Summary

ABSTRACT

Copper is probably the metal that the human race knows from more time, and in recent years its use is growing exponentially[1]. It is employed in every industry, from architecture to sculpture, from electronics to medicine, from food to musical instruments, and so on. The ultra-pure Copper then, for its characteristics of thermal and electrical conductivity, and corrosion resistance (all three exceeded only by Gold and Silver), is critical in special and advanced applications such as particle physics, the superconducting accelerators and all the components involved in high value-added applications.

For the latter components, the surface finish is not only an aesthetic whim, but a necessary request.

Roughness plays an important role in determining how a real object will interact with its environment. Rough surfaces usually wear more quickly and have higher friction coefficients than smooth surfaces. Roughness is often a good predictor of the performance of a mechanical component, since irregularities in the surface may form nucleation sites for cracks or corrosion. Although a high roughness value is often undesirable, it can be difficult and expensive to control in manufacturing. Decreasing the roughness of a surface will usually increase its manufacturing costs.

This project work focuses on the ultra high cleaning protocol of Copper components for particle physics, superconducting cavities and technology transfer of this knowledge to anodes for X-ray tubes.

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[1] http://www.icsg.org/index.php/component/jdownloads/finish/170/2202

INTRODUCTION

During my period of Master thesis, I worked on three main projects:

A. THE **ULTRA HIGH CLEANING PROTOCOL** OF COPPER FOR NEUTRINOS DETECTION

B. THE **DEVELOPMENT OF A NEW SPINDLE FOR** THE REALIZATION OF 6 GHZ COPPER **SEAMLESS CAVITIES**, AND THEIR SURFACE TREATMENTS FOR NIOBIUM SPUTTERING

C. THE STUDY OF A **SIMPLE CHEMICAL BATH** FOR POLISHING OF ANODES FOR X-RAY TUBES OF C.E.I COMPANY, IN ORDER TO **REPLACE** A BATH OF ELECTROPOLISHING A BASIS OF **CHROMIC ACID**

A. In the field of fundamental interactions neutrino physics has become progressively more important in recent years, after the discovery of their mass. In particular, its "ultimate nature" is of considerable importance in view of the fundamental interactions of the particles that make up the entire universe. The only way to discover this unique property is to look for the so-called double beta decay without neutrino emission. To do this the CUPID experiment, following the road opened by the experiment CUORE, wants to combine the proposed bolometric technique, with the simultaneous detection of the light emitted by the detector. The bolometric technique allows a good energy resolution (key to this type of research) while the – simultaneously – measuring light emitted provides an important tool for fund reduction induced by natural radioactivity. The CUPID scientific Goal is not just to look for the double beta decay, but to lay the foundations for a – high – third generation experiment that takes full advantage of the innovative potential introduced in CUPID.

For greater sensitivity of the detector it is necessary to differentiate from the ^{82}Se decays and the decays from the materials that make up the detector. To satisfy the requirement of very low radioactive background of the detector it is necessary to decrease the levels of radioactive contamination of the copper components which hold the Zinc Selenide crystals and surround the detector. Radioactive contamination can be present in natural origin, i.e. in metallurgical phase copper ingot, or provided during the machining process of the components that make up the detector. The isotope ^{238}U, ^{232}Th and their products of decay chains are primarily responsible for radioactive contamination.

B. Advantages of SRF cavities for accelerators are well known but the fabrication of these cavities using the traditional way will cost much time and is expensive. The spinning technology for seamless cavities invented in INFN-LNL is an answer for this challenge. Inter alia, 6 GHz spun seamless Superconducting Radio Frequency (SRF) cavities are a very useful tool for testing alternative surface treatments. However, the spinning technique has also some drawbacks like contamination, surface damage in internal part due to the collapsible mandrel line.

To solve these problems has been realized a new spindle made of ONION'S. As drawback, this new mold can not be removed from the cavity immediately after the turning and reused to create another one, but must be suitably dissolved and recovered.

C. Cyanides and Chromic Acid (i.e. Chromium VI) based bath are historically the most utilized in the field of Copper electrochemistry. Unfortunately, both are extremely toxic (the cyanides are lethal and chromium VI is a carcinogen) and involve considerable costs, not only for the purchase, but also for safety in process and waste disposal. There is the real possibility that in a short time will be banned from the European community.

Hence the need to develop alternative bath, safer, cheaper, and easier to handle.

1. ABOUT COPPER

1.1 GENERAL

Occurs as a native element, usually of secondary origin and found in many localities but seldom in commercial quantities. It is found in beds and veins associated with copper compounds, such as malachite, green copper ore, and azurite, blue copper ore, both being hydrated carbonates of copper. The iron pyrites containing copper and sulphur, and the mineral cuprite, Cu_2O, all occur in copper veins. The symbol, Cu, is from the Latin cuprum, which comes from the Greek cyprium (Cyprian bronze) as, in ancient times, the island of Cyprus was noted for its copper mines. It is thought that copper was the first metal employed by man, after gold, as both occur in fair quantity in the free state of southern Europe and the Mediterranean area. The two sulphides chalcopyrite, $CuFeS_2$, and chalcocite, Cu_2S represent about 75% of the copper ore mined in the world.

It is a soft, malleable and ductile metal with very high thermal and electrical conductivity. It is used as a conductor of heat and electricity, as a building material and as a constituent of various metal alloys, such as sterling silver used in jewellery, cupronickel used to make marine hardware and coins and constantan used in strain gauges and thermocouples for temperature measurement.

Copper is found as a pure metal in nature, and this was the first source of the metal to be used by humans, c. 8000 B.C. Bronze, Cu:Sn, was the first metal alloy used by man, leading him out of the Stone Age into the Bronze Age about 5000 B.C. Brass, Cu:Zn, is not as brittle as bronze, and artefacts are said to have been discovered in Egyptian tombs, circa 4000 B.C. but, with the discovery of tin in Great Britain - the Tin Isles of ancient Rome - bronze was the major metal alloy until the discovery of iron smelting by the Hittites of Asia Minor around 1350 B.C.

Today there are a large number of alloy mixtures of both bronze and brass. About one third of the copper mined in the world is used for electrical wiring as an alloy to improve hardness. It is fabricated as rods, tubing, sheet, and as bulk material for a wide number of products. As sheeting, it is used in building construction, such as a roof covering or as rain gutters which, with time and exposure to the atmosphere, can turn green - Verdigris - a copper sulphate. It also is available as high purity copper (OFHC copper) used in electronics and Solid State processing. Copper is easily electroplated, and many products are so plated.

1.2 TECHNICAL APPLICATION

In Solid State processing copper is used as an n-type dopant in some compound semiconductors. As a thin film metallization along with other metals, such as gold, used in device construction as a contact pad on semiconductor devices as well as for circuits on substrate dielectrics. Thin film can be deposited by standard vacuum evaporation, E-beam evaporation, RF sputter from a solid target or by electrolytic plating. The latter method is used in plating PC boards (PCBs) and some of the metal parts used in test and package assembly. Solid copper parts, as copper alloys or OFHC copper, to include wire or strap contacts, or copper pins are used for both their electrical and heat dissipation characteristics. As a clad material, such as copper nickel cold-welds or resistance weld packages, the copper is the seal metal. Single crystal copper has been grown, as have several copper alloys, all studies for their general physical characteristics, and trinary and quaternary compound semiconductors containing copper are under study: $CuIn_xGa_{1-x}Se_2$; Cu_2ZnSnS_2; and $CuInTe_2$, as examples.

1.3 COPPER OFHC

Oxygen-free copper (OFC) or Oxygen-free high thermal conductivity (OFHC) copper is a group of wrought high conductivity copper alloys that have been electrolytically refined to reduce the level of oxygen to .001% or below.

Oxygen-free high thermal conductivity (OFHC) copper is widely used in cryogenics. OFHC is produced by the direct conversion of selected refined cathodes and castings under carefully controlled conditions to prevent contamination of the pure oxygen-free metal during processing. The method of producing OFHC copper ensures extra high grade of metal with a copper content of 99.99%. With so small a content of extraneous elements, the inherent properties of elemental copper are brought forth to a high degree. These characteristics are high ductility, high electrical and thermal conductivity, high impact strength, good creep resistance, ease of welding, and low relative volatility under high vacuum.

2. STATE OF ART

Many materials or components or products after fabrication are not suitable for consumer use. The surfaces are too rough, not corrosion or wear resistant enough, not aesthetically pleasing in appearance, have too high coefficient of friction, have poor absorptivity or emissivity, and so on. To achieve these desirables properties some form of surface modification or coating is required. These are known as “surface finishing” steps.

Because the topic area is so broad, it is necessary to have some sort of classification scheme.

	MECHANICAL	**CHEMICAL**	**ELECTROCHEMICAL**
MECHANICAL	Blasting Brushing Buffing Burnishing Deburring Grinding Honing Lapping Mass finishing Polishing Scanding Tumbling	Ultrasonic Cleaning Vibratory Finishing Chemical Mechanical Planarization Deburring	Deburring Grinding Honing Shaping Electrolytic lapping
CHEMICAL		Cleaning Conversion Degreasing Descaling Dipping Etching Milling Pickling Polishing	
ELECTROCHEMICAL			Activation Cleaning Deburring Descaling Etching Pickling Polishing

TABLE 2.1 – CLASSIFICATION OF SURFACE FINISHING

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 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.

Generally, mechanical methods are used to remove burrs, flash, contour (radius) sharp corners or control dimensions. Mechanical methods also are used to provide a desired surface finish (polish) or texture before subsequent finishing steps. Chemical methods are most often used to remove soil, but they can also brighten a surface, or activate a surface prior to electroplating so that an adherent coating is obtained. Electrochemical methods provide a combination of cleaning and metal removal actions, and are useful for certain metals that are difficult to finish by conventional means.

Cover all possible techniques is out of the purpose of this paper. Here are presented only the ones used in our work.

2.1. DIFFERENCE BETWEEN CLEANING, ETCHING AND POLISHING

Depending on the final aspect of the surface of our sample we can make a distinction between:

- Cleaning
- Polishing
- Etching

2.1.1 Cleaning

Cleanliness is an important requirement for successful sample preparation. It does not affect the surface finishing but is crucial for the following treatments.

For example, all remnant grinding and polishing compounds have to be removed completely from the sample after each step to avoid cross contamination, which would be reduce the efficiency of the next preparation step.

After chemical reactions, clean the sample is necessary to neutralize traces of chemicals that could hurt the final user or interfere with the next step of the surface treatment.

This is done by rinsing the sample under running water and by additional wiping or by ultrasonic cleaning; other methods can be used in specific cases.

Ultrasonic cleaning is the most effective cleaning technique. Ultrasonic cleaning uses cavitation bubbles induced by high frequency pressure waves (usually from 20 to 400 kHz) to agitate a liquid. The agitation produces high forces on contaminants adhering to substrates like metals, plastics, glass, and ceramics. This action also penetrates blind holes, cracks, and recesses. The intention is to thoroughly remove all traces of contamination tightly adhering or embedded onto solid surfaces. Water or solvents can be used, depending on the type of contamination and the work piece. Contaminants can include dust, dirt, oil, pigments, rust, grease, lime scale, polishing compounds, flux agents, fingerprints, soot wax, and so on. Ultrasonic cleaning can be used for a wide range of work piece shapes, sizes and materials, and may not require the part to be disassembled prior to cleaning[2].

The object to be cleaned is placed in a chamber containing a suitable solution (in an aqueous or organic solvent, depending on the application). In aqueous cleaners, surfactants are often added to permit dissolution of nonpolar compounds such as oils and greases.

2.1.2 Polishing

Polishing refers to the process of creating a **smooth and shiny surface** by rubbing it or using a chemical action, leaving a surface with a significant specular reflection. In some materials (such as metals, glasses, black or transparent stones) polishing is also able to reduce diffuse reflection to minimal values. When an unpolished surface is magnified thousands of times, it usually looks like mountains and valleys. By repeated abrasion, those "mountains" are worn down until they are flat or just small "hills." The final result is a mirror-like surface.

2.1.2.1 Mechanical Polishing

These surface preparation techniques involve the use of abrasives and cutting tools to remove unwanted metal, such as burrs and flash.

Some hand finishing is done on parts with complex geometry, or which are delicate and require special handling. Most parts are mechanically finished on automatic machines, either individually while being held in a fixture, or in bulk, where they are free to move in the finishing media. The latter is known as tumbling.

Most mechanical methods use rotating or oscillating equipment driven by electric motors. Mechanical methods can be divided also into precision and no precision methods. In the former category fall polishing and buffing; while grinding, lapping and broaching, which are done with machine tools, fall into the latter category.

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[2] Robert H. Todd, Dell K. Allen, and Leo Alting; *Manufacturing Processes Reference Guide*

Grinding precedes polishing, which in turn precedes buffing. Each technique is less aggressive than the former and removes less metal.

SUMMARY OF FEATURES OF MECHANICAL FINISHING TECHNIQUES FOR SURFACE PREPARATION

Technique	Application	Cutting Action	Type of Abrasive	Type of Finish
A. Individual Parts				
Grinding	Excess metal removal	Abrasive bonded to rigid wheel or belt	Coarse alumina, silica, silicon carbide and zirconia-alumina particles	Rough with grinding marks depending on coarseness of abrasive
Brushing	Deburring, rust and scale removed, inorganic soil, paint removal	Impact of wires mounted on a wheel with or without loose abrasive	Metal (wire) brushes, plain, crimped or knotted, emery paste	Rough, only burrs, flash, soil knocked off
Blasting	Cleaning, rust scale removal, paint dry soil, carbon removal, straightening	Stream of abrasive particles in air or slurred in a liquid	Minerals such as alumina, sand, flint, garnet, also silicon carbide, glass and metal shot	Rough, uniform texture suitable for painting or subsequent finishing
Polishing	Surface smoothing, simple shapes, satin finishing	Abrasive bonded to flexible wheel or belt	Medium alumina, silicon carbide, emery particles	Smooth or textured
Sanding	Cutlery and tableware finishing	Abrasive dropped onto soft wheel	Sand, lightly oiled	Smooth, fine texture or bright
Honing	Finishing surfaces to close tolerances, especially inside cylindrical surface, gear teeth, valves	Abrasive bonded to a rotating rigid tool	Medium to fine alumina, silicon carbide, diamond particles	Smooth, fine cross hatched abrasive marks
Lapping	Finish surfaces to close tolerances, removing small surface imperfections	Low speed movement of abrasive particles against lap or mating surface	Fine silicon carbide, alumina, boron carbide particles	Smooth, flat surfaces
Buffing	Improve appearance, complex shapes	Abrasive held in flexible wheel	Fine alumina, silica, silicon carbide, emery particles	Bright, lustrous, very smooth or special textures
Burnishing	Improve tolerances	None: tool provides smoothing action by mechanical force	None used	Smooth, cold-worked
B. Mass Finishing				
Berrel	Scale removal, deburring, edge and corner rounding, shaping (some metal removal	Impact (sliding, tumbling action) of parts mixed with abrasive medium	Pumice, alumina, sand, shot, corn cobs, wood, etc. in wet media	Smooth, bright or special textures suitable for painting or plating
Vibratory	Edge and corner removal, finishing to close tolerances (little metal removal)	Impact (sliding action) of parts mixed with abrasive medium	Pumice, alumina, sand, shot, corn cobs, wood, etc. in wet media	Smooth, bright suitable for painting or plating

TABLE 2.2 - SUMMARY OF FEATURES OF MECHANICAL FINISHING TECHNIQUES FOR SURFACE PREPARATION

2.1.2.2 *Chemical Polishing*

This is a very simple technique. The sample is immersed into a polishing solution and agitated for several seconds or minutes and then rinsed. The polishing solution dissolves the surface at uniform rate and rapidly forms a barrier layer saturated with metal ions. The peaks of the surface are the ones exposed first to the fresh and agitated solution and dissolve first. The same action occurs at a much slower rate in the grooves of the sample surface; the result is an overall flat and deformation-free surface.

The polishing solutions are usually mixture of highly oxidizing reagents, such as nitric, sulphuric, phosphoric and chromic acids or hydrogen peroxide. Viscous agents are also added to control diffusion and convection rates, making the process more uniform.

Most polishing solutions are quite insensitive to concentration variations.

ADVANTAGES	**DISADVANTAGES**
• Simplicity and economy • Little initial preparation is required • Simple post-treatment of the sample; generally, rinsing in water is adequate • Polished surface is free of deformation and smeared layers that may occurs after mechanical polishing • The specimen does not to be electrically conductive	• Edge are heavily attacked, causing rounding • Only small surface roughness is smoothed; larger grooves or peaks are rounded but not flattened • A surface layer is formed on the polished surface by reaction products

2.1.2.3 Electro Polishing

Electro Polishing (EP) is commonly used as a sample preparation technique. During EP, which is also called electrolytic polishing or anodic polishing, the smoothing action is caused by the anodic dissolution of the sample surface in an electrolytic cell.

