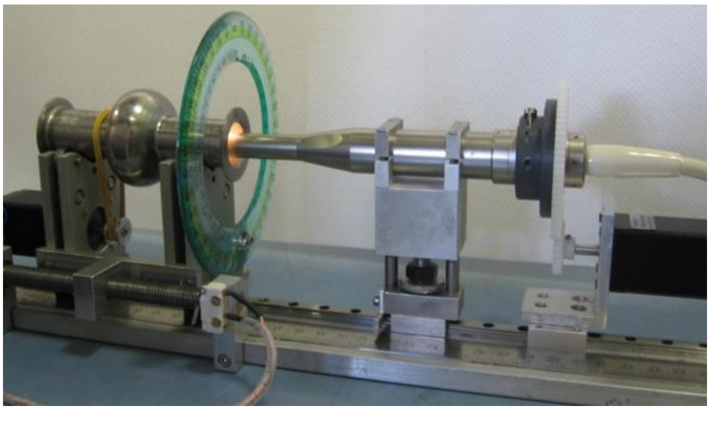


Figure 3.7 – Minicamera to study an internal surface of cavities

3.3.3 SUBU treatment and passivating

SUBU treatment was at CERN. The name comes from its main components – SUlfamic acid and BUtanol. The exact recipe and conditions is given below in table 3.2:

Each component of the bath plays sufficient role for optimal cleaning regime. Sulfamic acid H_2NSO_3H strongly reacts with copper under 70 °C with the presence of oxidizing agent (H_2O_2 hydrogen peroxide) yielding copper sulfamate $Cu(NH_2SO_3)_2$ and releasing hydrogen. Hydrogen peroxide permits the dissolution of copper.

Table 3.2 Recipe for SUBU-5 treatment

Compound	**Formula**	**Concentration**
Sulfamic acid	H_3NSO_3	5 g/l
Ammonium Citrate	$(NH_4)_2C_6H_6O_7$	1 g/l
Hydrogen peroxide	H_2O_2	50 ml/l
n-Butyl alcohol	C_4H_9OH	50 ml/l
Time	5 mins	
Temperature	70 ± 2 C°	
Mixing	Always maxim possible rpm	

At certain concentration of active oxygen, the copper oxide on the copper surface is formed, limiting the metal dissolution. The resulting shining and smooth surface is formed due to the two competing reactions of dissolution of copper and oxidation that form a passive layer. Ammonium citrate dibasic $HOC(CO_2H)(CH_2CO_2NH_4)_2$ is added to prevent obtaining brown layer, that sometimes occurs on the surface. And the last component - n-Buthanol C_4H_9OH is added to moderate, regulate and limit the strong effect of decomposition of peroxide action to the surface.

Figure 3.8 – SUBU treatment of Cu cavity

The SUBU process is performed following the steps hereby described:

1. The deionized water is heated at (72±2) [°C] in water baker under hood.
2. The components (sulfamic acid, ammonium citrate) are weighed [g].

3. The liquids of the recipe (hydrogen peroxide and butanol) are measured in [ml].
4. The copper pieces are fixed to a samples holder through copper wire.
5. The sulfamic acid solution is prepared with a concentration of [10 g/l] to perform the passivation of the copper surface after SUBU.
6. The SUBU solution is prepared once the bath temperature reaches (72±2) °C, first introducing the powders and then, the liquids.
7. The solution is stirred to mix all the elements of the recipe.
8. The copper components are placed inside of the SUBU solution for 5 minutes.

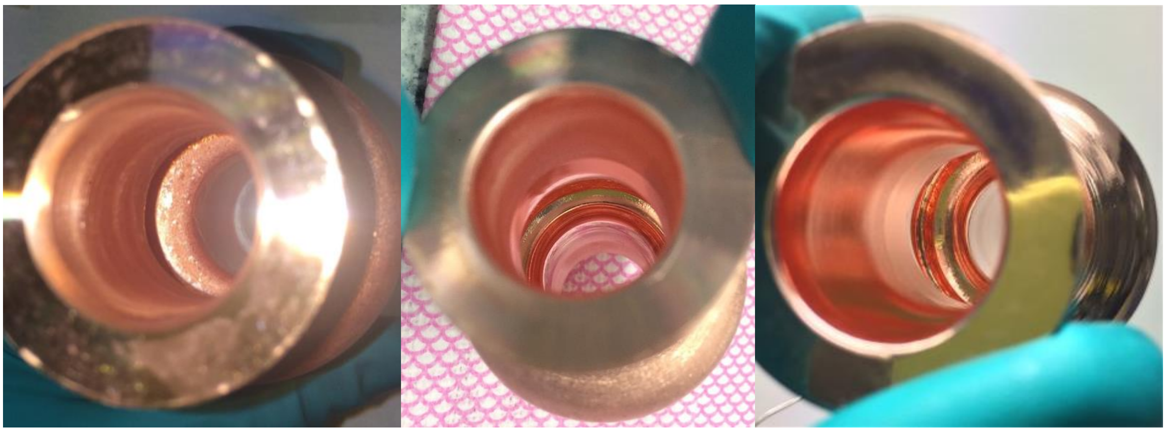


Figure 3.9 – Internal surface: a – after etching, b – after EP, c – after SUBU

3.3.4 Cleaning protocol and packaging

Almost after every operation it's required to carry out cleaning procedure, as it was explained earlier (see 2.4). During the spinning process, oil or grease are used to increase the tribological properties of the copper. The degreasing process is done with an ultrasonic cleaning process. For other stages of technological process, it is vital to remove all other contamination that could remain from aggressive medias. As well, to prevent oxidation, degradation and corrosion cleaning protocol must be followed.

Standard cleaning protocol consists of such operations:

1. Water rinsing
2. Ultrasound cleaning
3. Water rinsing
4. Alcohol drying (Ethanol)
5. Drying with high pressure nitrogen N_2.

Figure 3.10 – Final overview of the Cu

Last cleaning operation before final packaging is High Pressure Water Rinsing (HPWR) – several minutes ~ 100 bar. Then it is packed in special plastic case, after sealing top and bottom with aluminium foil to prevent dust attach on internal surface.

Figure 3.11 – Cleaning equipment: water cannon, ultrasound bath, ethanol rinsing, high pressure N_2.

3.4 Niobium SRF cavity treatment protocol

Niobium is an element of the fifth group of the fifth period of the periodic system of chemical elements. The atomic number is 41. Denoted by the symbol Nb (Latin Niobium). A simple niobium substance is a shiny silver-grey metal with a cubic, body-centered crystal lattice of the α-Fe type, a = 0.3294.

John Winthrop discovered mineral, which he has sent from Massachusetts to the British Museum in 1734. The mineral was a mixture of Tantalum and Niobium that was called columbite, and the chemical element was called Colombium (Cb) in honor of the country from which the sample was obtained - Colombia (at that time a synonym for the USA). Later, Niobium was identified as a self-element in 1801 by the English scientist Charles Hatcht [29].

For the first time pure niobium was obtained in the late XIX century by the French chemist Henri Moissan by electrothermal way: he restored the oxide of niobium with carbon in the electric furnace [30].

The metal takes on a bluish tinge when exposed to air at room temperature for extended periods. 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.

The unique properties of niobium make it a vital component in a wide 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 from 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. Niobium is also used in mobile cellphones, superconducting magnets, glass and camera lens coatings, superalloys and functional and structural ceramics. And those are not all applications of niobium.

The surface chemistry of niobium is dominated by high reactivity toward oxygen. The outermost layers are always found to be Nb_2O_5. Suboxides NbO_2, NbO and Nb_2O are also known and, in various combinations and morphologies, are proposed to be between the Nb_2O_5 and the underlying metal. While Nb_2O_5 is an insulator, NbO is a conductor ($T_c = 1.6$ K) and may seriously impair SRF performance by increasing surface resistivity, especially if the oxides have a morphology of spikes down into the bulk. Since many of the materials are prepared by aqueous chemistry and still others have been exposed to the ambient atmosphere, the hydroxide should be considered as well [1].

3.4.1 Standard protocol of Nb treatment

The protocol for Nb treatment is very similar to Cu one, in the same way require cleaning procedures before and after each step (see chapter 2.4). Listed below protocol is simplified according to this fact.

Empirically, an abrasion of at least 100–200 μm of the surface is necessary in order to obtain optimal cavity performance (see the discussion on the damaged layer below). Two main treatments exist, namely Buffered Chemical Polishing (BCP) and ElectroPolishing (EP) (see fig. 3.12). EP has supplanted BCP somewhat, at least in the hope of reaching record accelerating gradients, but is more difficult to reproduce. A huge quantity of information is available in the literature about the optimization of each process, as well as on the research of alternative ‘recipes’. In this chapter, it is described most common techniques of treatment that is applicable for Nb SRF cavities. [31].

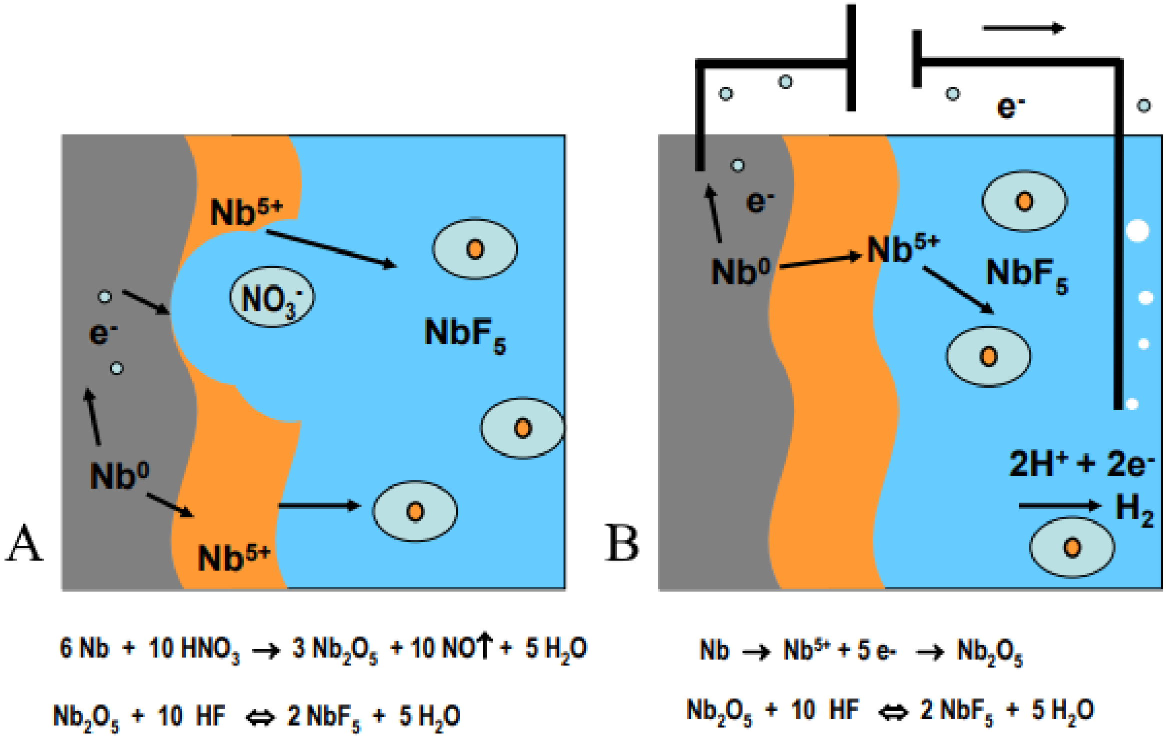


Figure 3.12 – Schematic difference between BCP (A) and EP of Nb (B)

In both cases, niobium is oxidized into Nb^{5+}. In the case of chemical polishing, oxidation occurs due to the presence of a strong oxidant NO^{3-} in the solution, while in electropolishing oxidation occurs due to the bias applied to the anode. Because of the presence of water, the stable form of Nb is Nb_2O_5; this compound is attacked by HF, and the oxides converted into NbF_5, which is soluble in the solution.

In this work have been done several treatments to the 6 GHz Nb cavities, with the idea of minimizing any type of contamination and at the same time providing maximum quality of electropolishing the surface using

1. BCP (Buffered Chemical Polishing) for 1 hour.
2. Cleaning protocol.
3. EP for 1,5 hours per one side.
4. Cleaning protocol.
5. High pressure rinsing.