Figure *2.1* shows a schematic of a simple electrolytic cell that can be easily assembled. The shape and the position of the anode and the cathode can be adapted to suit the particular application.

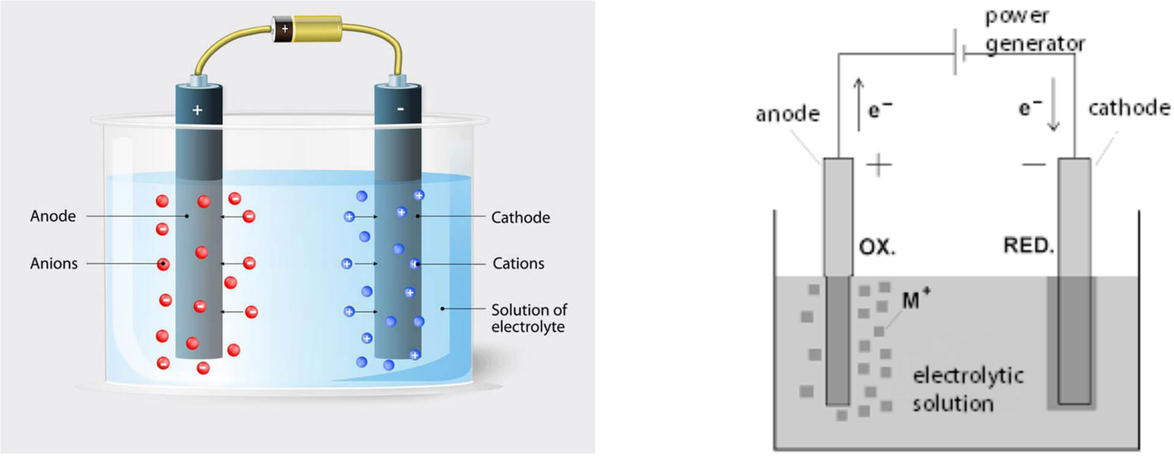

FIGURE 2.1 – SCHEMATIC OF ELECTROPOLISHING CELL

Suitable electrolytes for EP are usually mixture of phosphoric, sulphuric, and perchloric acids in ionizing solutions such as water, acetic acid or alcohol. Glycerol, butanol, urea and so forth are added to increase the viscosity. Alkaline solutions are used for metals that forms highly soluble hydroxides, and cyanide solutions are used for metals that form soluble cyanides.

The polishing action for a given combination of electrolyte and sample material is controlled by:

a. the current density
b. the voltage
c. distance between anode and cathode
d. size ratio of cathode and anode
e. surface condition of the anode
f. temperature of the electrolyte
g. polishing time
h. agitation of the solution
i. concentration of the electrolyte

A typically ideal relationship between current density and applied voltage for many common electrolytes is shown in Figure 2.1

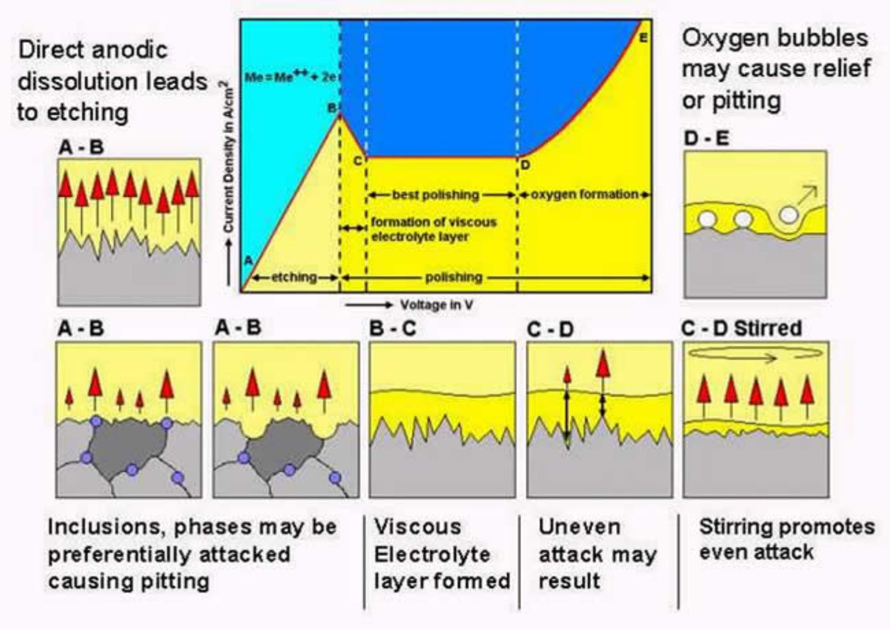

FIGURE 2.1 – RELATIONSHIP BETWEEN CURRENT DENSITY (VERTICAL AXE) AND VOLTAGE (HORIZONTAL AXE)

The current-density/voltage curve includes four characteristic parts:

A. anodic material dissolves between A and B by releasing electrons:

$$Me \leftrightarrow Me^{2+} + 2e^{-}$$

A layer with an increased concentration of metal ions forms at the anode surface. The portion A-B of the curve is important for electrolytic etching

B. at B, a potential that deposits a reaction product is attained, and a passive layer forms on the sample surface. As a result, the current density drops to a constant value:

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

C. the electrolyte composition must be able to dissolve the passive layer:

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

The formation and dissolution of the passive layer reaches an equilibrium through alternating diffusion and electrolytic process that form the plateau C-D in the current-density/voltage diagram. Electrolytic polishing takes place in this range.

D. oxygen evolution begins at D:

$$4OH^- \leftrightarrow O_2 + 2H_2O + 4e^-$$

The initial oxygen evolution is low and the settling time of the gas bubbles is relatively long. This interrupts the polishing process and pitting occurs. By increasing the voltage (D-E portion of the diagram), the oxygen evolution increases as well, and the settling time of the gas bubbles on the anode is then reduced.

Though EP takes place from point B of the diagram, it is only between C and D where other effects no longer interfere. Therefore, most metallographic polishing recipes refer to the C-D portion of this diagram. The D-E portion is rarely used, and if then only for industrial type electropolishing (anodic-brightening). The different regions of the current-density/voltage diagram are in most cases not very pronounced; sometime it is impossible to distinguish individual points when using electrolytes with very high resistivity. The original surface condition of the anode (sample) affects the polishing time: typically, the time becomes shorter, the higher the current density and the better prepared the sample surface. A prerequisite for electrolytic polishing is that the sample is electrically conductive. All single phase metal and alloys can be successful electrolytically polished without any problems. Multiphase alloys are less suitable for anodic polishing because of the different electrolytic potentials between their individual phases.

ADVANTAGES	**DISADVANTAGES**
• No deformation and smeared surface • Short time and good reproducibility • No or only little heat generation of the sample • Possibility of subsequent treatments (cleaning, etching, passivation, etc.) with the same equipment	• Edge are especially heavily attacked. Conductive mounting materials with good adhesion properties may help to protect the edges. However, good edge retention is very difficult to obtain • Only slight surface roughness is being levelled; large, uneven areas are not well polished • A surface layer is formed on the polished surface • Electrical contact can be lost with samples that oxidize easily • At the interface of non-metallic inclusions, the matrix metal is preferentially attacked, resulting in heavy relief and gap formation

2.1.2.4 Combined Polishing Methods

A combination of mechanical polishing with chemical or electro polishing methods can often produce better result than using only one technique.

Chemical-Mechanical Polishing

Chemical-Mechanical Polishing, also called Chemical-Mechanical Planarization (CMP) is a process of smoothing surfaces with the combination of mechanical material removal and a simultaneous chemical attack; highly diluted etchants for the material to be polished are used[3].

This technique is especially useful for:

- Soft and ductile materials, to promote the removal of deformed and smeared layers
- Materials with high abrasion resistance (e.g., refractory materials)
- Multiphase alloys
- Coated materials

A sample surface finish of 15 µm is usually satisfactory. The process uses an abrasive and corrosive chemical slurry (commonly a colloid) in conjunction with a polishing pad and retaining ring. Suitable polishing equipment are vibratory disks with a retaining rim and an automatic sample holder attachment [Figure 2.2]

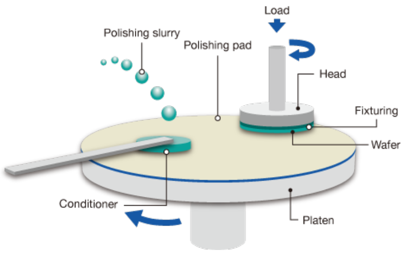

FIGURE 2.2 – CMP MACHINE

Chemical-Mechanical Electro Polishing

Better known as *Electrolytic Lapping* is the simultaneous electrolytic and mechanical removal of material. In this technique, the specimen (anode) is placed on a cloth saturated with electrolyte and mounted on a support or wheel that serves as the cathode. Although direct current is most frequently used for electrolytic lapping, an alternate current at low

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[3] Mahadevaiyer Krishnan, Jakub W. Nalaskowsk, Lee M. Cook, *Chemical Mechanical Planarization: Slurry Chemistry, Materials, and Mechanisms*, Chem. Rev., 2010, vol. 110, pp 178–204.

frequency produces better results with some special materials like molybdenum, rhenium, and tungsten.

Electrolytic lapping combines the advantages, but also some of the disadvantage of the electrochemical and mechanical polishing. It is well suited for homogeneous metals and alloys. As a complementary technique, it has been proven successful when the electrolytic or the mechanical polishing alone fails.

In reference [**4**] are listed the various types of electrolytic grinding that are used in industry.

2.1.3 Etching

Etching is a general term for revealing the **microstructure of a surface**. It is a sort of induced corrosion.

The etching solutions are those that have been developed for the processing and study of artificially grown single crystals. They are able to bring out some particular aspects as of the surface as of the bulk material, such as grain boundaries, dislocations, different compositions, etc.

Polished unetched samples can show macroscopic cracks, pits, and so on, but no microstructural details because there is not yet any contrast producing feature on the surface. These will be revealed by the etching process. The term etching is generally used to mean physical or chemical peeling of atomic layers. However, in the context of surface etching for microstructural evaluation, the idea is to expose the lowest-energy surface by chemical or thermal means. This will expose defects such as grain boundaries and bring out the contrast between different phases or different crystallographic orientations that etch at different rates. Specimen etching is a vast and matured area in itself, and several handbooks are available that describe and tabulate recipes for final polishing and etching of specific materials [**5**,**6** and **7**].

Etching could be both chemical or physical (e.g. plasma etching)

A wide variety of *etchants* are available, including acids, base alkaline solutions, neutral solutions, molten salts, and gases; many examples of etching solution are listed in section

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[4] T. Lyman, *Metals Handbook Vol. 3: Machining*, 8th Edition, American Society for Metals 1967.

[5] B. L. Gabriel, *SEM: A User's Manual for Materials Science*, ASM International, 1985.

[6] *Metals Handbook, 8th ed., Vol. 7, Atlas of Microstructure of Industrial Alloys*, ASM,1972.

[7] B. J. Kestel, *Polishing Methods for Metallic and Ceramic TEM Specimens*, ANL- 80-120, 1981.

2.2. Most of these recipes were derived empirically. Their composition and mode of application can easily be varied and modified and also are useful for materials other than those mentioned in the recipes.

The rate of the etch attack is mainly determined by the degree of dissociation and the electrical conductivity of the etchant. Both can be adjusted in a certain way by adding other chemicals.

The stability of many etching solutions is limited, since redox potentials change with time. Changes may also occur while the etchant is not in use, so that it must be discarded after limited time.

Etching times range from seconds to hours. Time and temperature are closely related; by increasing temperature, the time can usually be decreased.

2.2. CHEMICAL ETCHING/POLISHING BATHS

2.2.1 Ferric Chloride bath

Iron(III) chloride, also called ferric chloride, is an industrial scale commodity chemical compound, with the formula $FeCl_3$ (FC).

When dissolved in water, FC undergoes hydrolysis and gives off heat in an exothermic reaction. The resulting brown, acidic, and corrosive solution is used as etching solution began to be applied in PCBs in the 1960s[8].

A solution of $FeCl_3$ dissolves copper metal fairly quickly. It is used as PCB etchant in electronics and the hydrated form, $FeCl_3.6H_2O$ can be purchased at many electronics parts and hobby shops.

$FeCl_3$ acts as an etchant, because of two reasons:

- Fe^{3+} is a fairly strong oxidizer.
- Cl^- is a strong complexing agent for copper (II) ions.

The reaction in solution often is written as

$$2FeCl_3 + Cu \rightarrow 2FeCl_2 + CuCl_2$$

This, however, is a too strong simplification. If you put copper in a solution of iron (III) sulphate, $Fe_2(SO_4)_3$, then it does not dissolve. The chloride plays an essential role[9]:

$$2Fe^{3+} + Cu + 4Cl^- \rightarrow 2Fe^{2+} + {CuCl_4}^{2-}$$

In reality even this is simplified, because iron also is present as complex with chloride. So, a slightly better description of the reaction may be:

$$2{FeCl_4}^- + Cu \rightarrow 2Fe^{2+} + {CuCl_4}^{2-} + 4Cl^-$$

When all iron (III) is converted to iron (II), then the $CuCl_4^{2-}$ ion in turn also oxidizes copper metal quite well, where copper (I) species are formed:

$${CuCl_4}^{2-} + Cu \rightarrow 2{CuCl_2}^-$$

When all iron (III) is used up, these copper (I) species form very dark-colour mixed oxidation-state species with copper (II) species. This causes the etchant liquid to turn very dark, when it is near exhausted. This method can cause pollution and thus cannot be recycled[10].

Some recipes for etching copper based on $FeCl_3$ are listed above.

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[8] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements (2nd ed.)*, Oxford, 1997.

[9] Wang, Z., Che, J., Ye, C., 2010, *Application of ferric chloride both as oxidant and complexant to enhance the dissolution of metallic copper*, Hydrometallurgy 105, 69e74.

[10] Miao Yu, Xianlai Zeng, *Examining regeneration technologies for etching solutions: a critical analysis of the characteristics and potentials*, Journal of Cleaner Production 113 (2016) 973e980

Recipe: *Cu_01* **Ref**: Economou, N A & Trivich, D - *Electrochem Acta, 3,292(1961)*

Type: *removal/preferential*

Composition: Ferric Chloride $FeCl_3$ … saturated solution

Time:

Temperature:

Discussion: This ferric chloride solution was used to develop dislocations and other structure after specimens were subjected to deformation.

Recipe: *Cu_02* **Ref**: *Mackliet, C A - Phys Rev, 109,1964 (1958)*

Type: *etching*

Composition:
Ferric Chloride $FeCl_3$ … 10 g
H_2O demi … 90 ml

Time:

Temperature: hot

Discussion: Cu single crystal specimens used in a study of dislocation density after specimen deformation. A diluted ferric chloride solution was used to develop dislocations and other structures

Recipe: *Cu_03* **Ref**: *Skeist, I - Epoxy Resins, Reinhold, New York, 1950, 190*

Type: *polishing*

Composition:
H_2O demi … 82 ml
Nitric Acid 65% HNO_3 … 10 ml
Ferric Chloride sol. 40% $FeCl_3$ … 5 ml

Time:

Temperature:

Discussion: Cu and Cu alloys as sheet or foil were cleaned in this solution prior to being plastic laminated. Metal surface cleanliness is essential to obtain a good plastic/metal adhesion seal. This solution gave the best adhesion results. Several types of plastic sheet were evaluated and also were applied to aluminium.

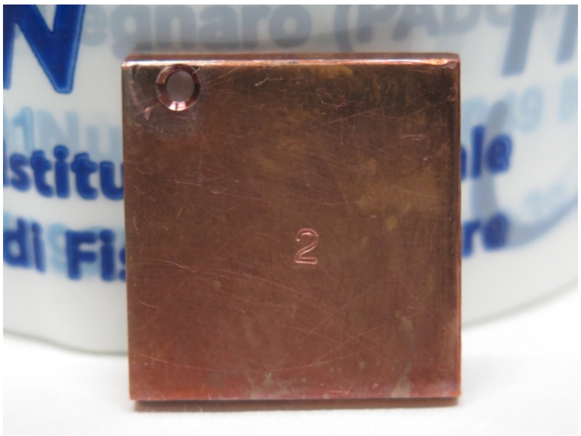
Historically, ferric chloride ($FeCl_3$) was first used in PCBs fabrication, and it remains a common etchant for small production lines and the hydrated form, $FeCl_3.6H_2O$ can be purchased at many electronics parts and hobby shops. During the past twenty years, however, a variety of new etchants have been utilized for copper etching, the most popular one being cupric chloride ($CuCl_2$) etching solution. At present, $CuCl_2$ has been a favourite etchant for its advantages of the high etching rate and natural regeneration properties[11]. It is also quite attractive because of its stable characteristics and lower processing cost. Acid etching solution began to be applied in PCB manufacturing starting in the late 1980s. It can make CuCl oxidated with hydrogen peroxide renewable and recyclable. The simple chemical reaction mechanism is:

$$Cu + CuCl_2 \rightarrow 2CuCl$$

Recipe: *Cu_04*	**Ref**:			
Type: *etching*				
Composition:		H_2O demi	…	60%
	Copper(II) Chloride	$CuCl_2$	…	5%
	Hydrochloric Acid 37%	HCl	…	10%
	Hydrogen Peroxide 35%	H_2O_2	…	25%
Time:	10 min			
Temperature:	30-40 °C			
Warnings:	Exothermic reaction. Wash in demi water in US and rinse in Ethanol			
Discussion:	Copper etching with $CuCl_2$ produces a stable, high etch rate and low undercut, demonstrating a desirable high etch factor			

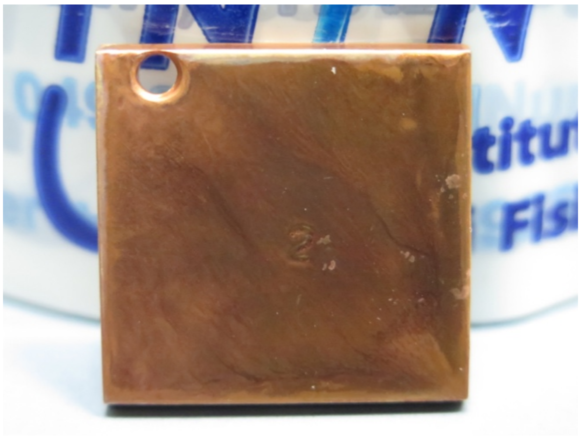
Photos

Before



m_i = 15,889 g

After



m_f = 13,824 g

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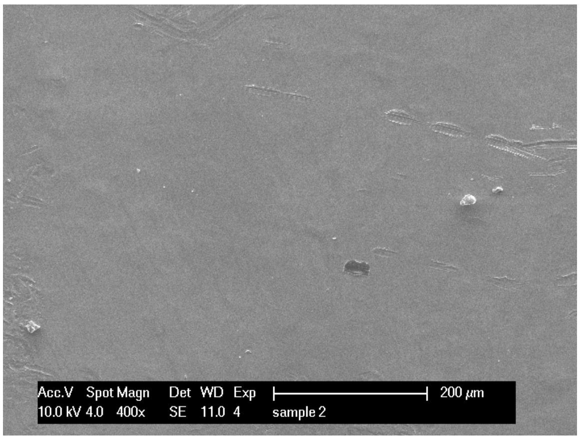
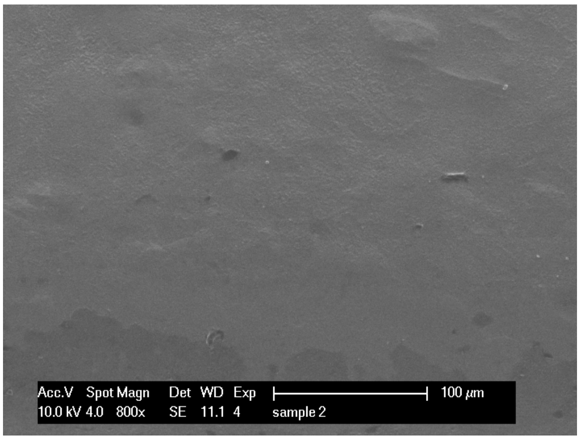
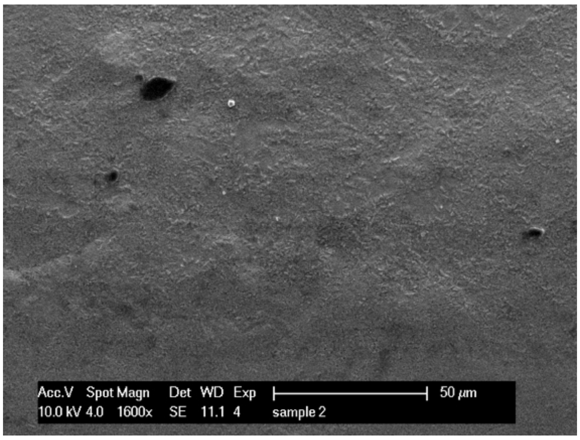
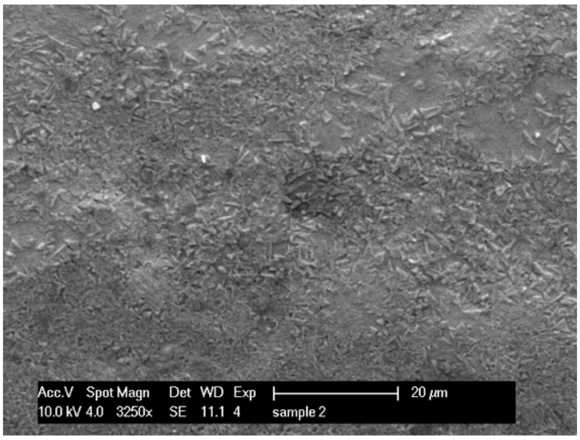
[11] Cakir, 2006; Keskitalo et al., 2007; Lee et al., 2008

Scanning Electron Microscope photos of surface after treatment









2.2.2 Ammonium Persulfate bath

The ammonium persulfate is the inorganic compound of $(NH_4)_2S_2O_8$. It is a white highly soluble salt in water and it is a strong oxidizing agent. For its powerful oxidizing property, it is used to etch copper on printed circuit boards from 1970s. When the copper is oxidized by persulfate, a blue soluble copper sulphate is formed, as indicated in the following chemical reactions:

- Copper Oxidation:

$$Cu + S_2O_8{}^{2-} \rightarrow Cu^{2+} + 2SO_4{}^{2-}$$

- Formation of copper sulphate:

$$Cu^{2+} + 2SO_4{}^{2-} \rightarrow CuSO_4 + SO_4{}^{2-}$$

- Completed reaction:

$$(NH_4)_2S_2O_8 + Cu \rightarrow CuSO_4 + (NH_4)_2SO_4$$

The dissolution rate and ability are worse than those of chlorides, and it readily decomposes. Its higher cost is also prohibitive for most applications.

Because of this, the original recipe calls for the addition of sulphuric acid (H_2SO_4), and mercuric chloride ($HgCl_2$). Then the mercury has been replaced with the silver[12].

The vapour or powder dispersing in the air may be irritating to eye, nose, throat, lung or skin upon contact. Exposure to high concentration may cause difficulty in breathing and asthma related effects[13].

Recipe: *Cu_05*	**Ref**: Baur, J. P. et all, *Acta Metall*, 103, 273 (1956)
Type: *etching*	
Composition:	Ammonium Persulfate $(NH_4)_2S_2O_8$ … 2 – 5 %
Time:	15 min
Temperature:	Room Temperature
Discussion:	Cu, OFHC copper single crystal specimens used in a study of the formation of fatigue cracks using an electron microscope (EM) for observation. An ammonium sulphate solution was used to develop cracks.

---

[12] Ye, B.R., *Talking about PCB etching solution with $(NH_4)_2S_2O_8$ as major etchant*. Print. Circuit Inf. 4, 34e37, (2009)

[13] Ammonium persulfate, "Sigma Aldrich," Material Safety Data Sheet, available online.

Recipe: *Cu_06* **Ref**: G. Petzow – Metallographic Etching 2nd Ed, pg. 93

Type: *microetching*

Composition: Ammonium Persulfate $(NH_4)_2S_2O_8$ … 300 g/L

Time: 1 h

Temperature: Room Temperature

Discussion: Etches the 100 texture of Cu crystals

Photos

Before

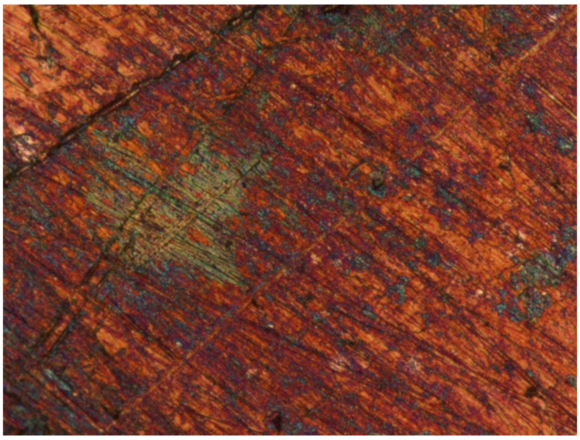
m_i = 16,122 g

After

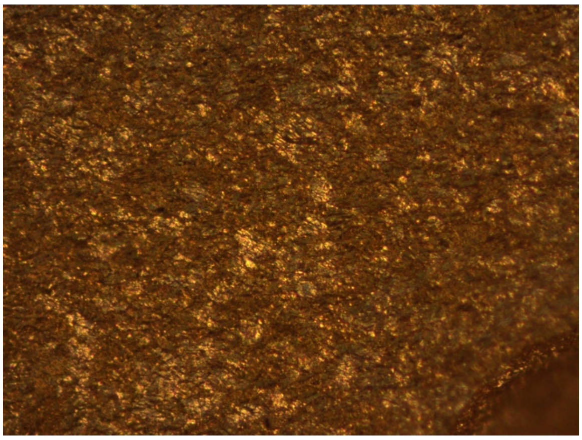
m_f = 15,442 g

Metallographic Microscope photos

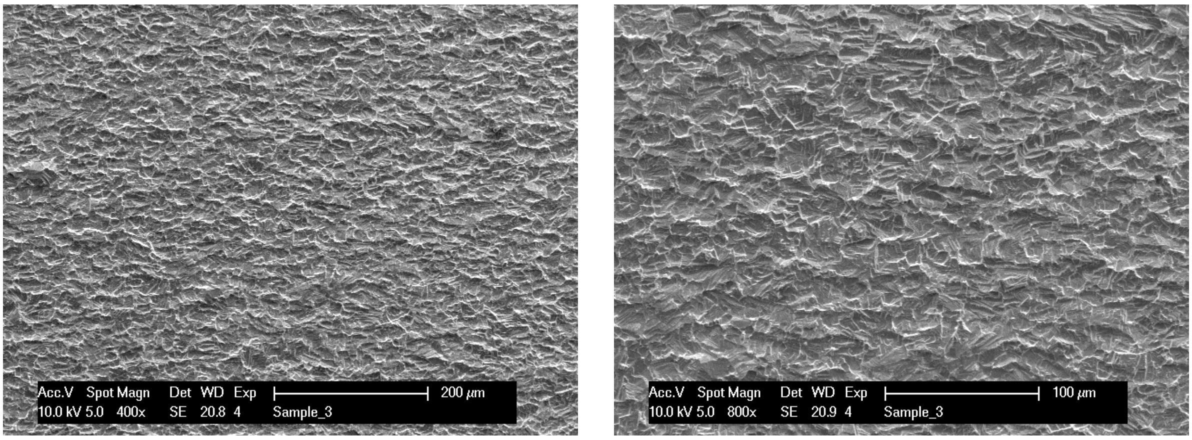
Before



After



Scanning Electron Microscope photos of surface after treatment



Recipe: *Cu_07* **Ref**: CUORE/CUPID protocol

Type: *microetching*

Composition: Ammonium Persulfate $(NH_4)_2S_2O_8$ … 20 g/L

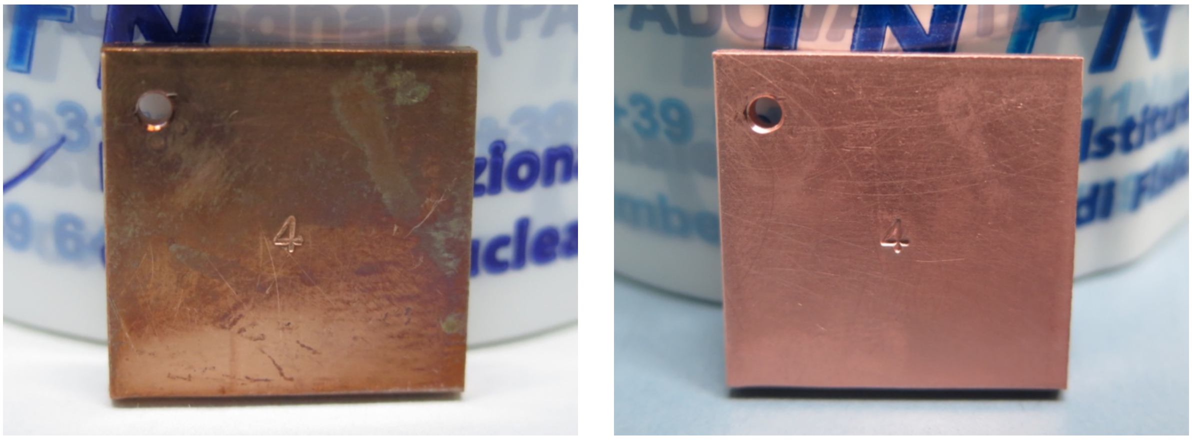
Time: 1 h

Temperature: Room Temperature

Discussion:

Photos

Before **After**

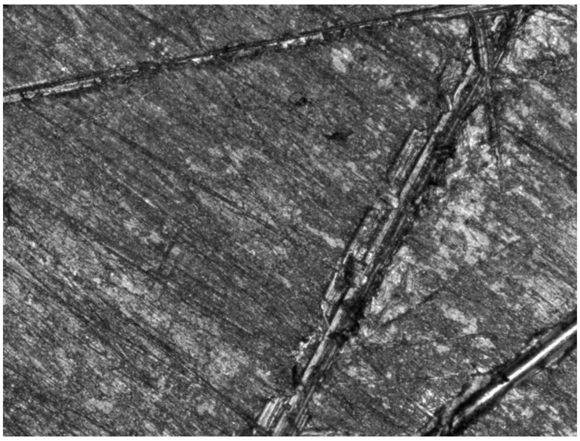


m_i = 16,825 g

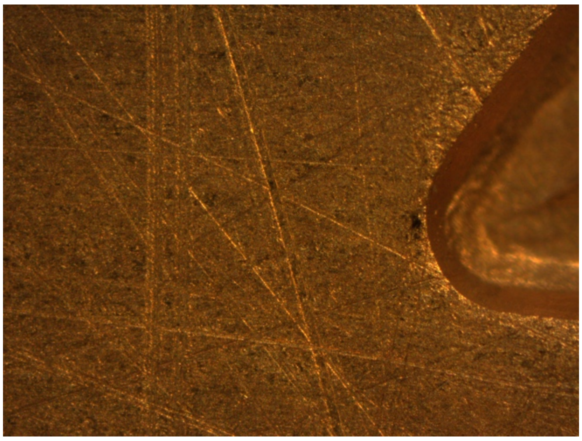
m_f = 16,810 g

Metallographic Microscope photos

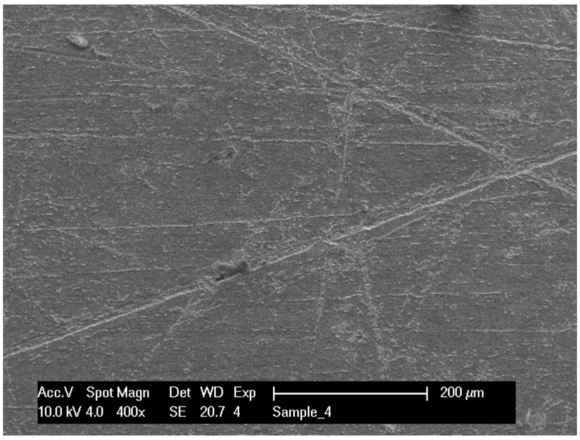
Before

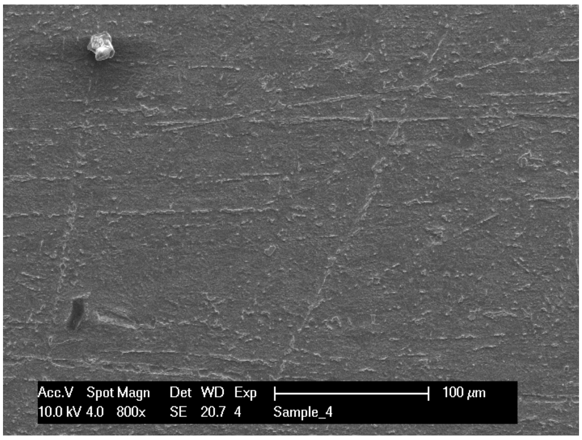


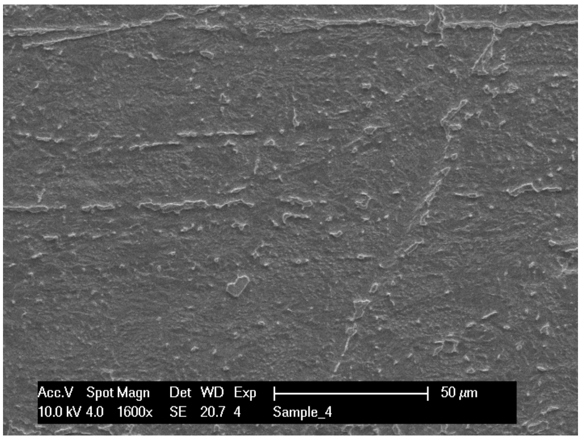
After



Scanning Electron Microscope photos of surface after treatment







2.2.3 Alkaline Etching Solution

AES began to be applied to PCBs after 1977. This method uses Sn/Pb as an etch-resistant alloy, and chlorine, hydrogen peroxide or sodium chlorate provides a continuous regeneration reaction medium. It is cheaper than ferric chloride and has more waste recycling value. This etching liquid's main ingredients are copper chloride ($CuCl_2$):15%, ammonia ($NH_3 \cdot H_2O$):10-20%, ammonium chloride (NH_4Cl) and stabilizer. Etching temperature is 40-60 °C, and its pH is 9.5-9.8. The chemical reaction mechanism of AES is shown from

$$\mathrm{Cu(NH_3)_2Cl_2 + Cu \rightarrow 2Cu(NH_3)_2Cl}$$

$$\mathrm{4Cu(NH_3)_2Cl + 4NH_4Cl + 4NH_3 \cdot H_2O + O_2 \rightarrow 4Cu(NH_3)_4Cl_2 + 2NH_4 + 6H_2O}$$