3.4.2 BCP (Buffered Chemical Polishing)

Electropolishing of niobium, as for many pure metals, produces both levelling and brightening simultaneously, while chemical polishing on niobium leaves the surface bright, but provides little or no levelling. It is noted that the brightness, as measured by e.g. specular reflection, is a function of both small scale roughness, and also of large scale roughness and has been largely superseded by more quantitative techniques. The mechanisms for electro- and chemical polishing have been generally understood since decades, but have been studied in more detail for niobium only recently. For both processes, there are multiple competing reactions by which oxides of niobium are converted into a soluble niobium salt. In general, a nanometer-scale oxide is formed at the niobium surface which is, subsequently, decomposed into a soluble niobium-fluoride salt and carried away into solution. Two examples of balanced reactions which take place at the cavity surface are as follows.

$$6Nb + 10\ HNO_3 = 3\ Nb_2O5 + 10\ NO\uparrow + 5H_2O$$

$$3\ Nb_2O_5 + 18\ HF = 3\ H_2NbOF_5 + 3\ NbO_2F + 6\ H_2O$$

$$3\ NbO_2F + 12\ HF = 3\ H_2NbOF_5 + 3\ H_2O$$

Buffered chemical polishing, which is the name given to controlled niobium etching, has been studied, though in somewhat less detail than electropolishing. Empirical observations show that with commonly used mixtures and typical conditions of temperature and stirring, a layer of reaction products is also formed at the niobium surface. For both the standard phosphoric acid buffer and the alternative mixture, the etch rate is determined by a combination of diffusion and convection of the active species through the layer of reaction products. Other empirical facts are clear. For the process to be well-controlled and to produce surfaces without pitting, a ‘buffer’ acid, such as phosphoric or sulfuric acid, is required. The etch rate is greatly reduced compared to the unbuffered solution, due to the increased viscosity and a decrease in the concentration of the active species. The surface roughness due to chemical polishing on fine-grained niobium over a length scales from 0.1 μm to 100 μm is roughly an order of magnitude higher than for electropolishing.

Composition: ~2 Volumes of H_3PO_4 (buffer, very viscous).

~1 Volume of HNO_3 (oxidant, transforms NbO into Nb^{5+})

~1 Volume of HF (complexant of Nb^{5+}, dissolves the oxide layer formed by HNO_3 into NbF_5)

Advantages:

- Easy to handle, middle stirring is necessary.
- Fast etching rate.
- Very reproducible.

Disadvantages:

- This is not 'polishing', but 'etching': all crystalline defects are preferentially attacked (etching pits, etching figures).
- Grains with various orientations are not etched at the same rate, which induces roughness!

3.4.3 Electropolishing of Nb cavities

The EP process now applied to cavities was inherited from Siemens Company in the 1970's and was further developed by KEK in collaboration with Namura Plating. Typically, a mixture of hydrofluoric (49%) and sulfuric acid (95 ~98 %) at a volume ratio of 1:9 is used with a temperature range of 30 ºC ~ 40 º C, a current density of 30 ~ 100 mA/cm^2, and a total cell voltage of 10~20 volts. The surface area ratio of the Nb cavity (anode) to the high purity Al tube cathode is 10:1 during practical cavity EP processing [32].

$$2\ Nb + 5\ SO_4^{2-} + 5\ H_2O = Nb_2O_5 + 10H^+ + 5\ SO_4^{2-} + 10e$$

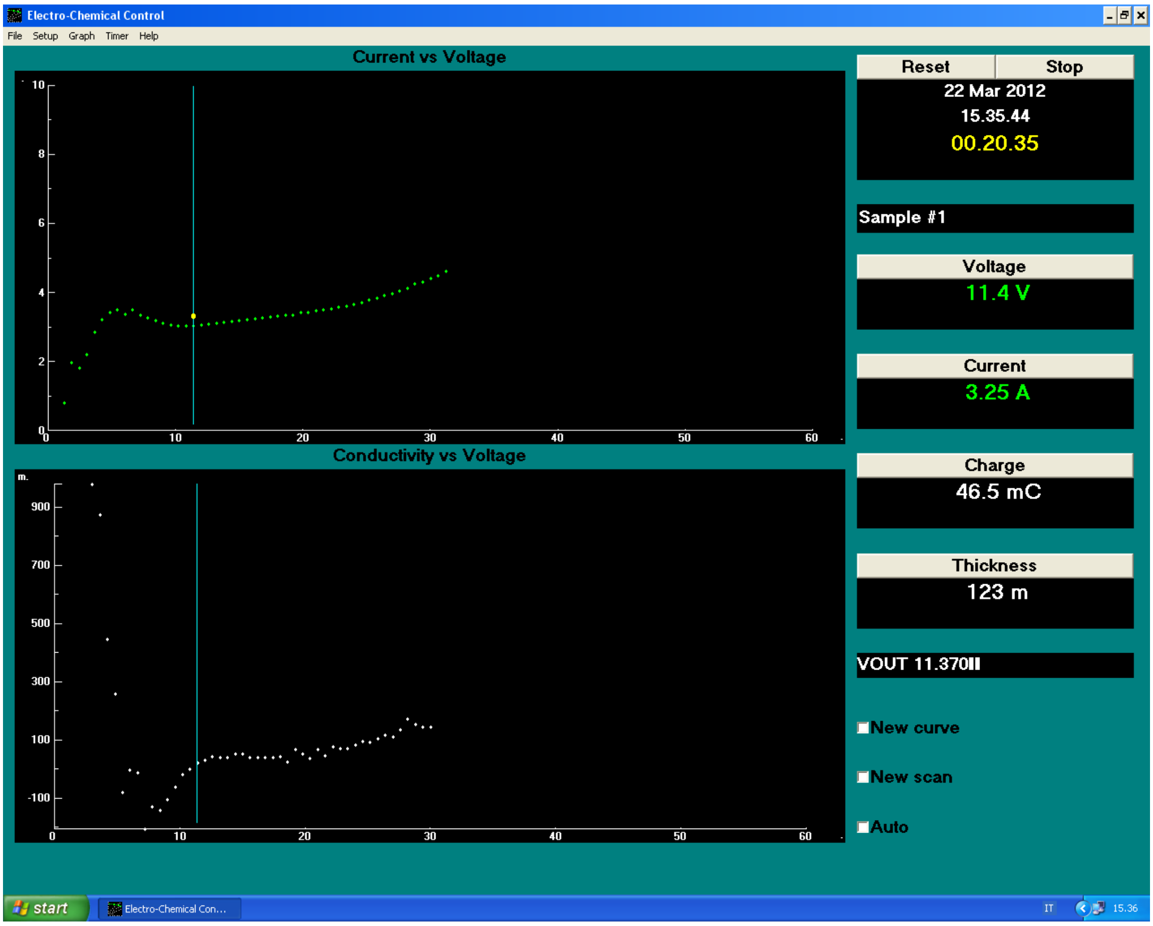
$$Nb_2O_5 + 6\ HF = H_2NbOF_5 + NbO_2F{\cdot}0{,}5HO + 1{,}5\ H_2O$$

$$NbO_2F{\cdot}0{,}5H_2O + 4\ HF = H_2NbOF_5 + 1{,}5\ H_2O$$

For electropolishing 'viscous' layer, or for purposes of electrochemical modelling Nernst diffusion layer, is required to achieve levelling. The concentration profiles for the active species, in this case niobium metal ions, fluoride ions and water, determine the rate limiting mechanism. Recently, experimental measurements indicate that the electropolishing rate for ideal or near ideal conditions is limited by diffusion of fluoride ions in the electrolyte toward the (cavity) anode surface. Empirically it is observed that the levelling effect is disrupted by vigorous agitation of the electrolyte which impedes formation of the viscous layer [33].

Table 3.3 Electropolishing parameters for bulk niobium cavities

Parameter	Value
Electrolyte composition	1 part by volume Hydrofluoric acid (48%) 9 parts by volume Sulfuric acid (96%)
Anode-to-cathode voltage	max. 18 V
Anode-to-cathode distance	max. 12 cm
Anode current density	typical 25 mA/cm2
Cathode material	Aluminum (1100, 3003)
Surface area ratio anode/cathode	max. 10
Niobium surface temperature	max. 35 °C (25 °C final polishing)
Removal rate	0.3 µm/min



22 Mar 2012
15.35.44
00.20.35

Sample #1

Voltage
11.4 V

Current
3.25 A

Charge
46.5 mC

Thickness
123 m

VOUT 11.370

☐ New curve
☐ New scan
☐ Auto

Figure 3.13 – Typical I-V and dI/dV of 6 GHz Nb cavity EP

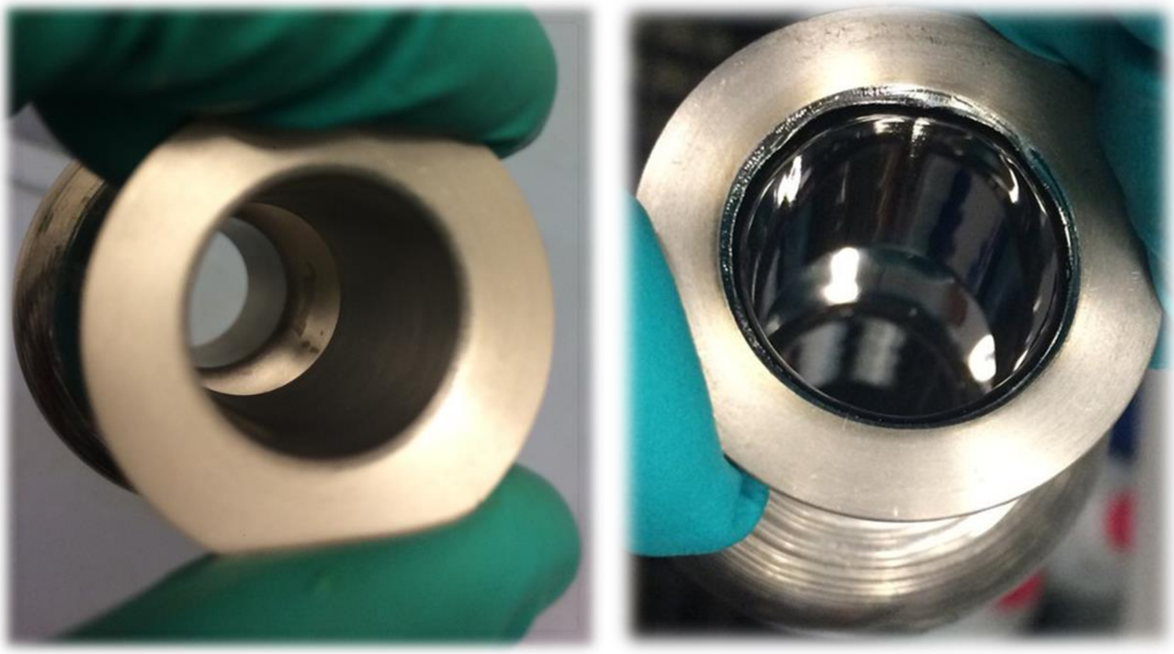


Figure 3.14 –Before and after the whole procedures of Nb treatment

3.5 Cavity treatment activity

During my master course I have proceeded several times standard treatment of both Cu and Nb cavities, that were studied by the team who performs RF measurements. As for the Cu cavities, the main purpose was to study and find possible way to resolve Q-slope problem. After treatment, Nb thin film was sputtered before the RF measurements. This work wasn't much deep scientific, but was of exceptional importance because of collected statistics, that are applicable for proving recently published theory by R.Vaglio and V.Palmieri [34] that described possible reason for Q-slope problem.

Since February 2017 13 cavities were treated both copper and Niobium. All the data collected are shown below in table 3.4, including approximately calculated removed thickness

Table 3.4 Experimental data of cavity treatment.

Material, ID, date	Process and time	Mass removed, g	Approximately removed, µm
Copper C014 05.02.2017- 10.02.2017	Persulfate	0,00	0,00
	EP 110min	6,86	186
	EP 60min	3,72	101
	SUBU 5min	1,57	11
	Total∑	12,145	297
Copper C015 05.02.2017- 10.02.2017	EP 100min	6,15	167
	EP 90min	4,07	110
	SUBU 5min	1,41	10
	Total∑	11,632	287
Copper C008 22.02.2017- 02.03.2017	Persulfate	0,00	0,00
	EP 60min	2,57	70
	EP 50min	2,35	64
	SUBU 5min	1,39	10
	Total∑	6,299	143
Copper C010 22.02.2017- 02.03.2017	Persulfate	0,00	0,00
	EP 60min	2,68	73
	EP 60min	0,00	0,00
	SUBU 5min	0,98	7
	Total∑	3,657	79
Copper C012 03.03.2017- 23.03.2017	Persulfate	0,96	7
	EP 60min	1,79	73
	EP 1000min	2,08	56
	SUBU 5min	1,41	10
	Total∑	6,242	146

Continuation of Table 3.4

Material, ID, date	Process and time	Mass removed, g	Approximately removed, µm
Copper C014b 21.03.2017- 24.03.2017	Persulfate	0,53	4
	EP 60min	2,20	73
	EP 60min	1,92	52
	SUBU 5min	1,41	10
	Total∑	6,058	138
Copper C016b 27.03.2017- 30.03.2017	Persulfate	0,54	4
	EP 60min	3,15	73
	EP 60min	1,97	53
	SUBU 5min	1,36	9
	Total∑	7,023	140
Niobium 180 16.05.2017- 19.05.2017	BCP 6min	0,00	0,00
	EP 1,5h	6,12	168,23
	EP 1,5h	0,00	0,00
	Total∑	6,12	168
Niobium 184 17.05.2017- 19.05.2017	BCP 6min	0,00	0,00
	EP 1,5h	5,50	151,11
	EP 1,5h	4,64	127,49
	Total∑	10,14	279
Niobium 174 01.06.2017- 03.06.2017	BCP 6min	0,00	0,00
	EP 1,5h	6,88	189,06
	EP 1,5h	0,00	0,00
	Total∑	6,88	189
Copper C011 21.03.2017- 24.03.2017	Persulfate	0,00	0,00
	EP 60min	0,00	0,00
	EP 60min	0,00	0,00
	SUBU 5min	1,26	9
	Total∑	1,257	9
Copper C015 10.10.2017- 15.10.2017	Persulfate	0,002	0
	EP 180min	4,838	137,79
	SUBU 5min	1,149	8,21
	Total∑	5,989	146
Copper C018 10.10.2017- 15.10.2017	Persulfate	0,004	0
	EP 90min	2,552	69,35
	EP 90min	2,342	67,08
	SUBU 5min	1,201	8,57
	Total∑	6,099	145

4 ARIES PROJECT

During my master course I faced several experimental works, which I should resolve. I describe only the main two, which are referred to ARIES project and to the preparation of Copper and Nb cavities.

The main work is connected with the ARIES project, that is already described previously in 1.1 chapter. All works are divided into 4 sub-chapters. The first is connected with chemical treatment of OFHC Copper samples.

4.1 ARIES project introduction.

On this project we explored 4 different polishing techniques for copper

a) SUBU treatment (5 samples);
b) Electrochemical polishing (8 samples);
c) Combination of SUBU + Electrochemical polishing (4 samples);
d) Tumbling (8 samples).

During all of the treatments, in order to perform more identical treatments, we have set the thickness or Copper to be removed. The treatment time is set to remove 40 µm of Copper focused to remove the same amount of average thickness of copper. The treatment has been done in more than one step.

The planar samples have been characterized by the following techniques:

- SEM – scanning electron microscopy; for characterization of the surface morphology.
- EDS (EDX) - energy-dispersive x-ray spectroscopy; for energy analysis.
- Profilometer – Veeco Dektak 8.

The profilometer characterization analysis returns two parameters

The obtained data from profilometer were described by two parameters: Ra and Rq. The Mean Roughness (Roughness Average Ra) is the arithmetic average of the absolute values of the roughness profile ordinates. Ra is one of the most effective surface roughness measures commonly adopted in general engineering practice. It gives a good general description of the height variations in the surface.

The Root Mean Square (RMS) roughness (Rq) is the root mean square average of the roughness profile ordinates.

$$Ra = \frac{1}{L}\int_{x=0}^{x=L} lyi \cdot dx; \quad Rq = \sqrt{\frac{1}{L}\int_{0}^{L} y^2(x)dx}.$$

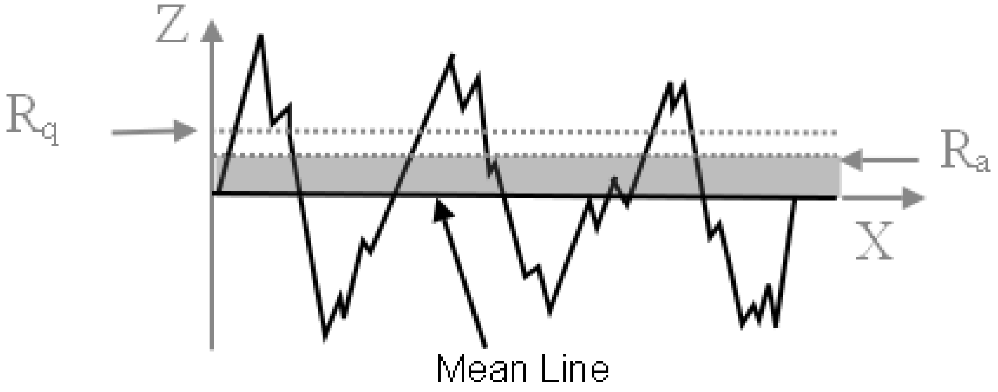


Figure 4.1 – Visualization of Ra and Rq parameters

Both test and final copper samples were square shaped with a side length of 53 mm and thickness of 1 mm. Samples also had one hole with diameter of 3 mm in front of one corner on the ~2,5 mm distances from both edges.

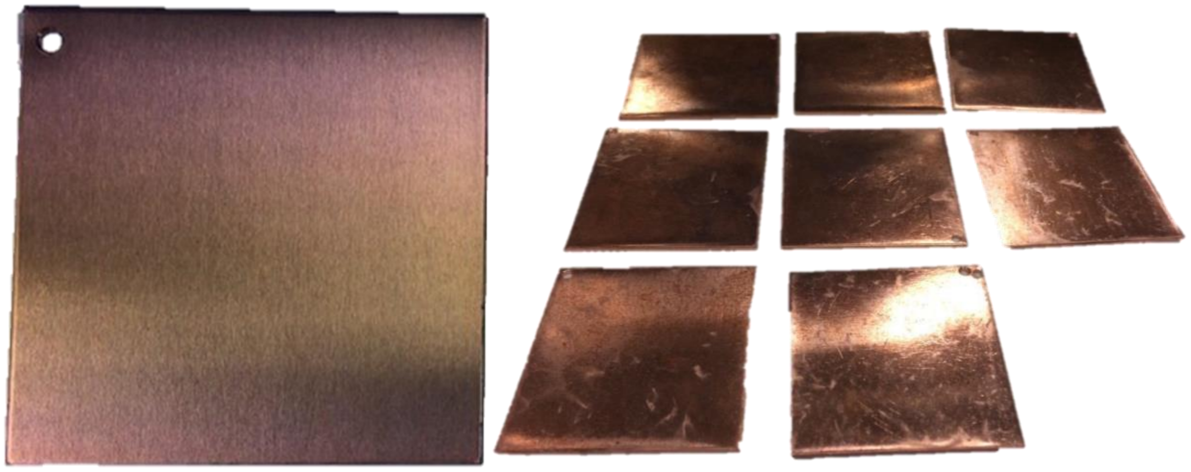


Figure 4.2 – Final and test Cu samples

Test samples were numerated. Measuring the mass Δm of the sample, we are able to calculate approximate value of thickness δ, which has been removed, due to chemical or electrochemical process.

$$\delta = \frac{10^6 \cdot \Delta m}{\rho \cdot S} = \frac{10^6 [kg]}{[kg/m^3] \cdot [m^2]} = [\mu m],$$

where ρ *is density of copper (8920 kg/*m^3*) and S – total surface of one sample, calculated as* $53^2 \cdot 2$ *mm*^{2} *and converted to m*^{2}*.*

Next step of ARIES project is to implement the polishing treatments tested on the real samples 3 different treatment batches are foreseen by the experiment:

1. Only SUBU (twice for 30 min to remove 40 µm). 5 Samples
2. Only EP (time is variable, to reach 40 µm removed layer). 8 samples
3. EP + SUBU = 5 samples

Before treatment, almost all samples were studied under SEM, profilometer, EDS. We were interested only on one side of samples. Final copper samples were prepared by lamination technology, and it presents a typical texturing, as it is possible to see on SEM analysis (see fig. 4.3 and fig. 4.4).

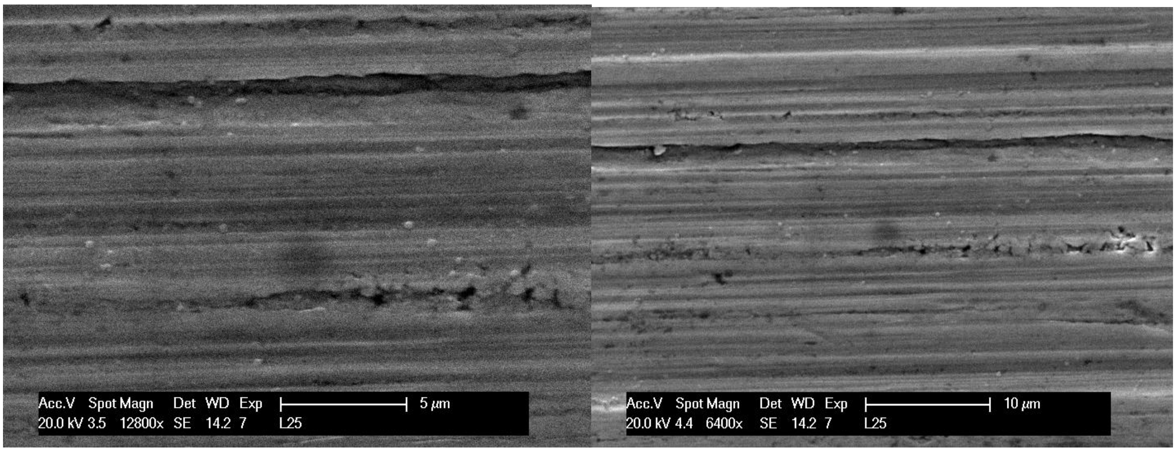


Figure 4.3 – SEM pictures of the sample L25 with magnifications: a)12800x; b)6400x

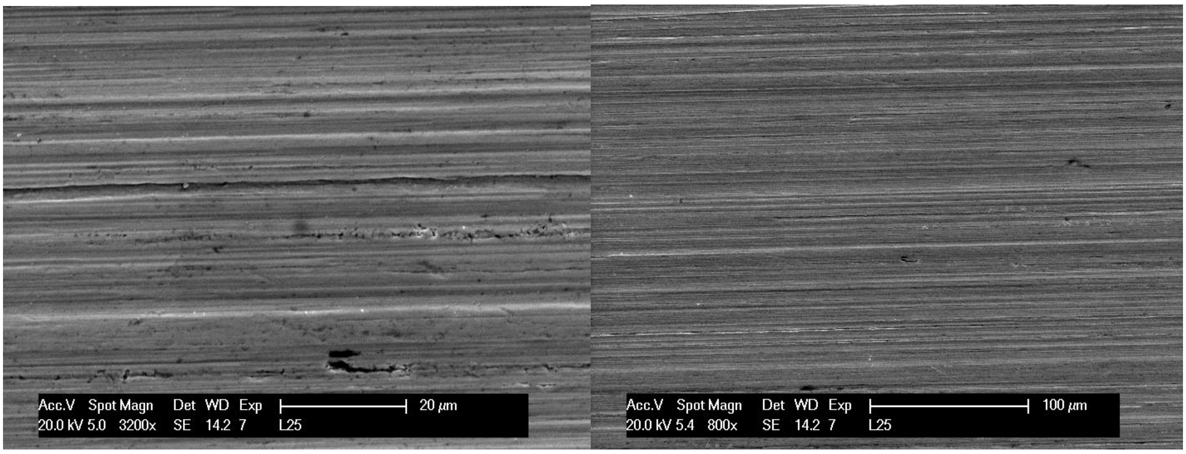
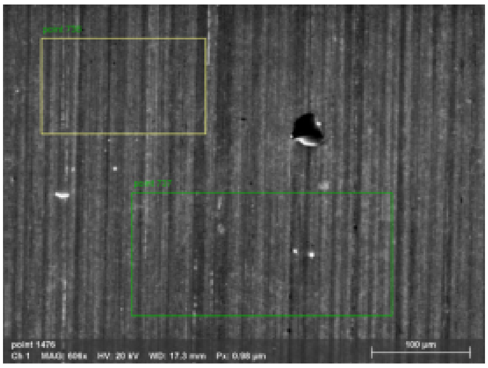
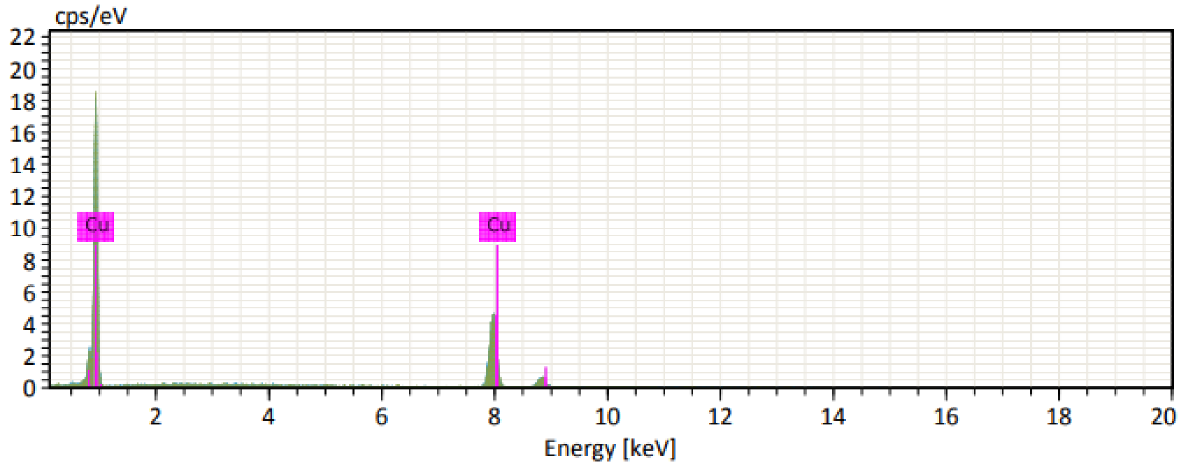