Shanghai Lvcheng Environmental Protection Technology Co., Ltd patented an efficient extraction of copper etching solution with oxidized copper and recycled ammonia and salts from copper extraction waste residue. This method simultaneously produces PCBs and protects the environment by extracting valuable metal by-products from the alkaline etching liquid waste. With the rapid development of the PCB industry, the total amount of generated spent etchant is continually increasing. Based on market data from Singapore organized by Robert in 2002, it was estimated that it produced 70,000 L of spent ammoniacal etchant every month by local PCB plants[14].

---

[14] Kang, X., Yang, Y., 2011. *An experimental study on removal of copper ions from industrial wastewater by magnetic flocculation*. Ind. Water Wastewater 42, 24e27.

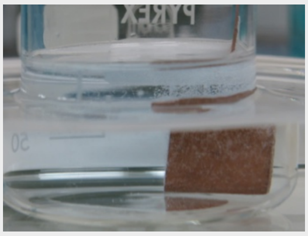
Recipe: *Cu_08* **Ref**:

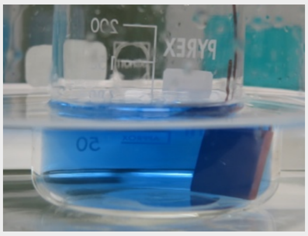
Type: *microetching*

Composition:		H_2O demi	... 3 pt
	Ammonium Hydroxide	NH_4OH	... 1 pt
	Hydrogen Peroxide	H_2O_2	... 1 pt
Time:	10 min		
Temperature:	Room Temperature		

Discussion: Exothermic reaction. Better to use a cooling bath.

Stirring may cause a strong bubble evolution. The reaction ends when the effervescence stops.





Photos

Before

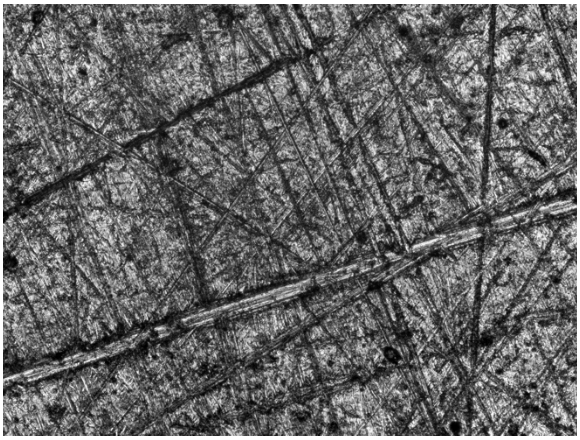
m_i = 15,752 g

After

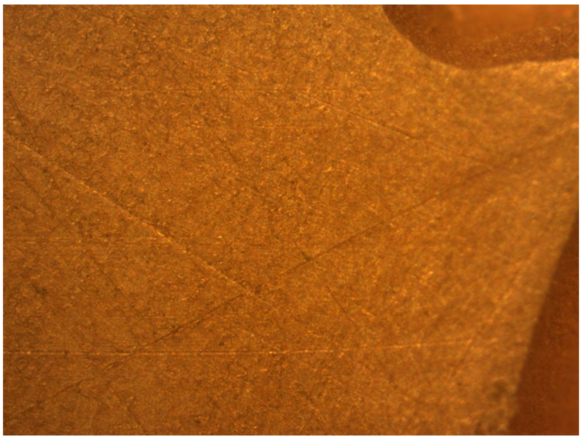
m_f = 15,735 g

Metallographic Microscope photos

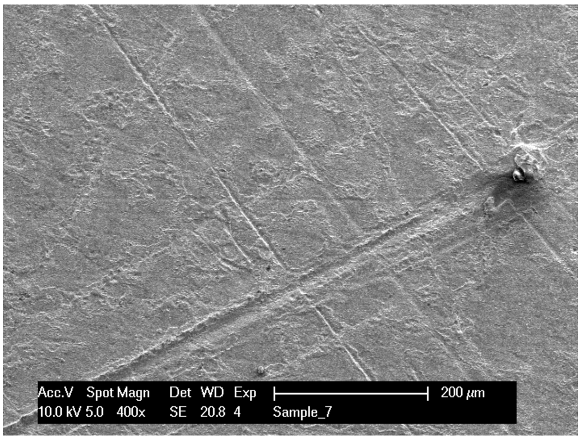
Before

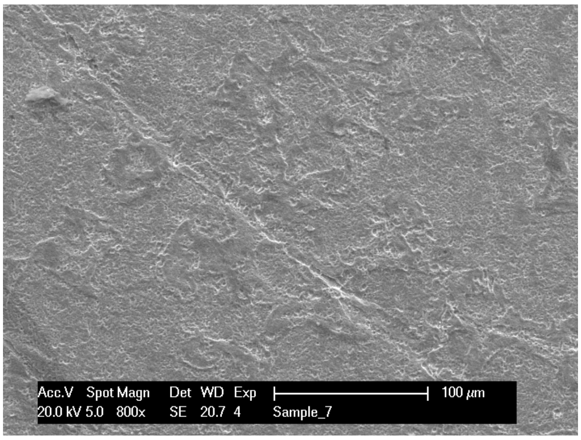


After



Scanning Electron Microscope photos of surface after treatment





2.2.4 Sulphuric/Chromic Acid bath

Sulfo-Chromic Acid (SCA) etching solution, etches well through the corrosion resistant tin-lead alloy layer of PCBs, but chromic acid is a first category hazardous substance in the national emission standards for three wastes and is harmful to people, animals, and plants. Therefore, it is no longer used to etch PCBs and in few years will be no longer suitable for any application. In fact, because of this dangerous pollution phenomenon as well as its high cost, it was only used for about a year and was then replaced by sodium chlorite. SCA etching liquid's main ingredients are chromium trioxide (CrO_3), sulphuric acid (H_2SO_4). The chemical reaction mechanism of SCA is shown from[15]:

$$\mathrm{CrO_3 + H_2O \rightarrow H_2CrO_4}$$

$$\mathrm{2H_2CrO_4 + 3Cu \rightarrow Cr_2O_3 + 3CuO + 2H_2O}$$

$$\mathrm{2Cr_2O_3 + 3CuO + 9H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 3CuSO_4 + 9H_2O}$$

The sulphuric acid is used to provide enough hydrogen ions; beware hydrochloric acid must not be used as toxic chlorine gas would be liberated.

Recipe: *Cu_09* **Ref**: Hu, Y.H., Zhao, G.P., Xie, S.L., Yuan, G.W., Zhang, Z.X., 2009. *Reuse of waste etching solution of printed circuit board with copper containing*. Electroplat. Finish. 28, 32e35.

Type: *etching*

Composition:	Cromic Acid	H_2CrO_4	…	240 g/L
	Sulphuric Acid 96%	H_2SO_4	…	180 g/L
	Sodium Sulphate	Na_2SO_4	…	40 g/L

Time:

Temperature:

Discussion: Chromic-Sulphuric etchant has only a slow etch rate and low copper holding capacity. The addition of sodium sulphate increases the etch rate.

---

[15] P. Patnaik , *Handbook of Inorganic Chemicals*, McGraw-Hill, New York, 2003.

Recipe: *Cu_10* **Ref**: Hu, Y.H., Zhao, G.P., Xie, S.L., Yuan, G.W., Zhang, Z.X., 2009. *Reuse of waste etching solution of printed circuit board with copper containing*. Electroplat. Finish. 28, 32e35.

Type: *etching*

Composition:	Sodium Cromate	Na_2CrO_4	…	113 g
	Sulphuric Acid 96%	H_2SO_4	…	340 g
		H_2O	…	3785 ml

Time:

Temperature:

Discussion: Solution will remove heavy oxides and leave a matte type surface finish.

Recipe: *Cu_11* **Ref**: Iker, P & campos, R – personal application 1962

Type: *etching*

Composition:	Cromic Oxide	CrO_3	…	12 pt
	Sulphuric Acid 96%	H_2SO_4	…	6 pt
		H_2O	…	82 pt

Time:

Temperature:

Discussion: Cu cryogenic trailer piping, including brass, bronze and stainless steels. Solution used as a "Brite Copper" dip.

Because of the high toxicity of Chromium (VI) and the problems inherent in the disposal of waste, none of these recipes have been tested.

2.2.5 Sulphuric/Peroxide bath

A straight mixture of Sulphuric and Peroxide, known as **PIRANHA ETCH**, makes a very fast etchant, but sadly is unstable and not safe to use. Additives are added such as Aryl Sulfonic acids to stabilize the peroxide in solution, and even Phosphoric acid which helps to retain a cleaner tin lead over the copper.

This solution is typically used to clean organic residues off substrates. Because the mixture is a strong oxidizing agent, it will remove most organic matter, and it will also hydroxylate most surfaces (add OH groups), making them highly hydrophilic (water-compatible).

Standard reaction is:

$$Cu + H_2O_2 + H_2SO_4 \rightarrow Cu_2SO_4 + 2H_2O$$

Its primary advantages are that its components are cheap and readily available and that it produces only high-purity copper sulphate crystals after etching.

However, piranha solution **must be prepared with great care**. Piranha solution should always be prepared by adding hydrogen peroxide to sulphuric acid slowly, never in reverse. Mixing the solution is extremely exothermic. If the solution is made rapidly, it will instantly boil, releasing large amounts of corrosive fumes. Even when made with care, the resultant heat can bring solution temperatures above 100 °C. It must be allowed to cool reasonably before it is used. The sudden increase in temperature can also lead to violent boiling of the extremely corrosive solution. Solutions made using hydrogen peroxide at concentrations greater than 50% may cause an explosion. Once the mixture has stabilized, it can be further heated to sustain its reactivity.

Due to the self-decomposition of hydrogen peroxide, the piranha solution must be prepared at the time, in addition, can not be stored, and must therefore be neutralized, instead of being stored. The oxygen produced by the decomposition of hydrogen peroxide, in addition to the products of oxidation of organic compounds may cause the breakage of the container[16].

The immersion of a surface (for example a wafer) in this solution must be done slowly to prevent thermal shock which could make the die material.

---

[16] *Piranha Solution*
https://ehs.princeton.edu/laboratory-research/chemical-safety/chemical-specific-protocols/piranha-solutions

2.2.6 Nitric acid-based bath

Not the safest of chemicals but a simple fast etchant. Often used as a quick fix for removing any remaining copper from a electroless copper tank prior to use.

Adding by weight 2% of *POTASSIUM CHLORATE* to a 10% NITRIC ACID solution allows it to etch brass.

Normal reaction as a copper etchant is:

$$3Cu + HNO_3 \rightarrow 3Cu^{2+} + 2NO_2 + 2H_2O$$

The action is rapid. It may be slowed down by adding small amounts of “inhibiting materials” such as 10g/L *SODIUM NITRIDE* plus 5g/L of *SODIUM CHLORIDE* to bath 50/50 or greater in *NITRIC ACID*, or by adding *CHROMIC ACID* to those of lower ratio. Additions of up to 50% *PHOSPHORIC ACID* improves the smoothing action and diminishes the tendency to tarnish.

Concentrated bath are most satisfactory for individually racked work. For bulk dipping the bath are usually diluted with water to slow down the action and minimize staining. Cold solutions with cooling coils to prevent any temperature rise are preferred by many.

For greater smoothing action so that a measurable amount of polishing take place, the dissolution process must be changed. *PHOSPHORIC- NITRIC- ACETIC* acid solutions provide brilliance and smoothing.

Preferred compositions ranges from[17]:

- 10 to 80% by wt. *PHOSPHORIC ACID*
- 10 to 50% by wt. *NITRIC ACID*
- 10 to 80% by wt. *GLACIAL ACETIC ACID*

Examples of typical bath are:

Recipe: *Cu_12* **Ref**: Metallographic etching. P.91

Type: *polishing*

Composition:	Acetic Acid glacial	CH_3COOH	…	25 ml
	Phosphoric Acid 85%	H_3PO_4	…	25 ml
	Nitric Acid 65%	HNO_3	…	25 ml
	Hydrochloric Acid 32 %	HCl	…	0.5 ml

Time: 3 min

Temperature: 40 °C

Discussion:

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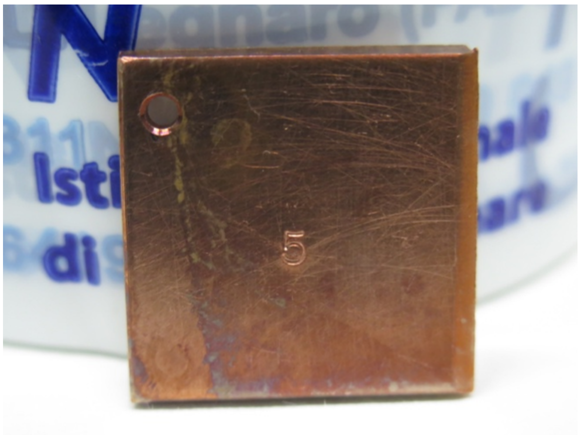
[17] NPCS Board of Consultants & Engineers, *Electroplating, Anodizing & Metal Treatment Hand Book*, 2003, p. 139