Figure 4.4 – SEM pictures of the sample L25 with magnifications: a)3200x; b)800x



Name	Date	Time	HV [kV]	Mag	WD [mm]
point 1476	9/21/2017	10:30:15 AM	20.0 keV	606x	17.3 mm



Name	Date	Time	HV [kV]	Real time [s]	Dead time [%]	Pulses [kcps]
point 737	9/21/2017	10:31:00 AM	20.0	6.000	2	4.002
point 738	9/21/2017	10:31:01 AM	20.0	5.816	2	4.020

Figure 4.5 – EDS scan of 25 sample done with 4 kcps

At the same time, samples were studied under EDS (EDX). No visible contaminations are present on the surface (see fig. 4.5). The profilometer characterization was performed in 3 parallel step scanning in the 2 directions X and Y(directions was parallel to the two perpendicular edges of the sample). Scanning carried out with stylus 2,5 µm, force – 12 mg applied for length of 6000 µm.

All data corresponding to the profilometer analysis is shown below (see table 4.1) for 7 samples in two directions.

Table 4.1 Initial data from profilometer

Sample	Direction	Ra, nm	Rq, nm	Ra, mean	Rq, mean
19	X	97,9	122,11	110,94	138,84
		106,64	134,66		
		128,29	159,74		
	Y	888,86	1055,14	1025,71	1197,59
		1114,2	1296,11		
		1074,06	1241,52		
20	X	148,08	177,91	151,09	181,73
		138,51	164,65		
		166,67	202,62		
	Y	251,64	306,59	238,82	289,84
		234,36	282,69		
		230,46	280,25		
21	X	412,52	510,61	395,19	477,33
		387,12	449,86		
		385,93	471,52		
	Y	176,01	217,08	176,28	218,3
		169,91	211,68		
		182,94	226,12		
22	X	335,33	386,46	321,61	371,43
		315,53	350,41		
		313,98	377,42		
	Y	155,13	192,37	139,4	169,82
		133,77	161,28		
		129,29	155,8		
23	X	390,6	466,26	413,24	490,34
		426,75	500,01		
		422,38	504,73		
	Y	176,12	212,14	275,91	322,15
		207,81	258,27		
		443,79	496,05		
24	X	204,01	263,86	193,38	242,79
		170,63	207,29		
		205,51	257,23		
	Y	174,73	215,25	195,24	241,46
		195,93	240,35		
		215,04	268,8		
25	X	266,93	325,22	263,26	323,61
		266,07	333,47		
		256,78	312,13		
	Y	177,4	218,72	247,23	306,43
		234,2	292,99		
		330,11	407,58		

4.2 SUBU treatment

In order to test and estimate approximately the etching rate, we did 3 SUBU bath with 5 samples each. Samples were weighted all together and 2 out of 5 separately one by one. As it was already described earlier SUBU solution were prepared with the volume of 4 liters, maintained at 70-72 °C temperature. To hold the 5 samples, were bended copper or niobium wire to build a circle and separate samples from scratching each other as it is shown on fig. 4.6

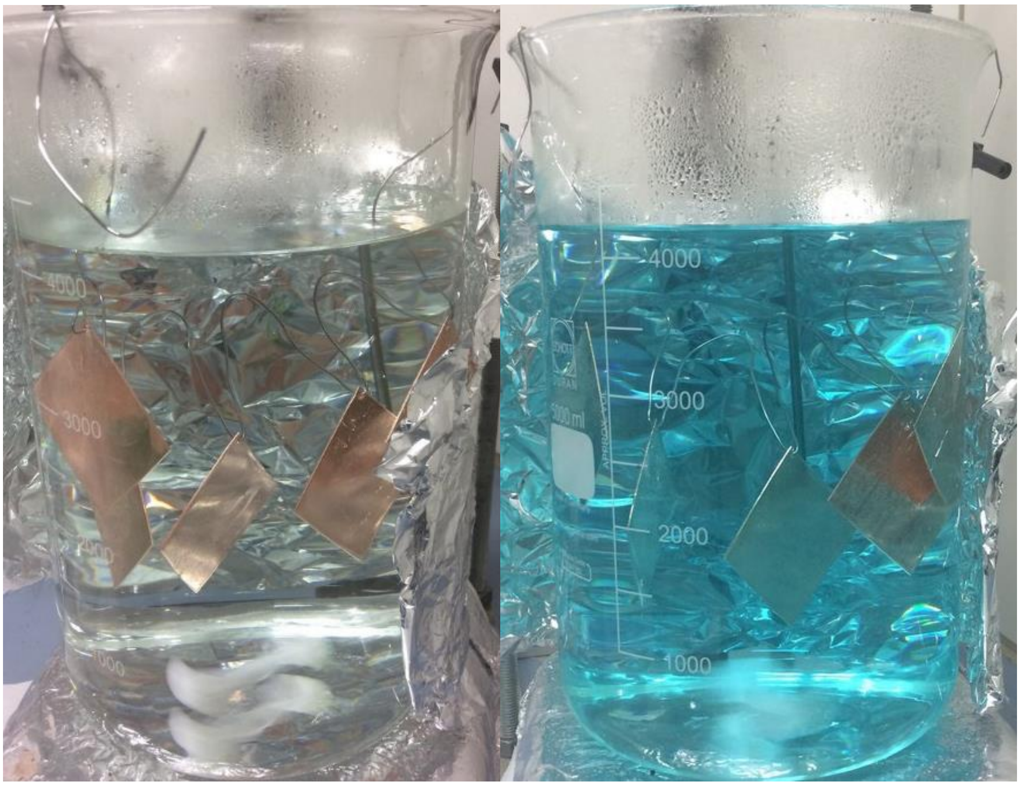


Figure 4.6 – Test copper samples fixed on Niobium wire under SUBU treatment
A – beginning of the procedure,
B – end of the procedure.

We performed three tests (see table 4.2), with different time of treatment. As a pretreatment it has been done degreased in GP 1742 solution at 40 °C for 15 minutes and deoxidizing in persulfate solution for half an hour (figure 4.7).

Analyzing obtained information, we decided for the final samples to perform not one long SUBU test to remove ~40 μm, but two baths for 30 min each. The main etching rate, of course, occurs at the beginning of the treatment, and decreases with saturating of the solution, due to decreasing concertation of main agents and etc. But, one of the main aspects, we didn't reach, is the quality of the surface (see fig. 4.8).

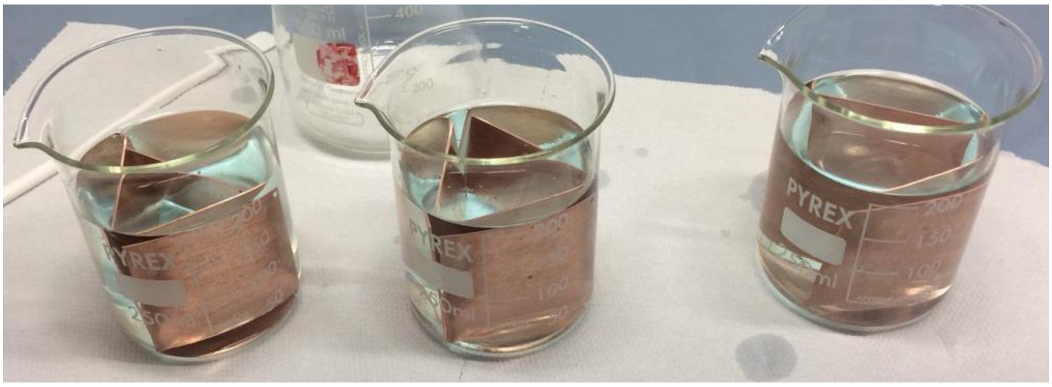


Figure 4.7 – Several samples were pretreated in $(NH_4)_2S_2O_8$ ~30 g/l solution

The surfaces were shinning and polished in some way, but big scratches, impurities and other defects remains from initial state. One of the possible explanations was the initial quality of the surface and as well purity of the copper material, that were tested. To prove this, we did the same conditions and treatment for other copper materials, such as 6 GHz cavity, other Cu parts that we usually make treatment. And as it has been shown (see fig. 4.8) the difference of the quality is easily observed by eyes.

Table 4.2 Results for test SUBU treatment

SUBU TEST	Samples	Substrate weight before(kg)	Substrate weight after (kg)	Delta weight (kg)	Average etched thickness (µm)	SUBU duration (min)
Batch 1 (29.08.2017) 5 samples	Test 5 samples	$1{,}3060\cdot10^{-1}$	$1{,}2624\cdot10^{-1}$	$8{,}712\cdot10^{-4}$	17,4	20
				Average =	17,4	µm
Batch 2 (30.08.2017) 5 samples	5 Test samples	$1{,}2623\cdot10^{-1}$	$1{,}2118\cdot10^{-1}$	$1{,}011\cdot10^{-3}$	20,2	30
	2 of previous 5 samples	$4{,}7655\cdot10^{-2}$	$4{,}5763\cdot10^{-2}$	$9{,}460\cdot10^{-4}$	18,9	30
				Average =	19,5	µm
Batch 3 (31.08.2017) 5 samples	5 Test samples	$1{,}2118\cdot10^{-1}$	$1{,}1869\cdot10^{-1}$	$4{,}984\cdot10^{-4}$	9,9	10
	2 of previous 5 samples	$4{,}5763\cdot10^{-2}$	$4{,}4830\cdot10^{-2}$	$4{,}665\cdot10^{-4}$	9,3	10
				Average =	9,6	µm

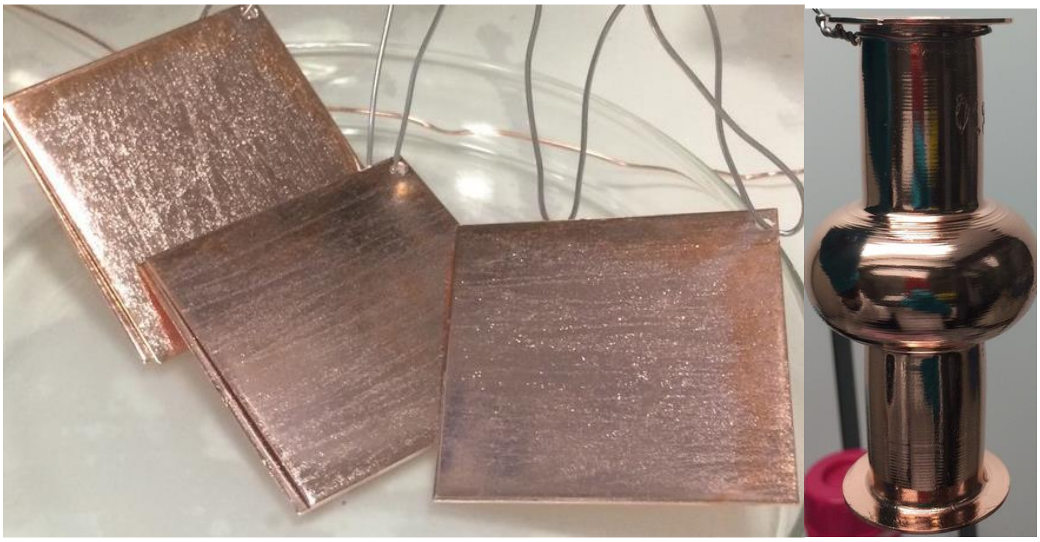


Figure 4.8 – Quality of the different Cu surfaces after SUBU treatment.

Samples that are showed on fig. 4.8 are polished, but initial quality of the cavity and samples differ so much, that effects on the final quality of the treatment. It means, that the same treatment can influence in a different way, that was what we observed in SUBU test treatment. However, samples are quite shining.

Overall, to summarize all steps we followed:

1. Degreasing in NGL1740 2 hours (first and last 3-5 min ultrasound);
2. Etching in $(NH_4)_2S_2O_8$ ~30 g/l solution for 30 minutes;
3. Activation in sulfamic acid (5 g/l) 3 min;
4. SUBU 72 °C (Sulfamic acid 5 g/l, $(NH_4)_3$Cit 1 g/l, H_2O2 -5 v.%, n-Butanol 5v.%);
5. Prerinsing in 5 g/l Sulfamic acid 1 min;
6. Rinsing with water 30 sec;
7. Alcohol cleaning;
8. High pressure N_2 cleaning.

For SUBU treatment were chosen 5 samples: L1, L2, L3, L19, L20. Last two samples will stay at laboratory as spare samples. The procedure of SUBU treatment is exactly the same, as of the test one. The only one difference, is that spare samples after treatment comes for studying the surface, and other samples immediately comes to be packaged inside plastic box, and vacuumed.

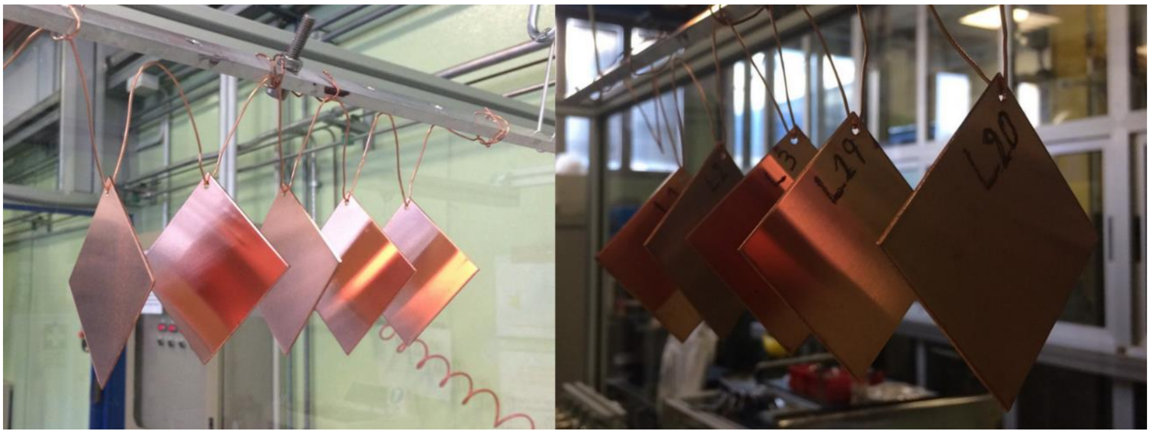


Figure 4.9 – Fixing samples for degreasing in ultrasound bath

To minimize any contaminations, Nb wire were changed to Cu (fig. 4.9). After first 30 minutes in SUBU bath, samples were prerinsed in 5 g/l sulfamic acid to passivate surface. The samples have been weighted and then treated in a new SUBU batch. All data presented in table 4.3.

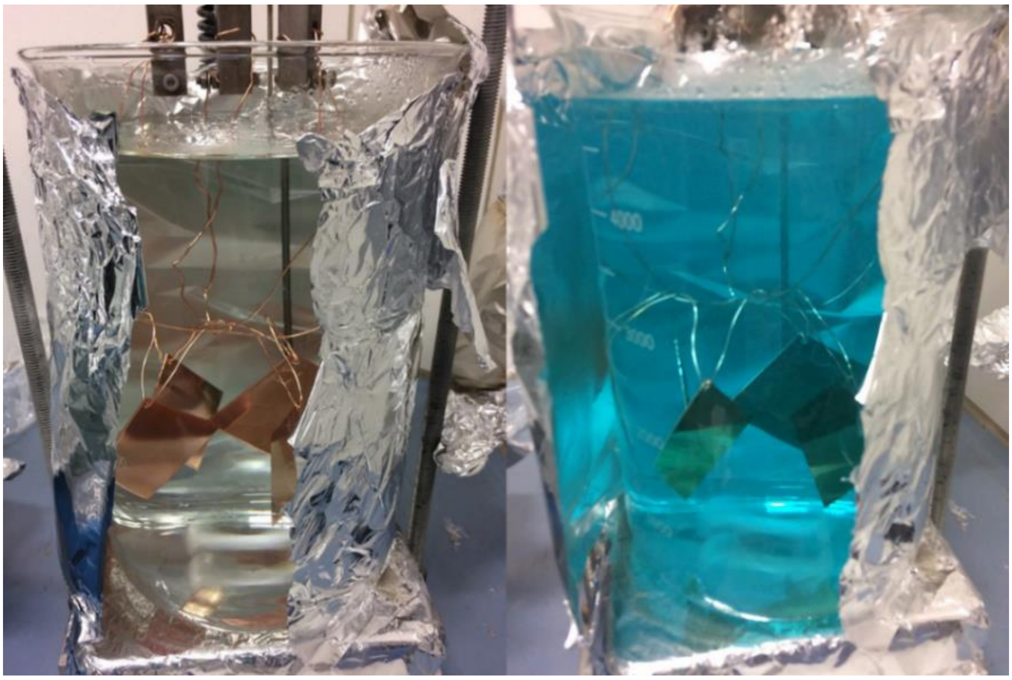


Figure 4.10 – SUBU treatment with ARIES samples

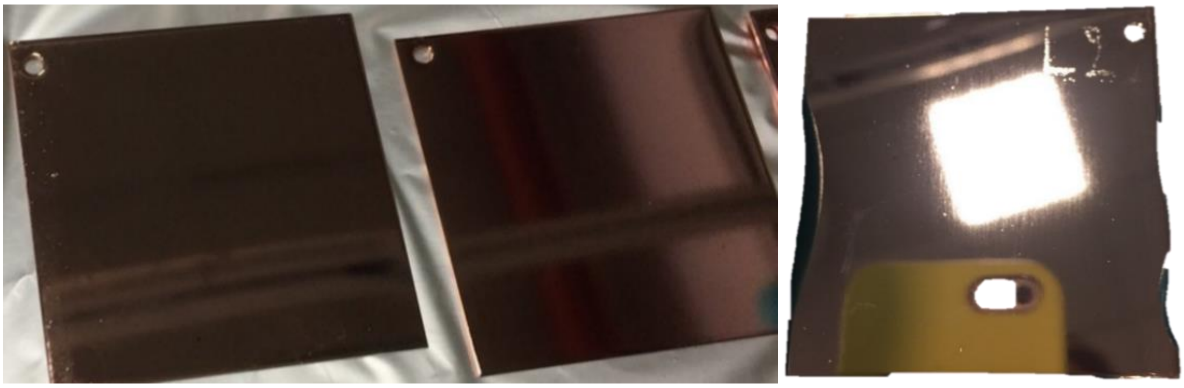


Figure 4.11 – Photo of samples, after SUBU treatment

As showed above on figure 4.10, surface after SUBU treatment became uniform, without initial texturing.

Characterization of SUBU treatment was carried out only on spare samples, that will remain at INFN-LNL. Also, we substituted L02 sample with L19, because L02 had a scratch on its surface. The roughness measurements were carried out, as well surface and spectrum analys. SEM pictures are listed below, profilometer data are shown in table 4.4, and spectrum is listed below on figure 4.13.

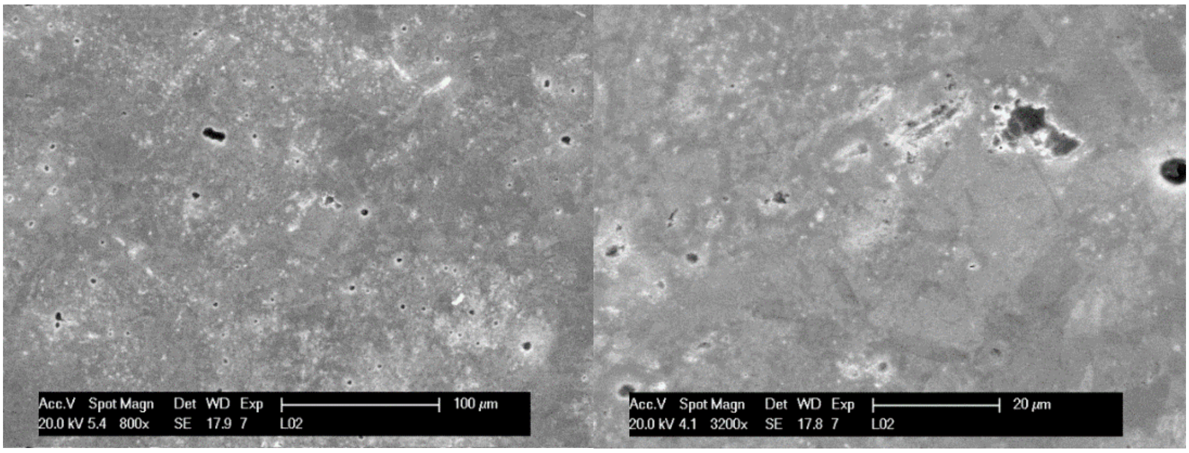


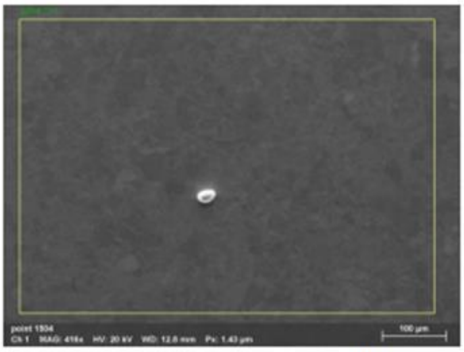
Figure 4.12 –SEM pictures of the sample L20 after SUBU treatment with magnifications: a)12800x; b)6400x

Table 4.3 Weighting data for SUBU treatment

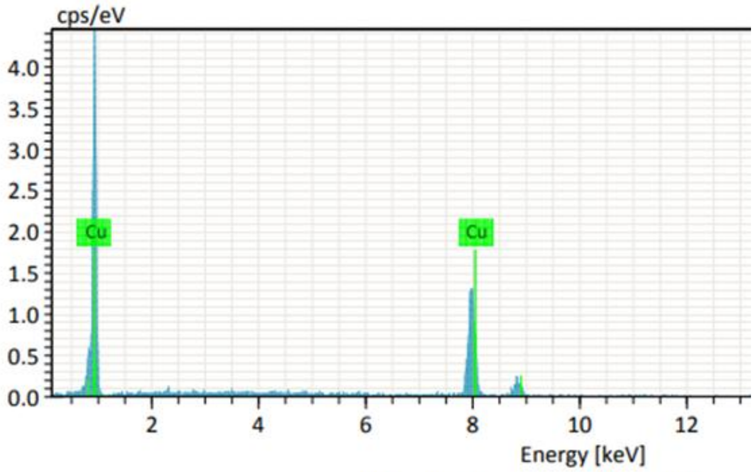
SUBU ARIES	Sample #	Substrate weight before(kg)	Substrate weight after (kg)	delta weight (kg)	Average etched thickness (µm)	SUBU duration (min)
Batch 1 (22.09.2017)	L01	$2,513\cdot10^{-2}$	$2,4178\cdot10^{-2}$	$9,540\cdot10^{-4}$	19,0	30
	L02	$2,501\cdot10^{-2}$	$2,4099\cdot10^{-2}$	$9,140\cdot10^{-4}$	18,2	30
	L03	$2,506\cdot10^{-2}$	$2,4099\cdot10^{-2}$	$9,660\cdot10^{-4}$	19,3	30
	L19	$2,498\cdot10^{-2}$	$2,4003\cdot10^{-2}$	$9,810\cdot10^{-4}$	19,6	30
	L20	$2,517\cdot10^{-2}$	$2,4200\cdot10^{-2}$	$9,740\cdot10^{-4}$	19,4	30
				Average =	**19,1**	**um**
SUBU ARIES	Sample #	Substrate weight before(kg)	Substrate weight after (kg)	delta weight (kg)	Average etched thick (µm)	SUBU duration (min)
Batch 2 22.09.2017	L01	$2,4179\cdot10^{-2}$	$2,3186\cdot10^{-2}$	$9,920\cdot10^{-4}$	19,8	35
	L02	$2,4099\cdot10^{-2}$	$2,3079\cdot10^{-2}$	$1,020\cdot10^{-3}$	20,4	35
	L03	$2,4099\cdot10^{-2}$	$2,3082\cdot10^{-2}$	$1,017\cdot10^{-3}$	20,3	35
	L19	$2,4003\cdot10^{-2}$	$2,3059\cdot10^{-2}$	$9,440\cdot10^{-4}$	18,8	35
	L20	$2,4200\cdot10^{-2}$	$2,3117\cdot10^{-2}$	$1,083\cdot10^{-3}$	21,6	35
				Average =	**20,3**	**um**

Table 4.4 Profilometer data, collected after SUBU treatment.