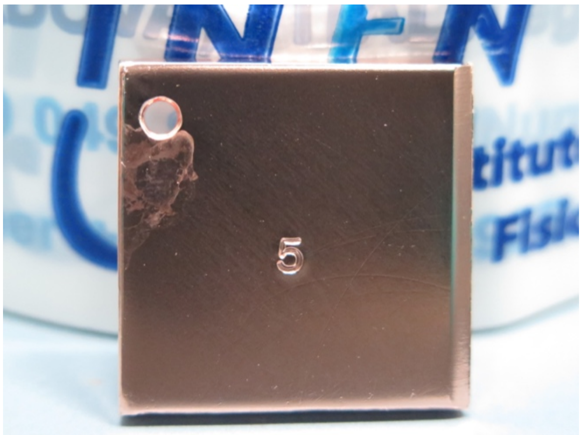
Photos

Before



m_i = 16,132 g

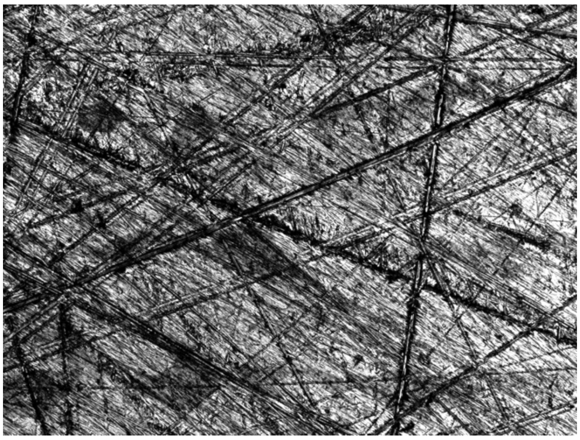
After



m_f = 15,896 g

Metallographic Microscope photos

Before



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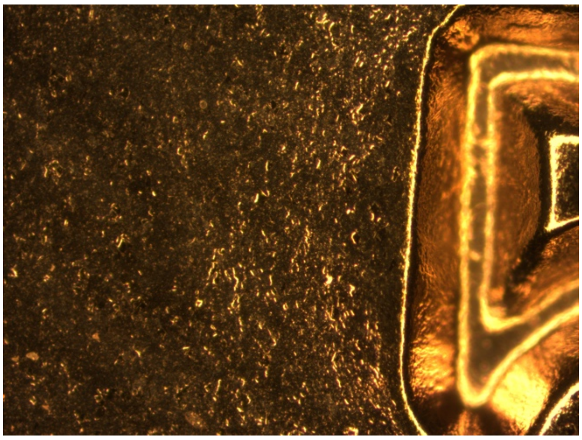
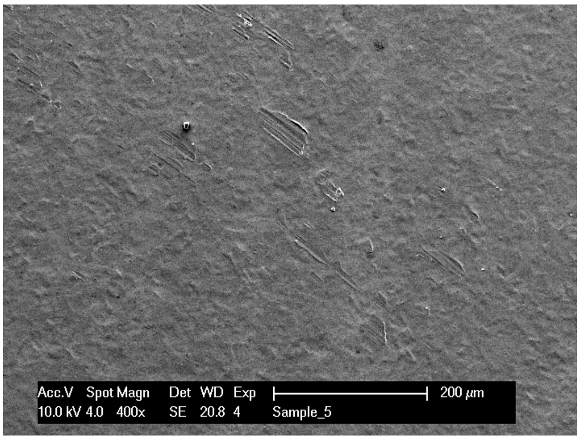
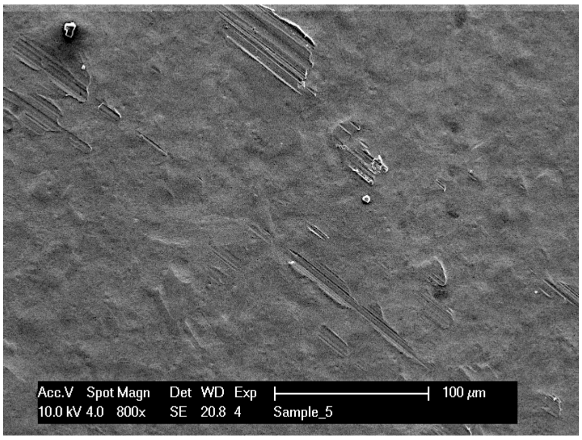


Scanning Electron Microscope photos of surface after treatment





Recipe: *Cu_13* **Ref**: Metallographic etching. P.91

Type: *polishing*

Composition:	Acetic Acid glacial	CH_3COOH	...	65 ml
	Phosphoric Acid 85%	H_3PO_4	...	27 ml
	Nitric Acid 65%	HNO_3	...	6 ml

Time: 1 - 2 min

Temperature: 60 °C

Discussion:

Photos

Before

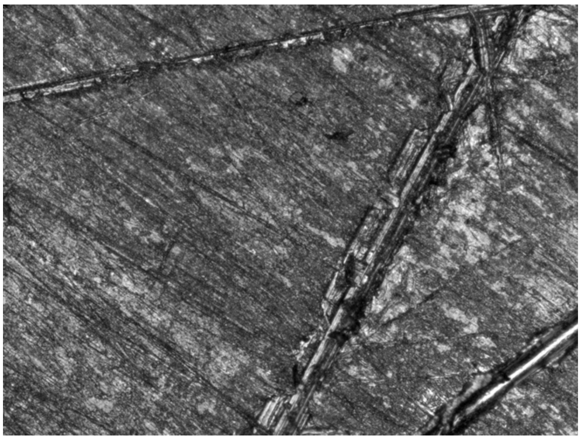
m_i = 16,491 g

After

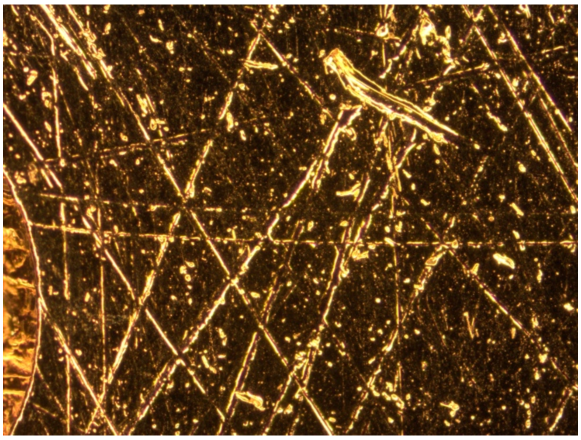
m_f = 14,457 g

Metallographic Microscope photos

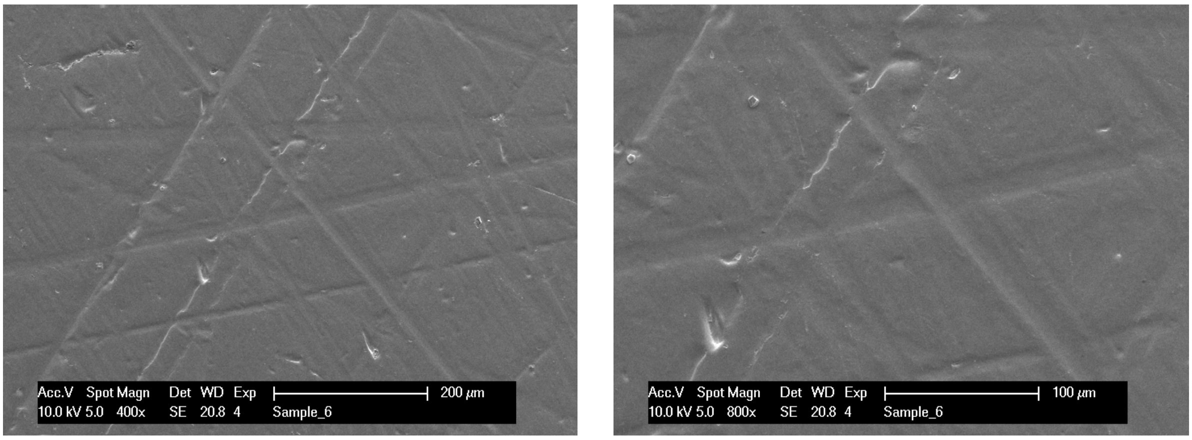
Before



After



Scanning Electron Microscope photos of surface after treatment



Recipe: *Cu_14* **Ref**: Metallographic etching. P.91

Type: *polishing*

Composition:	Acetic Acid glacial	CH_3COOH	…	50 ml
	Phosphoric Acid 85%	H_3PO_4	…	10 ml
	Nitric Acid 65%	HNO_3	…	30 ml
	Hydrochloric Acid 32 %	HCl	…	10 ml
Time:	1 - 2 min			
Temperature:	70 – 80 °C			

Recipe: *Cu_15* **Ref**: Metallographic etching. P.91

Type: *polishing*

Composition:	Acetic Acid glacial	CH_3COOH	…	30 ml
	Phosphoric Acid 85%	H_3PO_4	…	30 ml
	Nitric Acid 65%	HNO_3	…	40 ml
	Sodium Chloride	NaCl	…	1 g
Time:	4 min			
Temperature:	65 °C			

The hydrochloric additions are particularly suitable for treating alloys containing nickel, monel, and nickel silver. The metal removal rate ranges from 2µm/min a 7µm/min. Dipping usually is long enough to remove 2µm to 5µm of metal. Thereafter, no further increase brilliance occurs. Longer dipping may give some additional smoothing and thus improve surfaces which were initially very rough. An important fact is that etching does not occur regardless of the immersion time.

2.2.7 SUBU

The chemical etching based on SUBU process was invented by the research institute CERN (European Organization for Nuclear Research). Its name derived from Sulphamic Acid and Butanol. The exact recipe per 1 litre of deionized water is:

Recipe: *SUBU 5*	**Ref**:			
Type: *polishing*				
Composition:	Ammonium Citrate	$HOC(CO_2H)(CH_2CO_2NH_4)_2$	…	1 g/L
	Sulphamic Acid	H_2NSO_3H	…	5 g/L
	Butanol	C_4H_9OH	…	50 ml/L
	Hydrogen Peroxide	H_2O_2	…	50 ml/L
Time:	5 min			
Temperature:	(72±4)°C			

The role of each constituent of the bath is essential for the optimal cleaning surface. The **sulphamic acid** [H_2NSO_3H] at 70 °C in presence of an oxidant, heavily corrodes the copper forming a copper sulfamate [$Cu(NH_2SO_3)_2$] and releasing hydrogen. The **hydrogen peroxide** [H_2O_2] is decomposed oxidizing the environment and permitting the dissolution of copper. A certain concentration of active oxygen, the copper oxide on the copper surface is formed, limiting the metal dissolution. A smooth surface finish is the result of two competing reactions: dissolution of the metal and creation of a passive layer, due to the oxidation. A bath that contains sulphamic acid and hydrogen peroxide is the first condition to obtain a bright copper surface, but sometimes, a brown layer on the surface is created. The addition of a small amount of **ammonium citrate dibasic** [$HOC(CO_2H)(CH_2CO_2NH_4)_2$] prevents the occurrence of this layer. Nevertheless, when the bath contains sulphamic acid, hydrogen peroxide and ammonium citrate, a strong effervescence due to decomposition of hydrogen peroxide in contact with copper is produced. In order to regulate or limit the effervescence, the **n-butanol** [C_4H_9OH] reduces the action of the hydrogen peroxide[18].

---

[18] J.D. Adam, J.P. Birabeau, J. Guerin*, Procedes de preparation de surface de cuivre compatibles avec un depot de niobium realisé par pulverisation cathodique. Presentation d'un bain de polissage chimique repondant a ce critere*, CERN, Novembre 1985

2.3. ELECTROPOLISHING

For the electropolishing theory see section 2.1.2.3

Recipe: *EP_1* **Ref**: G. Petzow, Metallographic Etching, (1999), p. 91

Type: *electropolishing*

Composition:		H_2O demi	…	30 ml
	Phosphoric Acid 85%	H_3PO_4	…	70 ml
Time:	5 – 15 min			
Temperature:	Room Temperature			
Cathode:	Copper			
Voltage:	1.5 – 2 V DC			

Recipe: *EP_2* **Ref**: G. Petzow, Metallographic Etching, (1999), p. 91

Type: *electropolishing*

Composition:		H_2O demi	…	30 ml
	Phosphoric Acid 85%	H_3PO_4	…	67 ml
	Sulfuric Acid 95-97%	H_2SO_4	…	10 ml
Time:	15 min			
Temperature:	Room Temperature			
Cathode:	Copper			
Voltage:	2 V DC			

Recipe: *EP_3* **Ref**: G. Petzow, Metallographic Etching, (1999), p. 91

Type: *electropolishing*

Composition:		H_2O demi	…	100 ml
	Chromium Trioxide	CrO_3	…	1 g
Time:	3 – 6 s			
Temperature:	Room Temperature			
Cathode:	Aluminium			
Voltage:	6 V DC			

Recipe: *EP_4* **Ref**: G. Petzow, Metallographic Etching, (1999), p. 91

Type: *electropolishing*

Composition:	Methanol 99.8 %	CH_3OH	…	594 ml
	Phosphoric Acid 85%	H_3PO_4	…	406 ml
Time:	10 s			
Temperature:	Room Temperature			
Cathode:	Stainless Steel			
Voltage:	15 - 25 V DC			

Recipe: *EP_5* **Ref**: G. Petzow, Metallographic Etching, (1999), p. 91

Type: *electropolishing*

Composition:		H_2O demi	…	500 ml
	Phosphoric Acid 85%	H_3PO_4	…	400 ml
	Ethylene Glycol	$(CH_2OH)_2$	…	100 ml
Time:	5 s			
Temperature:	Room Temperature			
Cathode:	Stainless Steel			
Voltage:	8 - 15 V DC			

Recipe: *EP_6* **Ref**: CUORE/CUPID process. See section 3.1.1.4

Type: *electropolishing*

Composition:		H_2O demi	…	500 ml
	Phosphoric Acid 85%	H_3PO_4	…	400 ml
	Ethylene Glycol	$(CH_2OH)_2$	…	100 ml
Time:				
Temperature:	Room Temperature			
Cathode:	Copper			
Voltage:	3.5 – 3.9 V DC			

3. COPPER SURFACE TREATMENTS FOR NEUTRINOS

3.1. CUORE & CUPID

The **C**ryogenic **U**nderground **O**bservatory for **R**are **E**vents – **CUORE**, is a particle physics facility located at the Laboratori Nazionali del Gran Sasso in central Italy. CUORE was designed primarily as a search for neutrinoless double beta decay (0νββ) in 130Te, a process that consist in the simultaneous occurrence of two beta decays from the same nucleus. It is an extremely rare event and has been observed only in nuclides with life times around $10^{20}÷10^{21}$ years.

It uses 988 tellurium dioxide (TeO_2) crystals as both the source of the decay and as heat capacity bolometers to detect the resulting electrons. They are arranged in a circular configuration of 19 towers [Figure 3.1] and cooled in a large cryostat to approximately 10mK (the coldest m^3 in the universe[19]) with a dilution refrigerator.

The detectors are isolated from environmental thermal, electromagnetic, and other particle backgrounds by ultrapure low-radioactivity shielding.

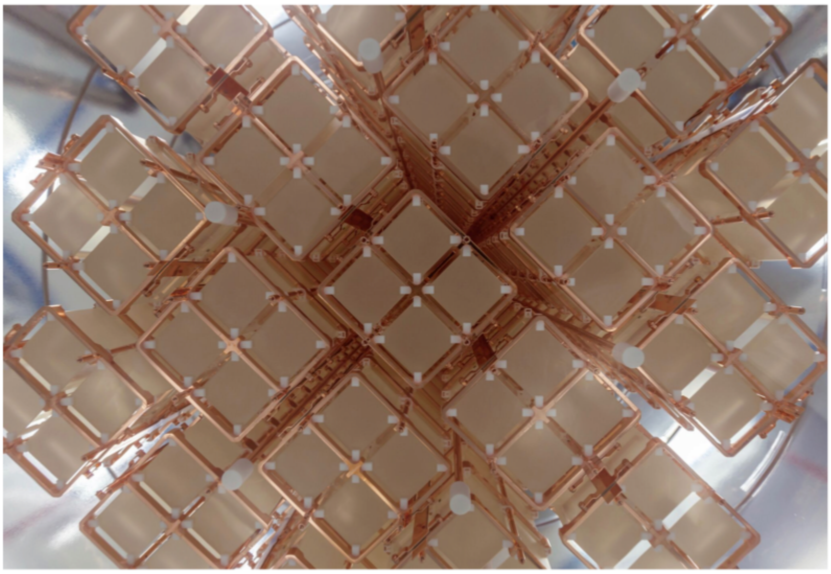


FIGURE 3.1 – BOTTOM VIEW OF THE TOWERS JUST BEFORE

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[19] Jonathan L. Ouellet, *The Coldest Cubic Meter in the Known Universe*, University of California - Berkeley, Oct 15, 2014

For the construction of CUORE, the collaboration followed several procedures to minimize radioactive contamination that can cause the detectors to register background events at energies close to the energy released in neutrinoless double beta decay.

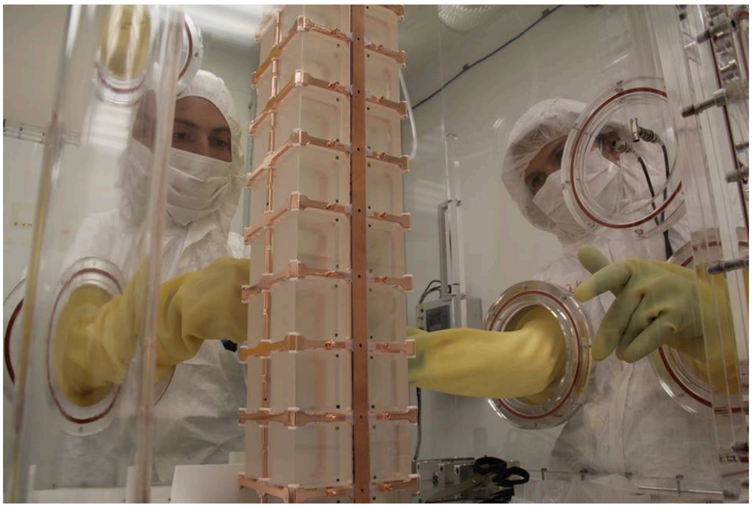

FIGURE 3.2 – ASSEMBLY OF A CUORE TOWER INTO THE GLOVEBOXE

The crystals are held in place by PTFE support in towers constructed from oxygen-free high thermal conductivity copper and were assembled under nitrogen inside gloveboxes in cleanrooms [Figure 3.2].