Sample №	Direction	Ra, nm	Rq, nm	Ra, mean	Rq, mean
L02	X	103	127,23	101,67	129,15
		102,67	128,48		
		99,32	131,73		
	Y	101,26	130,75	100,85	129,89
		111,92	145,56		
		89,37	113,37		
L20	X	160,83	188,75	145,68	173,59
		143,06	171,59		
		133,15	160,42		
	Y	105,86	149,72	90,82	116,19
		94,83	118,19		
		71,78	90,65		



Name	Date	Time	HV [kV]	Mag	WD [mm]
point 1504	10/2/2017	5:46:20 PM	20.0 keV	416x	12.8 mm



Name	Date	Time	HV [kV]	Real time [s]	Dead time [%]	Pulses [kcps]
point 771	10/2/2017	5:47:58 PM	20.0	6.744	1	1.046

Figure 4.13 – EDS spectrum of L20 sample after SUBU treatment

4.2 Electropolishing test

According to the plan of ARIES project, It should be treated 8 samples with EP in the same bath. To implement this task it was built the EP system consisting of PVC batch, designed holders for samples and cathode (see figure 4.14).

The procedure was identically to the one used for SUBU treatment, with only one obvious exception: SUBU procedure was substituted by EP process. For the first test, it was used old solution, that probably was contaminated by Fe^{2+} ions (see color on fig. 4.15). The solution has a lower etching rate, which forced us to prepare a new solution, and also to pre-work it for several hours in order to eliminate any type of mistakes

Figure 4.14 – Two bathes for EP and cleaning procedure, holders for samples, and holed copper cathode.

As we observed later, new solution showed us quite big values of EP points (we choose as minimum conductivity point from dI/dV graph). Big values could be dangerous, for future electropolished surface due to intensive bubble formation, especially in the case of non-agitated media. After first batch of EP, we obtained quite close surface quality as in SUBU test.

It was decided to pre-treat mechanically two test samples, to understand if initial roughness is so important in this step. One sample (T2) was polished with several abrasive papers starting with 200 µm and finishing with 30 µm. Second sample (T3) was polished under rotating wheel in local mechanical workshop. Other samples remained in the same state as before.

We tried to minimize any mistakes, by adjustments the position of samples and cathode to have the same distance from one row to another, and also the distance between each other and to cathode.

But, samples T5, T6 and T8 showed 3 an abnormal erosion rate. Other data is quite correlated.

Table 4.5 Experimental data of EP on test samples.

EP TEST	Sample №	Substrate weight before(kg)	Substrate weight after (kg)	delta weight (kg)	Average etched thickness (µm)	EP duration (min)
Batch 1 (13.09. 2017)	T1	$2,4771\cdot10^{-2}$	$2,2750\cdot10^{-2}$	$2,021\cdot10^{-3}$	40,3	90
	T2	$2,5029\cdot10^{-2}$	$2,2899\cdot10^{-2}$	$2,130\cdot10^{-3}$	42,5	90
	T3	$2,5067\cdot10^{-2}$	$2,3105\cdot10^{-2}$	$1,962\cdot10^{-3}$	39,2	90
	T4	$2,4799\cdot10^{-2}$	$2,3495\cdot10^{-2}$	$1,304\cdot10^{-3}$	26,0	90
	T5	$2,4835\cdot10^{-2}$	$2,0831\cdot10^{-2}$	$4,004\cdot10^{-3}$	79,9	90
	T6	$2,5064\cdot10^{-2}$	$2,1800\cdot10^{-2}$	$3,264\cdot10^{-3}$	65,1	90
	T7	$2,4698\cdot10^{-2}$	$2,1517\cdot10^{-2}$	$3,181\cdot10^{-3}$	63,5	90
	T8	$2,4808\cdot10^{-2}$	$2,2926\cdot10^{-2}$	$1,882\cdot10^{-3}$	37,6	90
	∑T1-8	$1,9907\cdot10^{-1}$	$1,7936\cdot10^{-1}$	$2,464\cdot10^{-3}$	49,2	90
				Average =	49,2	µm
Batch 2 (18.09. 2017)	T1	$2,4701\cdot10^{-2}$	$2,4127\cdot10^{-2}$	$5,740\cdot10^{-4}$	11,5	60
	T2	$2,4990\cdot10^{-2}$	$2,4247\cdot10^{-2}$	$7,430\cdot10^{-4}$	14,8	60
	T3	$2,4269\cdot10^{-2}$	$2,3508\cdot10^{-2}$	$7,610\cdot10^{-4}$	15,2	60
	T4	$2,4943\cdot10^{-2}$	$2,4314\cdot10^{-2}$	$6,290\cdot10^{-4}$	12,6	60
	T5	$2,4756\cdot10^{-2}$	$2,4120\cdot10^{-2}$	$6,360\cdot10^{-4}$	12,7	60
	T6	$2,5050\cdot10^{-2}$	$2,3909\cdot10^{-2}$	$1,141\cdot10^{-4}$	22,8	60
	T7	$2,4942\cdot10^{-2}$	$2,4302\cdot10^{-2}$	$6,400\cdot10^{-4}$	12,8	60
	T8	$2,2362\cdot10^{-2}$	$2,1326\cdot10^{-2}$	$1,036\cdot10^{-4}$	20,7	60
	∑T1-8	$1,9600\cdot10^{-1}$	$1,8985\cdot10^{-1}$	$7,693\cdot10^{-4}$	15,4	60
				Average =	15,4	µm
Batch 3 (19.09. 2017)	T1	$2,4127\cdot10^{-2}$	$2,3865\cdot10^{-2}$	$2,620\cdot10^{-4}$	5,2	30
	T2	$2,4247\cdot10^{-2}$	$2,3937\cdot10^{-2}$	$3,100\cdot10^{-4}$	6,2	30
	T3	$2,3508\cdot10^{-2}$	$2,3198\cdot10^{-2}$	$3,100\cdot10^{-4}$	6,2	30
	T4	$2,4314\cdot10^{-2}$	$2,4015\cdot10^{-2}$	$2,990\cdot10^{-4}$	6,0	30
	T5	$2,4120\cdot10^{-2}$	$2,3814\cdot10^{-2}$	$3,060\cdot10^{-4}$	6,1	30
	T6	$2,3909\cdot10^{-2}$	$2,3498\cdot10^{-2}$	$4,110\cdot10^{-4}$	8,2	30
	T7	$2,4302\cdot10^{-2}$	$2,3986\cdot10^{-2}$	$3,160\cdot10^{-4}$	6,3	30
	T8	$2,1326\cdot10^{-2}$	$2,0947\cdot10^{-2}$	$3,790\cdot10^{-4}$	7,6	30
	∑T1-8	$1,8985\cdot10^{-1}$	$1,8726\cdot10^{-1}$	$3,237\cdot10^{-4}$	6,5	30
				Average =	6,5	µm

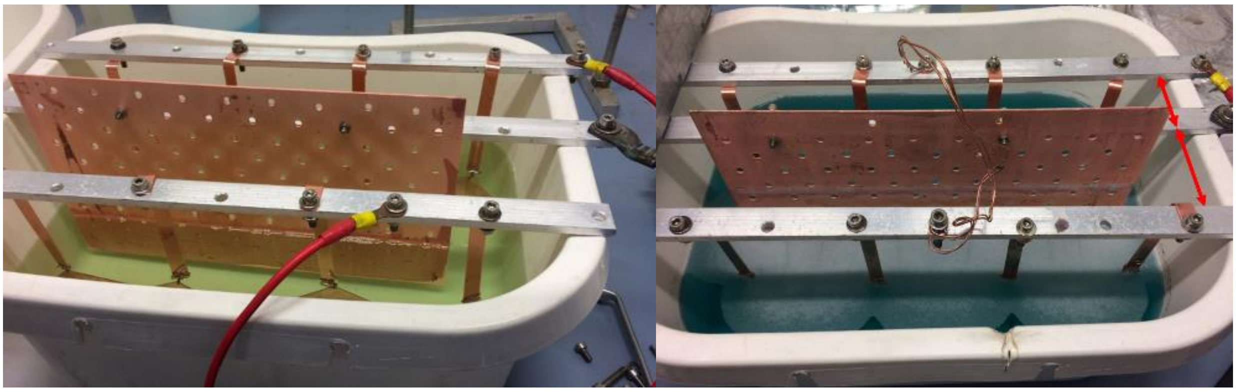


Figure 4.15 – Positioning of the samples and main view of the bath

As for the solution, nominal content was always the same: H_3PO_4:n-Butanol = 3:2 in volume, as described earlier. Temperature – room conditions, no agitation.

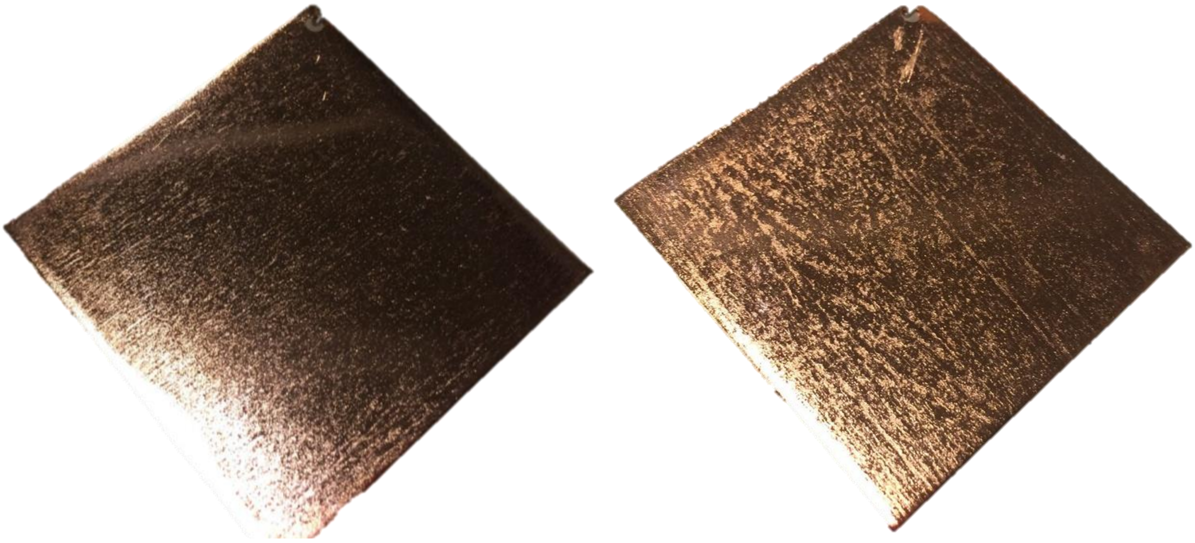


Figure 4.16 – Typical quality of the surface obtained with on samples

In general, quality of the surface after EP is similar to SUBU treatment. As it was already explained earlier, this could be due to bad initial quality of the surface and copper substrate. Even more, holders that partially were immersed inside the solution were EP as well, and the quality was better than the samples (see fig. 4.17)

Figure 4.17 – Holders after EP process

As described earlier, solution was prepared with the same composition and pre-worked for 3 hours with waste samples. After 3 hours of EP, the point of the minimum conductivity decreased from 5 V to 3,5 V. The less it is, the less will be production of Oxygen on anode (samples) and better result should be expected, as well, like in plating, slow removing rate is more preferable in terms of quality of the surface.

For the final EP stage, L10, L11, L12, L13, L14, L15, L21, L22 samples were chosen, from which the last two are spare samples. Procedure for EP was exactly the same, as it was described in test part earlier. To reach 40 µm, it was done ~5 hours of EP. During EP, it should be controlled the quality of the surfaces and also taken into account the average thickness that is removing. That’s why it was performed a stop, while all samples were rinsed with water, passivated with sulfamic acid. During these stops, spare samples were weighted. All data connected with mass change measurements is shown below in table 4.6. SEM pictures of the surface and roughness data from profilometer are shown in figure 4.18, 4.19 and table 4.7 respectively.