Copper OFHC, ancient low-radioactivity Roman lead, and borated polyethylene are used to shield the detectors.

One of the critical part of these experiments is to remouve the residual radioactive contamination due to the presence of Th, Po and U on copper surface.

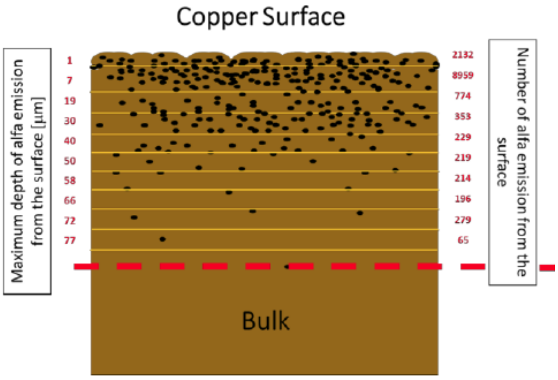

FIGURE 3.3 – DISTRIBUTION OF ALPHA EMITTING IMPURITIES ON COPPER SURFACE

From Figure *3.3* we can observe that the impurities emitting alpha particles are accumulate on the surface sample. Therefore, based on the assumption that the impurities concentration in the bulk and surface of OFCH copper is rather uniform, additional impurities were aggregated by handling the sample, the environmental interactions and the mechanical machining of the piece. The abundance of impurities in the surface and the high purity of the bulk generate a concentration gradient that cause a diffusion of the impurities through the first layers of thickness.

Lot of studies and work on this field have been done at the Laboratory of Superconducting and Surface Treatments @ INFN-LNL [for further informations see *Menegatti (2005/2006)*, *De Biasi (2007/2008*) and *Camacho (2013/2016)*].

CUPID is the **C**UORE **U**pgrade with **P**article **ID**entification, a research and development project for the CUORE detector. Several research groups worldwide are working together to develop materials for this upgrade. CUPID aims to use new detector materials in the same cryostat as CUORE.

In particular it tries the radioactive decay of ^{82}Se. For this reason, in order to increase the crystals of the search sensitivity, will be "grown" with If in isotopically enriched ^{82}Se. The single CUPID detector [Figure 3.4] will work as bolometer. A bolometer is usually constituted by a crystal coupled with a very particular thermometer. When a crystal is cooled to very low temperatures [-273.14 °C], close to absolute zero, a minimum and invisible energy release in it produces a measurable rise in its temperature. Moreover, if this crystal is chosen in a suitable manner, the release of energy can also produce a minimum production of light, that "exiting" from the crystal can be measured, providing an additional information from which it can be deduced the nature of the particle that has interacted in the crystal. This opportunity is a fundamental tool to break down the natural background radiation that "mimics" the expected signal. Given that in such extreme temperatures detectors "standard" do not work, have been developed ad hoc light detectors. It is bolometers "opaque" very sensitive: when the light (quantifiable in a few hundred photons) is emitted by the ZnSe crystal, is absorbed by the bolometer "opaque". This slight amount of light is sufficient to heat the bolometer-light detector and the measure to increase of temperature measurement in a precise manner the number of photons that have been issued.

The CUPID experiment consists of an array of individual detectors arranged in towers [Figure 3.4]. The single module will be constituted by a cylindrical crystal of diameter 45 mm and height 55 mm Zn82Se. The light detector will consist of a 45 mm diameter and 0.1 mm thick disc of germanium.

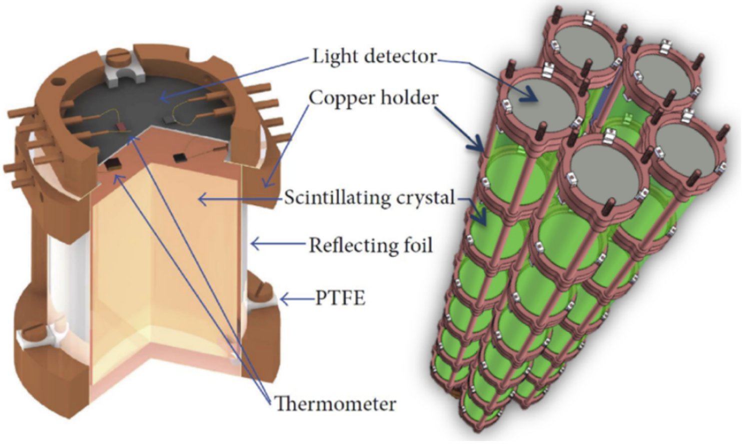

FIGURE 3.4 – CUPID DETECTOR

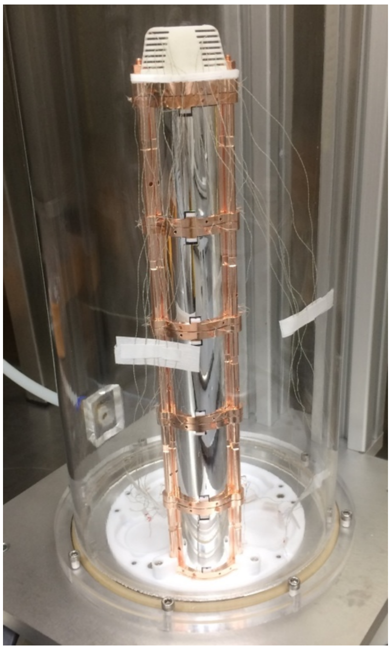

FIGURE 3.5 - FIRST TOWER COMPLETED ON 28-09-2016

3.1.1 Cleaning procedure established for the project

The previews protocol for polishing Cu OFHC CUORE and CUPID pieces consisted in 4 steps.

3.1.1.1 Pre-cleaning

Cleaning using solvents and ultrasound: suitable for coarsely remove residues due to mechanical processing, such as fats and oils processing (cleaning by means of solvents it is based on dissolution of the contaminants bringing them in solution).

In the specific case *TETRACHLOROETHYLENE* is used. Followed by rinsing in *ACETONE* and *ETHANOL* and treatment with alkaline soaps and ultrasound.

- The *TETRACHLOROETHYLENE*, or *PERCHLOROETHYLENE* (*PERC*) is an organic halide compound of formula $Cl_2C{=}CCl_2$, being an excellent solvent for organic materials. Moreover, it is volatile, highly stable, and non-flammable. For these reasons, it is widely used in dry cleaning. Recently the *International Agency for Research on Cancer* it has been classified in the Group 2A as carcinogen product, which means that it is harmful to humans[20].

- The *ACETONE* is an organic compound with the formula $(CH_3)_2CO$, being the simplest ketone; it is a colourless, volatile and flammable liquid. As a strong solvent, it may damage plastic materials and some synthetic fibres. As a heavy-duty degreaser, it is useful in the preparation of metal surface[21]. Surface treatments find important applications to degrease and remove the PERC from the copper surface.

- The *ETHYL ALCOHOL* [CH_3CH_2OH] is also widely used as a solvent, antiseptic and as a product that finds applications in many fields. It is a volatile, flammable, colourless liquid with a strong chemical odour. In cleaning process is used to dissolve the acetone from the copper surface.

The pre-cleaning process is performed rubbing the copper surface using different solvents and Texwipe - Alpha Wipe®, i.e. a special tissue. The process is carried out under fume hood, to reduce worker health impact due solvents PERC, acetone and alcohol. The Texwipe - Alpha Wipe® tissue is used since it does not leave any lint on the copper surface.

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[20] PERC," *IARC monograph,* vol. 63, p. 159, 2007

[21] Acetone, "National Institute of Standards and Technology," NIST Chemistry WebBook, 2011. [Online]. Available: http://webbook.nist.gov/cgi/cbook.cgi?ID=C67641&Mask=1

Following the applications of the three solvents mentioned above the copper pieces are cleaned in ultrasound (33 KHz) at 40 °C for 10 minutes with deionized water and NGL 17.40 P SUP®[22] powder soap. The copper parts are rinsed removing the soap and cleaned again only with deionized water at room temperature for 10 minutes. Immediately, the copper pieces are dried with alcohol and nitrogen flux.

NGL 17.40 P SP contains *SODIUM METASILICATE* and it is suitable for the micro finishing of the surface materials such as copper, titanium, steel and glass.

3.1.1.2 Tumbling or mechanical treatment

The tumbling is an abrasive technique for smoothing and polishing a rough surface when particles impact on it during a rotation, translation and inversion movements. The optimal speed of rotation depends on the size of the tumbler barrel and the materials involved. In a wet process, a compound, lubricant, or barrelling soap is added to aid the finishing process, prevent rusting, leaving the surface clean. The cleaning establishes a wet process using a special alkaline soap, called Rodaclean®, with pH 12, which contains corrosive potassium hydroxide. This soap is quite aggressive however excellent in removing attached particles, chemical residues and oxides present on the copper surface.

The tumbling barrel dimensions, the velocity of rotation, type and quantity of media, and liquid soap solution inside of the tumble barrel were given by De Biasi[23]. To obtain a uniform abrasion of the surface, the half of the tumbler barrel should be filled with the abrasive material, covered with deionized water and adding a drop of soap.

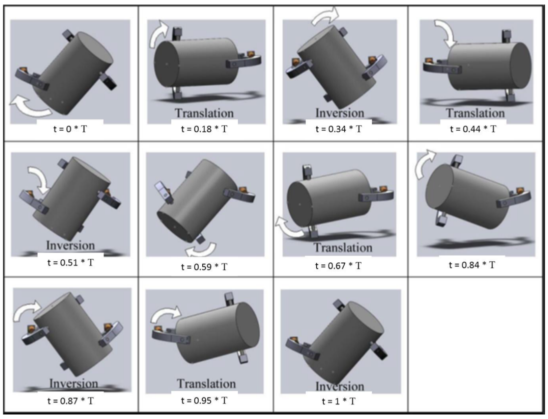

FIGURE 3.6 - BREAKDOWN OF THE TUMBLING MOTION WITH SOLIDWORKS®. (MAYER-LAIGLE, GATUMEL E BERTHINAUX 2015)

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[22] http://www.ngl-group.com/content/download/404/2383/file/Problema_I_21.02.11.pdf

[23] A. De Biasi, *Protocollo di pulizia superficiale di contaminanti radioattivi in ultratraccia sui componenti in rame per l'esperimento Cryogenic Underground Observatory for Rare Events (CUORE),* Surface Treatments for Industrial Application, INFN-LNL, 2007-2008

3.1.1.3 Chemical Etching – Ammonium Persulfate

Some delicate parts cannot undergo the tumbling process, due to their fragility and small thickness (< 1 mm). The wire trays can be bent or damaged during the tumbling process, losing their mechanical and structural function. Nevertheless, the surface must be prepared for the electropolishing process, therefore, they are chemically treated with *AMMONIUM PERSULFATE* at a concentration of 20 [g/l] for 2 hours @ RT.

For more details on *AMMONIUM PERSULFATE* see section 2.2.2

3.1.1.4 Electropolishing

The electropolishing is a critical phase to obtain good metal surface characteristics, in terms of reduction of radioactive contaminants. This process is set up to remove a surface layer of 100 µm for CUORE pieces and 50 µm for CUPID objects. The electropolishing is performed following the next steps:

1. The Teflon® protections are fixed to the copper pieces;
2. The copper pieces are connected to the positive terminal of a DC power supply;
3. The cathode is connected to the negative terminal of a DC power supply;
4. The tank is filled with electrochemical solution (40% of BUTANOL - 60% of PHOSPHORIC ACID) through a pumping system;
5. The copper pieces are placed inside the electrochemical solution following a configuration studied anode – cathode for each type of copper piece;
6. The power supply is turned on and the potential difference for optimal electropolishing process is found;
7. The stirring of the EP solution is turned on, if necessary;
8. The charge [c] required to remove the calculated thickness;
9. All the parameters along the electropolishing process and the copper surface quality are controlled;
10. The copper pieces are rinsed for at least 5 minutes with deionized water;
11. The Teflon® protections are removed;
12. The copper pieces are immersed in ultrasonic cleaning with Rodaclean® soap to remove and neutralize the residual electropolishing solution for 10 min;
13. The copper pieces are washed again in US with deionized water for 10 min.

14. The copper pieces are rinsed in ethanol, dried with nitrogen and packaged in a single PA/PE bags under vacuum.

The EP solution was changed with fresh one every three process cycles.

To perform the electropolishing process a chemical plant was used, specially designed for this aim. The chemical plant is composed of 4 tanks (see Figure 3.7). Each tank is equipped with doors that open automatically, heaters and plastics tubes for filling and draining the chemical solution. A toothed belt provides the movement of the copper pieces in two axes "X" and "Z". The pumping process of the chemical solutions is executed by 2 pneumatic diaphragm pumps. The aspiration of vapours is composed of 4 points above each tank, plus one aspiration point directly over the copper samples.

The electropolishing process is performed in the tank 1. The tank of PVDF (POLYVINYLIDENE FLUORIDE) with a capacity of 70 L, is ideal for the electropolishing solution of copper, due to its chemical resistance. The process of filling and draining the electropolishing solution is performed with all the caution necessary to prevent the risk of acid splashing.

The tank 2 is used to rinse the copper pieces in deionized water after electropolishing completion. This tank has got a capacity of 90 L and it is made of 316 stainless steel due to its resistance to acidic water. The waste of acid water is disposed into an external waste tank.

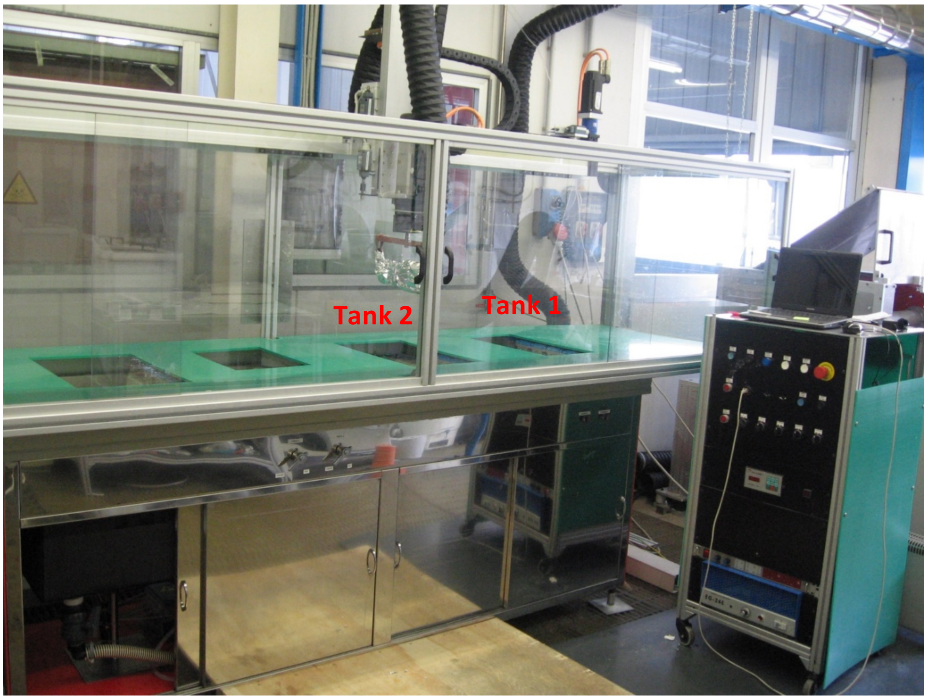
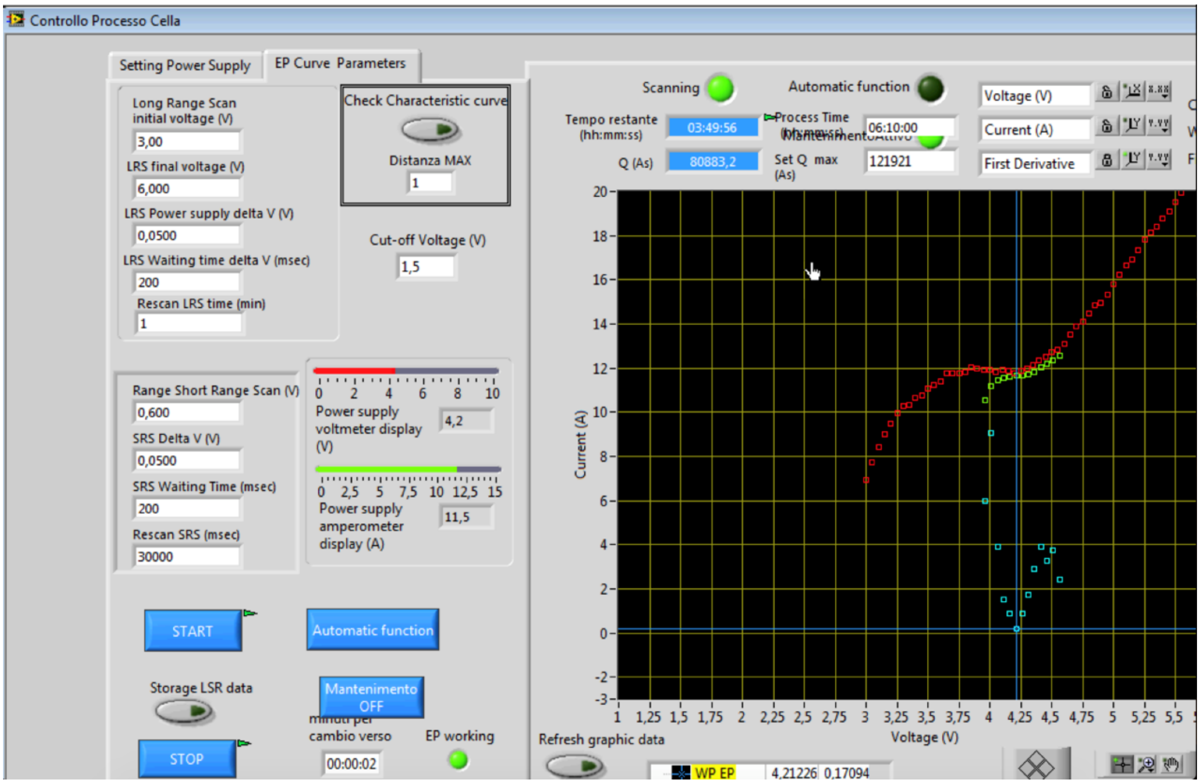


FIGURE 3.7 – CHEMICAL PLANT AVALIABLE @INFN-LNL, "CHIMICA ALPI" LAB.