Table 4.6 Experimental and calculation data after EP treatment

EP ARIES	Sample #	Substrate weight before(kg)	Substrate weight after (kg)	delta weight (kg)	Average etched thick (µm)	EP duration (min)
Batch 1 (26.09.2017)	L21	$2{,}5031\cdot10^{-2}$	$2{,}4594\cdot10^{-2}$	$4{,}370\cdot10^{-4}$	8,7	60
	L22	$2{,}5074\cdot10^{-2}$	$2{,}4594\cdot10^{-2}$	$4{,}800\cdot10^{-4}$	9,6	60
				Average =	9,1	µm
Batch 2 (27.09.2017)	L21	$2{,}4594\cdot10^{-2}$	$2{,}3918\cdot10^{-2}$	$6{,}760\cdot10^{-4}$	13,5	65
	L22	$2{,}4594\cdot10^{-2}$	$2{,}3905\cdot10^{-2}$	$6{,}890\cdot10^{-4}$	13,7	65
				Average = Total=	13,6 22,8	µm µm
Batch 3 (02.10.2017)	L21	$2{,}3918\cdot10^{-2}$	$2{,}3418\cdot10^{-2}$	$5{,}000\cdot10^{-4}$	10,0	93
	L22	$2{,}3905\cdot10^{-2}$	$2{,}3477\cdot10^{-2}$	$4{,}280\cdot10^{-4}$	8,5	93
				Average = Total=	9,3 32,0	µm µm
Batch 4 (02.10.2017)	L21	$2{,}3418\cdot10^{-2}$	$2{,}2960\cdot10^{-2}$	$4{,}580\cdot10^{-4}$	9,1	93
	L22	$2{,}3477\cdot10^{-2}$	$2{,}3120\cdot10^{-2}$	$3{,}570\cdot10^{-4}$	7,1	93
				Average = **Total=**	8,1 **40,2**	µm **µm**

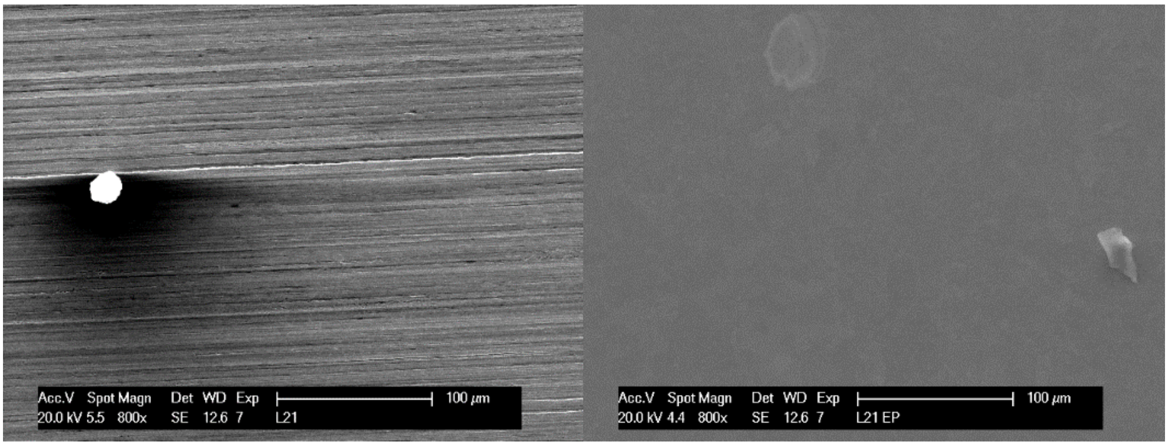


Figure 4.18 – Surface before and after EP of L21 sample, under 800x magnification

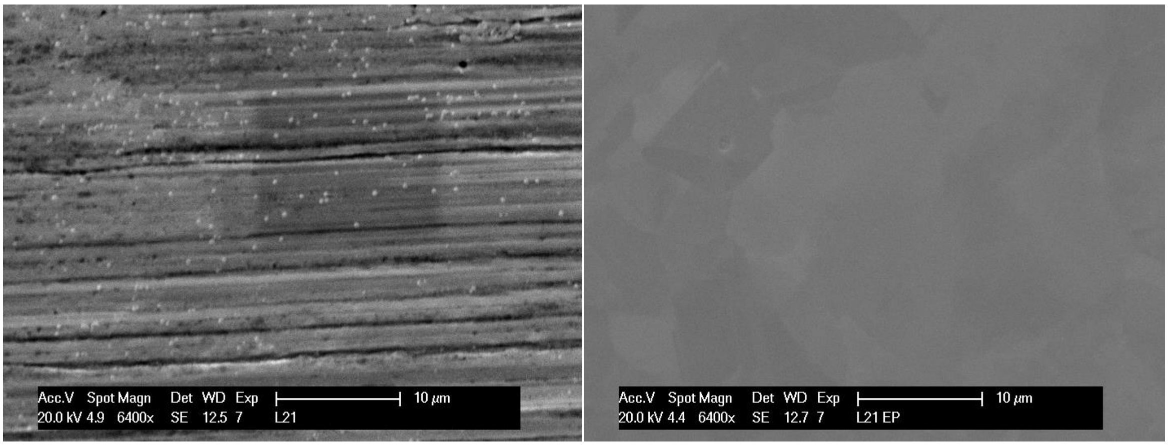


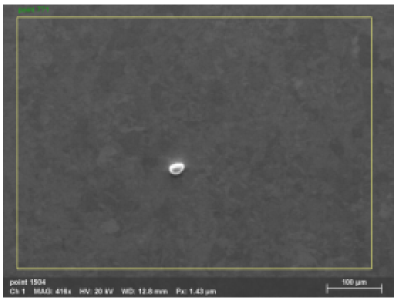
Figure 4.19 – Surface before and after EP of L21 sample, under 6400x magnification

Table 4.7 Roughness data after EP treatment

Sample	Direction	Ra, nm	Rq, nm	Ra, mean	Rq, mean
L21	X	600,13	781,46	540,07	671,38
		520,47	623,15		
		499,62	609,54		
	Y	520,99	657	513,89	645,82
		573,01	700,82		
		447,68	579,63		
	Z	418,23	540,83	320,09	399,01
		303,01	362,42		
		239,22	296,54		
L22	X	409,24	491,6	532,01	637,39
		440,85	548,74		
		745,95	871,83		
	Y	436,57	558,97	436,98	543,77
		371,72	469,02		
		502,63	603,33		
	Z	275,53	322,63	235,39	283,74
		232,48	275,83		
		198,57	252,04		

It should be said that all samples have a strong texturing on their surfaces clearly seen by eyes and it’s still unclear why they couldn’t be observed under SEM with minimum magnification. Probably, due to high smoothness of the surface, it becomes more difficult to observe, but at that time focusing on small objects (contaminations, pits or etc.) was still possible. In this experiment, it was considered about ways to mix the solution, to avoid bubble evolution effect. Therefore, by roughness measurements, in X and Y directions it was decreased statistics values. However, if it is taken into account Z direction, that is parallel to the texturing, it could be remained at the same level of initial roughness.

As before, spectrum measurements didn't show visible contaminations (see fig. 4.20).



Name	Date	Time	HV [kV]	Mag	WD [mm]
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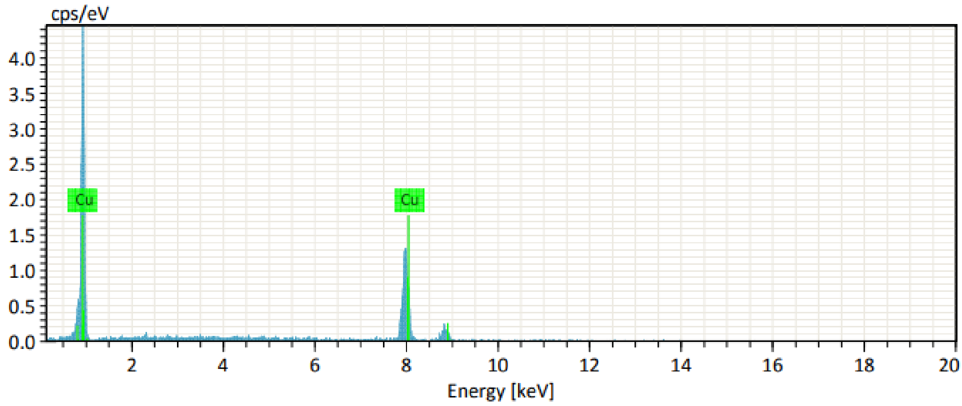


Name	Date	Time	HV [kV]	Real time [s]	Dead time [%]	Pulses [kcps]
point 771	10/2/2017	5:47:58 PM	20.0	6.744	1	1.046

Figure 4.20 – EDS spectrum after EP treatment

4.4 EP + SUBU treatment

For this treatment, L16, L17, L18, L23 samples were chosen. All stages of procedure are described below in table 4.8.

Observation: samples after EP treatment had texturing, however after SUBU treatment – texturing decreased. Shining effects after EP was clearly observed and after SUBU some samples had small defects in the part of connections. Small pitting and oxidation appeared due to transporting effects from SUBU bath to water bath. Solution of SUBU was stuck on surface, and slowly going down. To eliminate this imperfectness, we did for each sample additional 3 minutes of SUBU treatment over the standard 5 minutes procedure. We were unable to cancel all defects, however visually they were decreased.

Table 4.8 Full procedure list of EP+SUBU stage

№	Stage	Options	Time
1	Degreasing in GP 1742.	40 °C, 3 minutes at the beginning and ending at ultrasound.	1,5 h.
2	Cleaning	Rinsing with water, after ethanol cleaning and drying with N_2.	3 min
3	Weighting		1 min
4	EP	3:2 H_3PO_4:n-Butanol.	5,5 h.
5	Cleaning	Rinsing with water and fast passivation in 5 g/l Sulfamic acid, ultrasound, ethanol rinsing and N_2 drying.	10 min
6	Weighting		1 min
7	SUBU treatment	H_3NSO_3 – 5g/l; $(NH_4)_3$Cit – 1g/l; H_2O_2 – 50ml/l; n-Butanol – 50 ml/l. Total volume 4 litres.	8 min
8	Passivation	H_3NSO_3 – 10 g/l.	3 min
9	Cleaning	Rinsing with water, ultrasound cleaning, after ethanol rinsing and drying with N_2.	10 min
10	Weighting		1 min
11	Packaging	Samples were packed into plastic box, vacuumed under N_2 media.	2 min each.

All data collected are shown below: mass removal data – table 4.9, roughness measurements – table 4.10, SEM pictures of the surface fig. 4.21, EDS spectrum – fig. 4.22.

Observations: despite the fact it was used SUBU treatment, after EP texturing remains. Under SEM pictures pitting are clearly observed from SUBU treatment. Spectrum showed zero contaminations on the surface. Roughness on L17 sample is at least twice smaller comparing to L23. That probably adds big mistake inside statistic.

Table 4.9 Mass removal data, after EP+SUBU treatment

EP + SUBU	Sample #	Substrate weight before(kg)	Substrate weight after (kg)	delta weight (kg)	Average etched thick (μm)	Duration (min)
EP (04.10.2017)	L18	$2{,}50580\cdot10^{-2}$	$2{,}31910\cdot10^{-2}$	$1{,}867\cdot10^{-3}$	37,3	330
	L23	$2{,}50710\cdot10^{-2}$	$2{,}32510\cdot10^{-2}$	$1{,}820\cdot10^{-3}$	36,3	330
				Average=	36,8	μm
SUBU (04.10.2017)	L18	$2{,}31910\cdot10^{-2}$	-	-	-	8
	L23	$2{,}32510\cdot10^{-2}$	$2{,}28160\cdot10^{-2}$	$4{,}350\cdot10^{-4}$	8,7	8
				Average =	8,7	μm
				Total =	45,5	μm

Table 4.10 Roughness measurements data after EP+SUBU

Sample	Direction	Ra, nm	Rq, nm	Ra, mean	Rq, mean
17	X	188,2	249,67	229,84	292,79
		245,64	308,03		
		255,69	320,67		
	Y	244,98	288,81	221,43	266,99
		174,56	224,77		
		244,76	287,39		
23	X	389,61	491,08	476,8	572,66
		499,41	588,44		
		541,38	638,45		
	Y	423,11	533,49	480,52	629,08
		427,11	589,67		
		591,35	764,07		

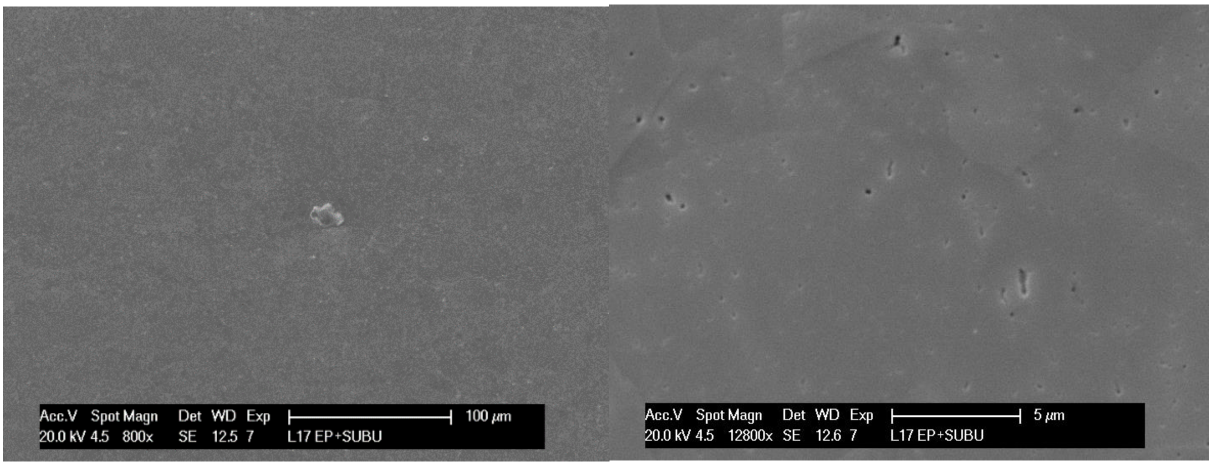
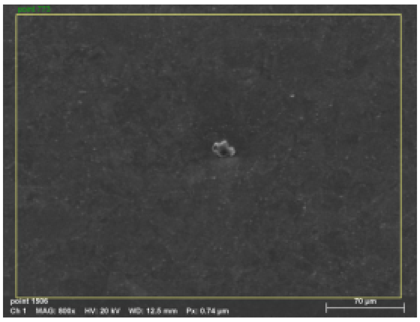


Figure 4.21 – SEM pictures of the L17 sample surface under 800x and 12800x magnification.

Discussion on results:

Synchronized and mixed test of ARIES project is a great way to optimize process, understand problems of contaminations and find weaker stages of procedure. As for EDS techniques, spectrum measurements didn't show any visible contaminations on any stage of the project. All data were collected with a good count rate per second, more than 1 thousand. This happened primary because of quality of Cu materials and anti-contamination rules.

Coming to roughness measurements, we obtained a good statistic for Ra and Rq parameters. However, it is supposed that data collected for initial roughness of L19 sample on Y direction seem to be affected by the fact that measurements were carried out very close to the hole, and in this region there is surely a local bending, due to formation of the hole, and so, overall differences in height is higher, and parameters Ra and Rq are also higher. Summarized statistic information is shown below in table 4.11 with average values and average error. Unfortunately, EP process without agitation decreased roughness parameters. However, SUBU treatment provides good results, which eliminate negative effect of EP in EP+SUBU treatment.



Name	Date	Time	HV [kV]	Mag	WD [mm]
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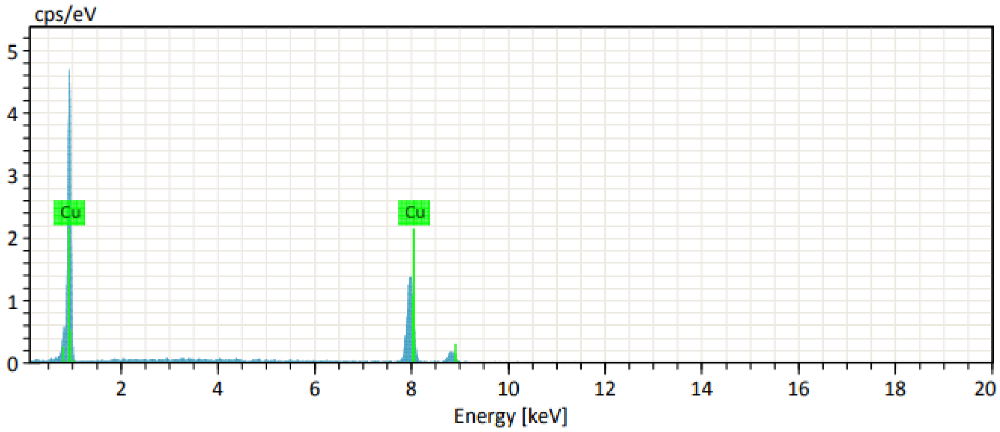

Name	Date	Time	HV [kV]	Real time [s]	Dead time [%]	Pulses [kcps]
point 773	10/5/2017	11:06:11 AM	20.0	16.599	0	1.048

Figure 4.22 – Spectrum of the L17 sample surface after EP+SUBU treatment

SEM scanning of the surface showed some aspects. The first, initial surface had texturing, probably due to lamination process. Second – EP process without agitation showed texturing, that should be absolutely avoided. SUBU process, however, decreased or absolutely removed (in case of initial process) texturing.

Table 4.11 Summarized data of roughness values

Process	Ra, nm	Ra error, nm	Rq, nm	Rq error, nm
Initial	240,12	±99,49	290,31	±115,11
SUBU	109,75	±18,32	138,04	±20,98
EP	429,77	±110,02	530,30	±138,00
EP+SUBU	352,15	±126,51	440,38	±160,49

4.4 Tumbling procedure

It is typically used for the mechanical removal of substrate residues (particularly burrs) resulting from processes like forging or casting. It is particularly suitable for giving a surface finish to a large number of small parts. It is carried out by placing the parts inside a tumbler together with a suitable abrasive material.

That process should be optimized for 8 samples. To feet with current tumbling machine dimensions (see fig. 4.23) and box (see fig. 4.24) we designed a new holder for samples.

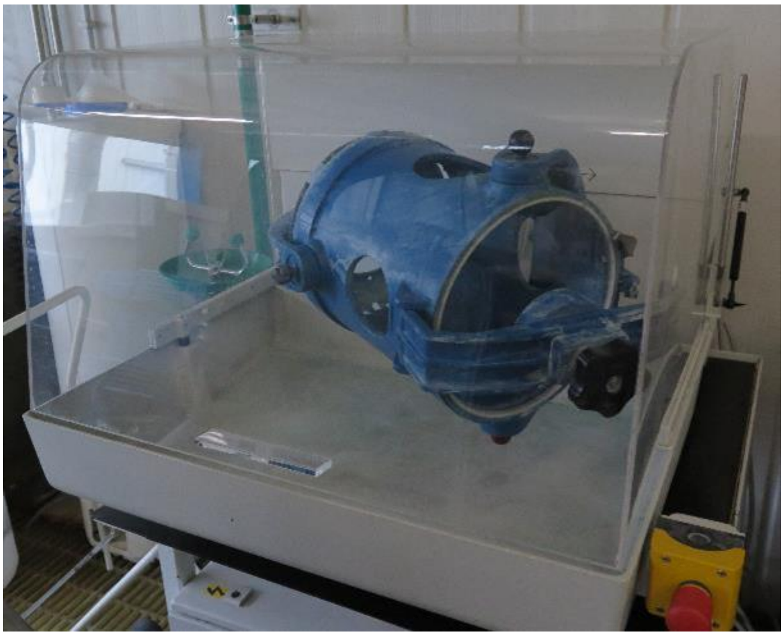

Figure 4.23 – Tumbling machine at LNL-INFN

Tumbling will be performed in aqueous media with abrasive material. The holder must fix the samples, and cover one side of the sample. The material of the holder was PVC, where abrasive media, water and soap Rodasteel were mixed to feel ~60% of volume. (see fig. 4.24).

Figure 4.24 – Tumbling box

It was carried out first try with test samples, for more than 16 hours. Etching rate was amounted to be ~1 µm/24 h (see table 4.12). But, unfortunately, test samples were bended. In future works other samples will be tested and probably some modification should be applied to the tumbling holder.

Table 4.12 Tumbling procedure data

Tumbling	Sample #	Substrate weight before(kg)	Substrate weight after (kg)	delta weight (kg)	Time	983 min	16,38 hours	0,685 days
Test samples					Etched (µm)	A_{sample} (m^2)	Rate (µm/h)	Rate (µm/day)
05-06.12.2017	1	0,019378	0,019364	$1,4\cdot10^{-5}$	0,5922	0,00265	0,036	0,868
	2	0,018338	0,018323	$1,5\cdot10^{-5}$	0,6340	0,00265	0,039	0,929
	3	0,01916	0,019143	$1,7\cdot10^{-5}$	0,7623	0,0025	0,047	1,117
	4	0,021935	0,021916	$1,9\cdot10^{-5}$	0,8037	0,00265	0,049	1,178
	5	0,019998	0,019983	$1,5\cdot10^{-5}$	0,7006	0,0024	0,043	1,027
	6	0,02012	0,020103	$1,7\cdot10^{-5}$	0,7785	0,00245	0,048	1,141
	7	0,018271	0,018257	$1,4\cdot10^{-5}$	0,6539	0,0024	0,040	0,958
	8	0,019456	0,01944	$1,6\cdot10^{-5}$	0,7321	0,00245	0,045	1,073
						Average	0,043	1,036

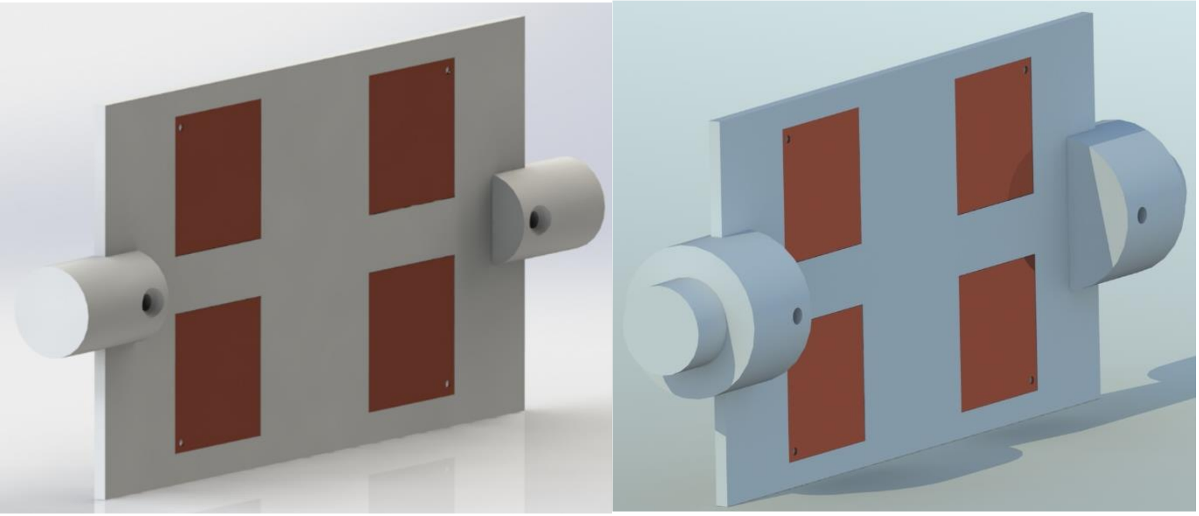

Figure 4.25 – Rendered photo of the holder version 1 and 2

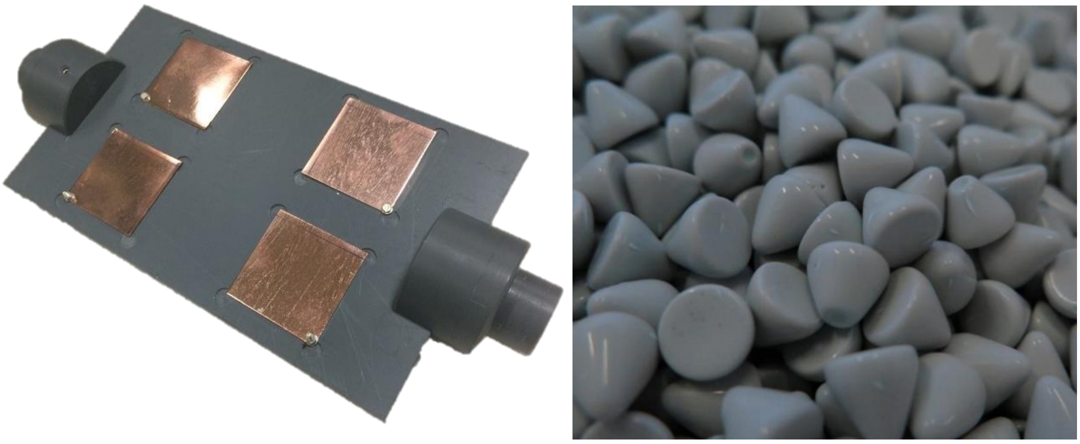

Figure 4.26 – Machined holder and abrasive material for finishing the surface

CONCLUSIONS

1. It was prepared 13 6 GHz cavities according to the standard LNL protocol.
2. It was studied chemical treatment of Cu samples in the framework of an international collaboration.
3. An optimization of 4 different treatments: SUBU, EP, EP + SUBU and tumbling were carried out. In accordance to it, 17 samples were treated.
4. EP without agitation cannot increase roughness parameters, in other hand, opposite to SUBU treatment, that can slightly improve the situation.

In the future works, tumbling treatment will be proceeded to the last 8 samples of ARIES project.

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