To find the optimal parameters to automatize the electropolishing process, the software LabVIEW® 7.1 was used. This software is connected to a DC power supply; it allows to set and control via PC all the parameters related to I-V curve of the electropolishing, as well as to control the movements of the copper pieces in the chemical plant. If necessary, it is possible to control everything manually with the control panel rather than the computer. Figure 3.8 shows the panel to set up the "*Electropolishing Curve Parameters*".

Initially, a LONG RANGE SCAN (LRS) is performed, selecting the initial and final voltage of the scan, the distance and time between the points of red curve (see Figure 3.8). After the LONG RANGE SCAN, the LabVIEW® software calculates the first derivative, f′(x) = 0, and selects the voltage corresponding to the derivative minimum value, f′′ (x) > 0. From now, the software uses the data in SHORT RANGE SCAN to find the appropriate potential difference for optimal voltage, V_c. Figure 3.8 illustrates the red curve obtained by the parameters of LONG RANGE SCAN, while the green curve represents the SHORT RANGE SCAN defining the voltage (V_c).



Long Range Scan initial voltage (V): 3,00
LRS final voltage (V): 6,000
LRS Power supply delta V (V): 0,0500
LRS Waiting time delta V (msec): 200
Rescan LRS time (min): 1
Distanza MAX: 1
Cut-off Voltage (V): 1,5
Range Short Range Scan (V): 0,600
SRS Delta V (V): 0,0500
SRS Waiting Time (msec): 200
Rescan SRS (msec): 30000
Power supply voltmeter display (V): 4,2
Power supply amperometer display (A): 11,5
minuti per cambio verso: 00:00:02
Tempo restante (hh:mm:ss): 03:49:56
Process Time (hh:mm:ss): 06:10:00
Q (As): 80883,2
Set Q max (As): 121921
4,21226 0,17094

FIGURE 3.8 – AUTOMATED ELECTROPOLISHING PROGRAM

With this software it is also possible to set up the total electric charge, Q, calculated using Faraday's law of electrolysis[24]:

1. *The mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at that electrode. Quantity of electricity refers to the quantity of electrical charge, typically measured in coulomb.*

2. *For a given quantity of DC electricity (electric charge), the mass of an elemental material altered at an electrode is directly proportional to the element's equivalent weight*. The equivalent weight of a substance is equal to its molar mass divided by the change in oxidation state it undergoes upon electrolysis (often equal to its charge or valence).

Faraday's laws can be summarized by the following expression:

$$m = \left(\frac{Q}{F}\right) \cdot \left(\frac{M}{z}\right)$$

Where:

- m is the mass of the substance liberated at an electrode in grams,
- Q is the total electric charge passed through the substance in coulombs,
- F = 96485 C·mol^{-1} is the Faraday constant
- $\left(\frac{M}{z}\right)$ is the equivalent weight, E_w, in g/equivalent. In this case E_w = 31.8 [g/eq]

Substituting the mass of the substance liberated at an electrode, **m**, by the density **ρ** and volume of the removed material **V**, $\boldsymbol{m = \rho \cdot V}$, and in turn, the volume of removed material is the surface layer thick removed, **h**, times the area of the copper surface, **A**, $\boldsymbol{V = h \cdot A}$, the following mathematical expression in function of the total electric charge **Q** is obtained:

$$Q = \frac{h \cdot A \cdot \rho \cdot F}{E_w}$$

Calculation of current charge is obtained using an Excel® Table like the following:

Frame	**A** [mm^2]	**ρ** [g/mm^3]	**h** [mm]	**n° pieces**	**Q_{TOT}** [A·s]

TABLE 3.1

The Area of each piece is calculated using SolidWorks®. When the copper pieces reach the current charge Q calculated to remove the surface layer thick desired, the LabVIEW® program stops the electropolishing process.

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[24] N. V. Suryanarayana, *Utilisation of Electric Power: Including Electric Drives and Electric Traction*, New Delhi, New Age International Publishers, 2005, p. 118.

3.1.1.5 Chemical Polishing – SUBU

The chemical polishing is applied to reduce the radioactive contaminants from the areas screened with the Teflon® protections and to enhance the shiny appearance of the surface. This cleaning step, it was found an erosion rate of 2 μm/min, which means 10 μm removed thickness during the 5 minutes of treatment.

The SUBU process is performed following the steps hereby described:

1. The deionized water is heated at (72±4) [°C] in water baker under hood
2. The powders which compound the recipe (sulfamic acid, ammonium citrate) are weighed [g]
3. The liquids of the recipe (oxygenated water 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 [20g/L] to perform the passivation of the copper surface after SUBU
6. The SUBU solution is prepared once the bath temperature reaches (72±4) °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;

3.1.1.6 Passivation

Immediately after SUBU process it is necessary to passivate the copper surface because it is completely reactive with the environment so that a layer protection avoids the fast oxidation and recontamination of the surface. So:

9. After the SUBU process, the copper pieces are passivated in a solution of sulfamic acid 20 g/L for 5 minutes @ RT;
10. The copper pieces are immersed in ultrasonic cleaning with Rodaclean® soap to remove and neutralize the residual solution for 5 min @ RT;
11. The copper pieces are washed again in US with deionized water for 10 min.
12. The copper pieces are rinsed in ethanol, dried with nitrogen and packaged in a double PA/PE bags under vacuum.

3.1.1.7 Plasma Cleaning

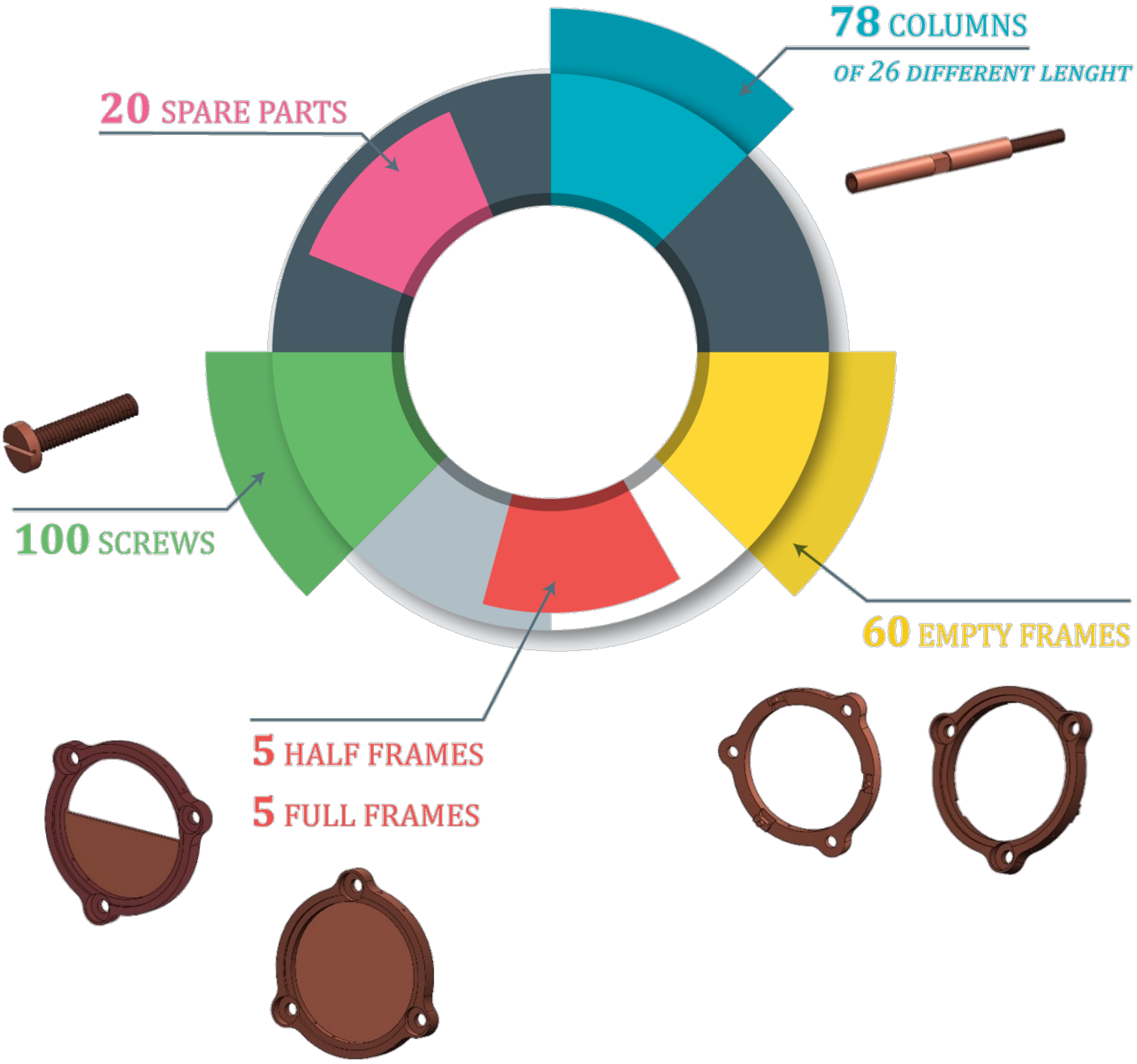
The plasma cleaning constitutes an important step because it is carried out in a vacuum system and is the last phase before the assembly of the towers (nothing is cleaner that vacuum systems). The erosion rate during plasma cleaning is around 1 m·h^{-1}. The copper components are positioned in special stainless chambers where the air is pumped by a system composed by a scroll and a turbo molecular pumps. The scroll pump is a dry pump allowing to reach a 10^{-3} mbar, while the turbo molecular pump is a magnetic levitation pump that reaches 10^{-10} mbar. This system was selected to avoid any trace of oil from the pumps. The system reaches a pressure of ~10^{-7} mbar, but to reduce this pressure, it is necessary to increase the temperature of the chamber around 100°C to degas adsorbed chemical substances in the inner walls of the chamber and copper components. After 12 hours of baking, the pressure reaches ~1x10^{-8} mbar. Metal surface mostly retains water, hydrogen, nitrogen and oxygen.

The procedure for plasma cleaning of the copper components follows these steps:

1. The copper pieces are fixed on the sample holder inside of a class 100 cleanroom. There is a different sample holder for each kind of component.
2. The holder is placed into the vacuum chamber using a crane. The chamber is in another class 1000 cleanroom. The cleanroom allows to handle the copper pieces in a controlled environment with low level of pollutants, such as dust and airborne microbes.
3. The chamber is pumped and baked out until it reaches a base pressure of 1x10^{-8} mbar.
4. The argon gas is fluxed using a leak valve.
5. DC current is applied into the external coil to generate a uniform magnetic field of 1.5x10^{-2} [T].
6. The electrical connections are performed in order to apply 30 watts during 5 minutes.
7. The system is cooled, stopping the pumping system, closing all the gates of the chamber and fluxing argon gas until the pressure of 10 mbar.
8. The copper pieces are transported again inside of the class 100 cleanroom, to be packaged using three PA/PE bags under vacuum. In turn, the bags are placed into plastic box under vacuum and delivered to the Gran Sasso Laboratory. Here the boxes are preserved inside the mountain, specifically, in a Part Storage Area (PSA), a room continuously kept under nitrogen flux. This accurate preservation of the copper parts reduces the possibility of recontamination from the environment.

3.2. EXPERIMENTAL SECTION

3.2.1 Materials Processed



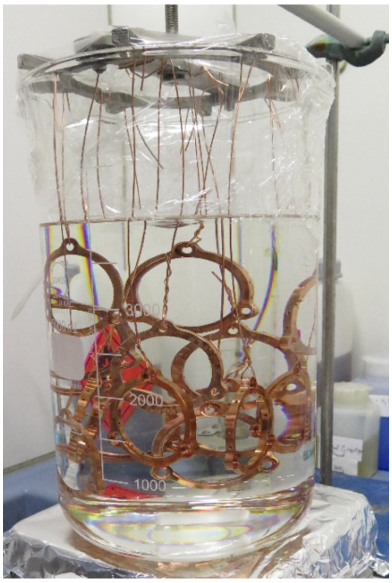
3.2.2 Methods & Problem Solving

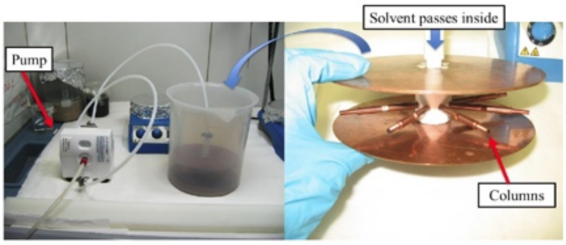
3.2.2.1 Pre Cleaning

Because of the difficulty of reaching with the alpha wipe some delicate areas of the frame, these are dipped in tetrachloroethylene @40°C for at least 2h under vigorous agitation, in order to ensure an effective degreasing.

After that the piece were usually cleaned like above.

Small holes were purged with the solution under pressure using a wash bottle.

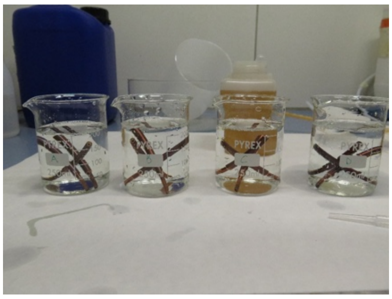


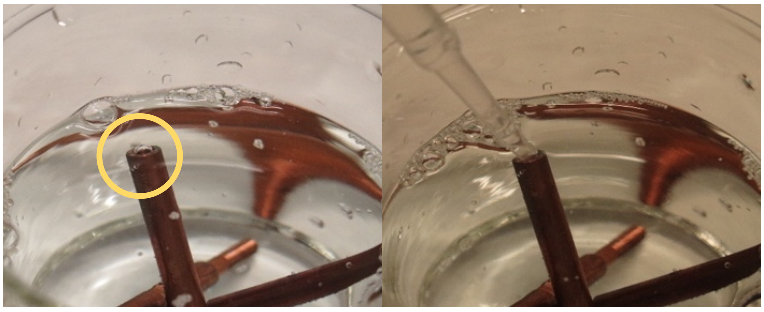


To remove the oil from mechanical machining, within the internal thread of the columns, it was constructed by A. Camacho a circular holder made of Teflon ®, inside which the PERC is pumped[25].

One of the main problems handling CUPIDs columns was to keep them separate by length.

To do this, each bench has been marked and treated separately. This cost a huge amount of time.





In order to eliminate the bubbles formed in the thread, the cleaning solution was taken and pushed inside by a pipette.

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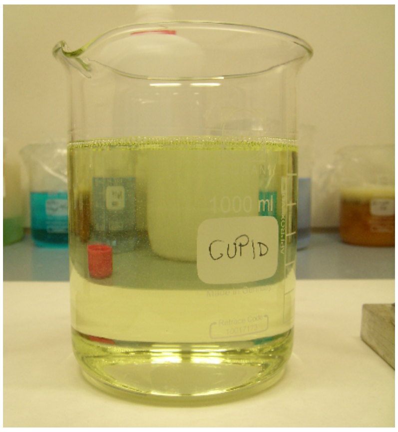
[25] A. Camacho, *Estudio y mejoras del proceso de descontaminación radiactiva de los componentes de detección del experimento CUORE,* 2016

3.2.2.2 Electropolishing

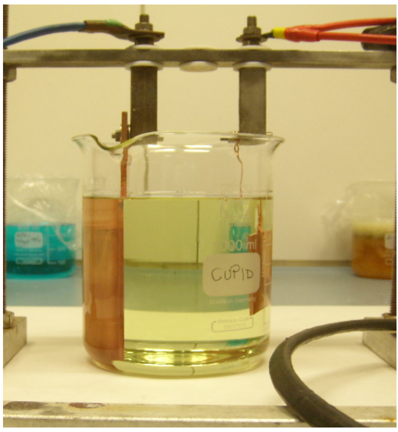
This was one of the most critical aspects.

The first issue with this step was the possible contamination of the electrolyte solution. In fact, during the tank refill with the TITOLCHIMICA mixture of phosphoric/butanol, it was noted that the solution had a yellowish glare. Suspecting a contamination of the solution, some tests were performed.

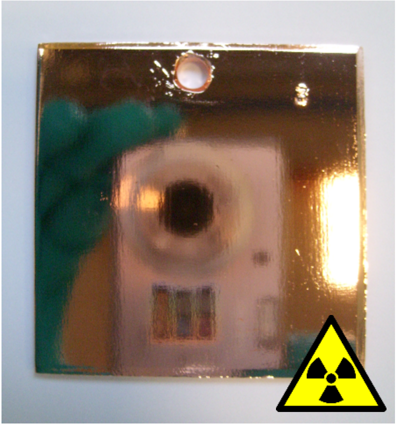
Two identical square of Cu OFHC were treated as usually (cleaning and ammonium persulfate), and then electropolished separately.



Suspect Contaminated Solution from TITOLCHIMICA



Test Electropolishing



The sample sent to Milan for the analysis revealed the presence of traces of ^{210}Po

At the same time, the same thing have been done with the solution from LABOCHIMICA and the sample electropolished with this solution results with no traces of residual contamination.

After that it was decided to empty the tank from the TITOLCHIMICA solution, clean accurately everything with demi water, dry the tank and refil with fresh transparent solution

Another problem that came up, was during the frames electropolishing.

In Figure 3.9 there is the sheme of the frames holder. Every component is made of teflon (except for the frame).

As it can be seen, the teflon screw that fix the frame to the structure, exceed the dimension of the hole. This caused a not uniform electropolishing due to the fact that neither the solution nor the electric field can reach the surface covered by the teflon. As consequence a circular step appeared around the hole. Since this is the point where the columns would have been mounted, there was a risk of misalignment of the tower.

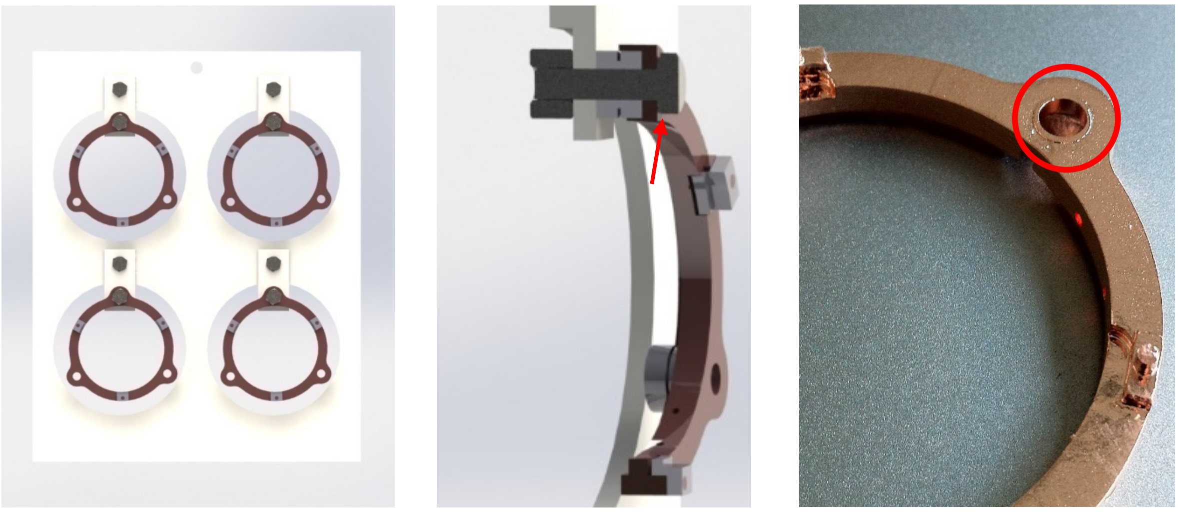

a b c

FIGURE 3.9 – (a) TEFLON FRAMES HOLDER. (b) PART OF THE FRAME COVERED BY THE SCREW. (c) PART NOT ELECTROPOLISHED. THIS DISK IS 50 µm HIGHER, AND THIS MAY CAUSE A MISMATCH DURING THE MAUNTING OF THE TOWER.

The solution proposed is shown in Figure 3.10, and the result in Figure 3.11. With this arrangement, both solution and electric field can reach every part of the surface.

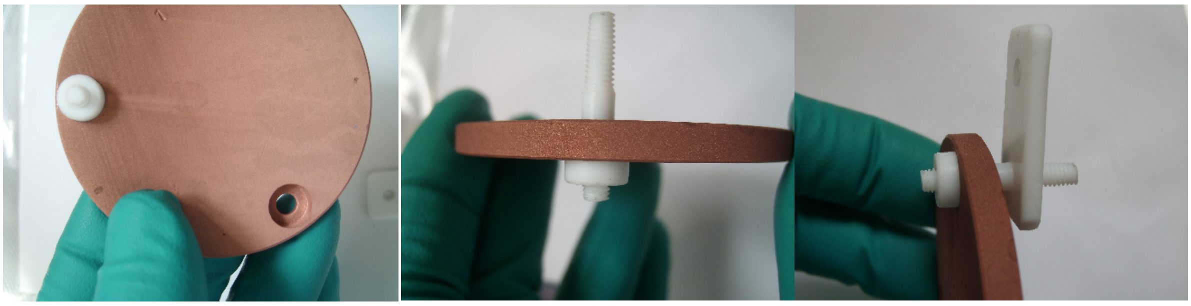

a b c

FIGURE 3.10 – NEW HOLDING SYSTEM. (a) FRONT VIEW. (b) AND (c) LATERAL VIEWS

FIGURE 3.11 – FINAL RESULT AFTER ELECTROCHEMISTRY WITH THE NEW HOLDING SYSTEM. THE SURFACE IS UNIFORM AND WITHOUT ANY STEP

Otherwise there were some thin part that had to be preserved from the electrochemical polishing. In Figure 3.12 are shown the teflon protection on the three back pins and in the front holes.

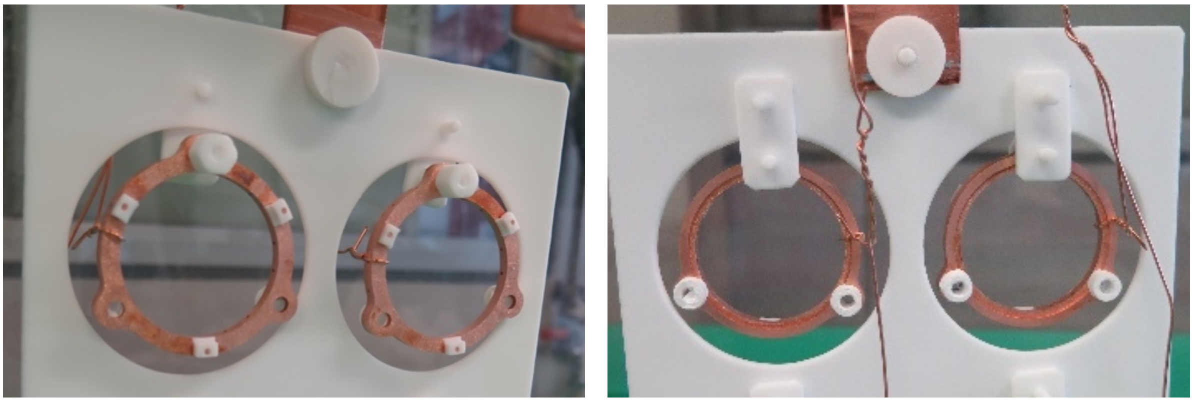


FIGURE 3.12 – FRAMES BEFORE EP WITH THE TEFLON PROTECTIONS

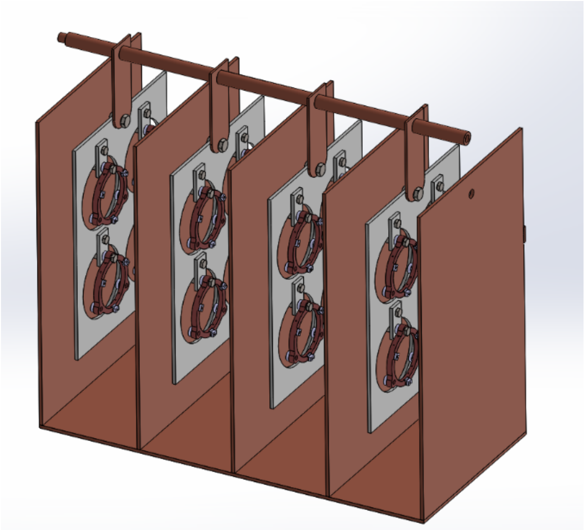
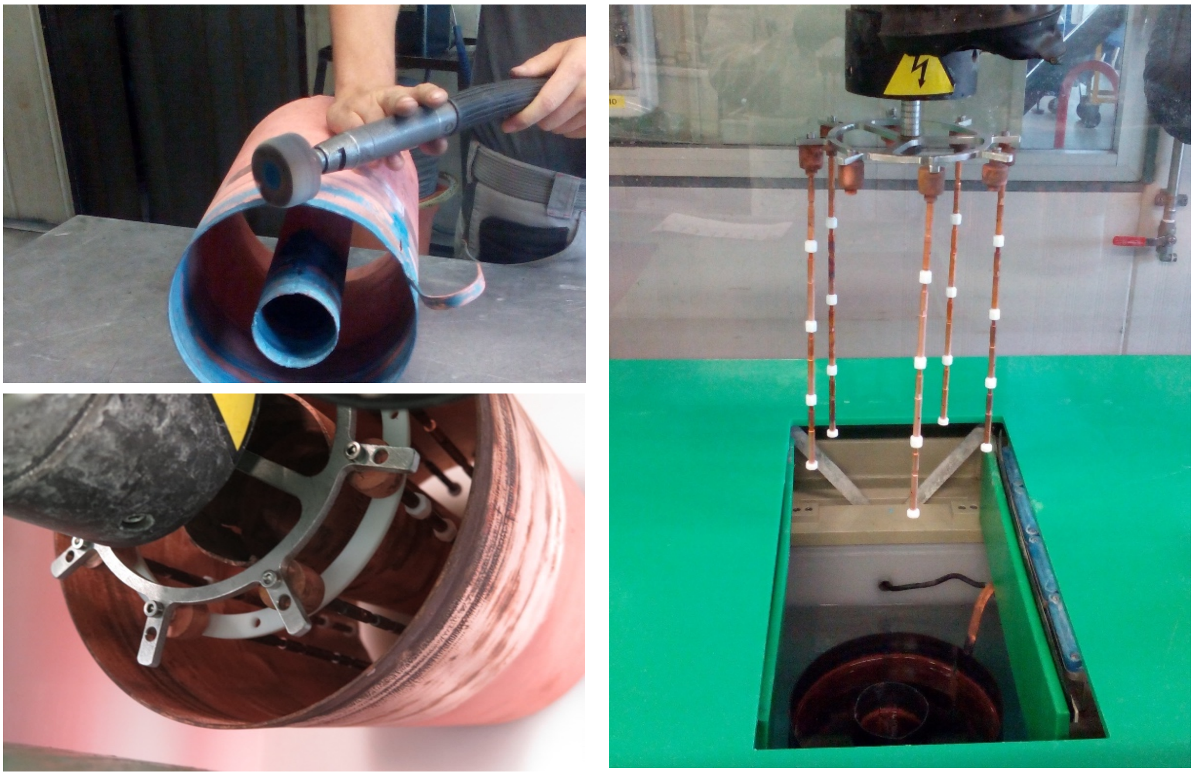


FIGURE 3.13 – COMPLETE APPARATUS FOR EP OF A BANCH OF 16 FRAMES.

To process the columns, the same cylindrical cathode employed for CUORE has been used. Since it was not used for some time, it had a thick scale of copper pyrophosphate [$Cu_2P_2O_7$]. the simplest way to remove this layer is mechanically by brushing with sandpaper [Figure 3.14]. Before to use, it was washed in an ultrasonic cleaner with GP 17.40 SUP to remove any trace of machining.



a

b

Figure 3.14 – Cylindrical Cathode used to process (a) during mechanical treatment, (b) just before EP. Fillets of the columns were protected by teflon bolts.

4. APPLICATION IN 6 GHZ CAVITIES FOR NIOBIUM SPUTTERING

In the past 50 years, electron-positron collisions have played a central role in the discovery and detailed investigation of new elementary particles and their interactions. ***S**uperconducting **R**adio **F**requency (**SRF**)* are resonating cavity that can provide high acceleration gradients[26], indispensables to this kind of studies.

The international ***TESLA** – **T**eV-**E**nergy **S**uperconducting **L**inear **A**ccelerator* project uses nine-cell 1.3 GHz niobium cavities [Figure 4.1], which reduce the cost per MeV by increasing the operating accelerating gradient by a factor of five from 5 MV/m to 25 MV/m, and reducing the cost per meter of the complete accelerating module by a factor of four for large-scale production[27].

Advantages of SRF cavities for accelerators are well known and a large number of 9-cells TESLA cavities is needed for the International Linear Collider (ILC). The fabrication of these cavities using the traditional way will cost much time and expensive. The spinning technology for seamless cavities invented in INFN-LNL is an answer for this challenge.

1.3 GHz SRF cavities still remain too large and expensive to do R&D on them, however, 6 GHz spun seamless SRF cavities are a very useful tool for testing alternative surface treatments in the fabrication of TESLA cavity. Anyway, the spinning technique has also some drawbacks like contamination, surface damage in internal part due to the collapsible mandrel line. Nevertheless, using this technology not only multi-cell 1.3 GHz resonators but also the 6 GHz cavity can be produced.

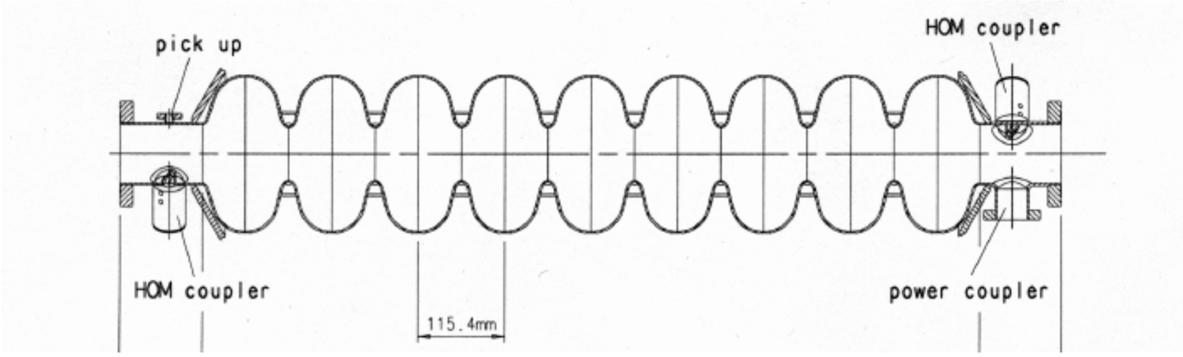


FIGURE 4.1 - 9 CELLS 1.3 GHZ SRF CAVITY

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[26] H. Padamsee, *RF Superconductivity for Accelerators*, John Wiley & Sons, Plenum Press, San Diego, 1998.

[27] International linear collider reference design report, *ILC global design effort and world wide study*, August, 2007

4.1 STANDARD FABRICATION TECHNIQUE[28]

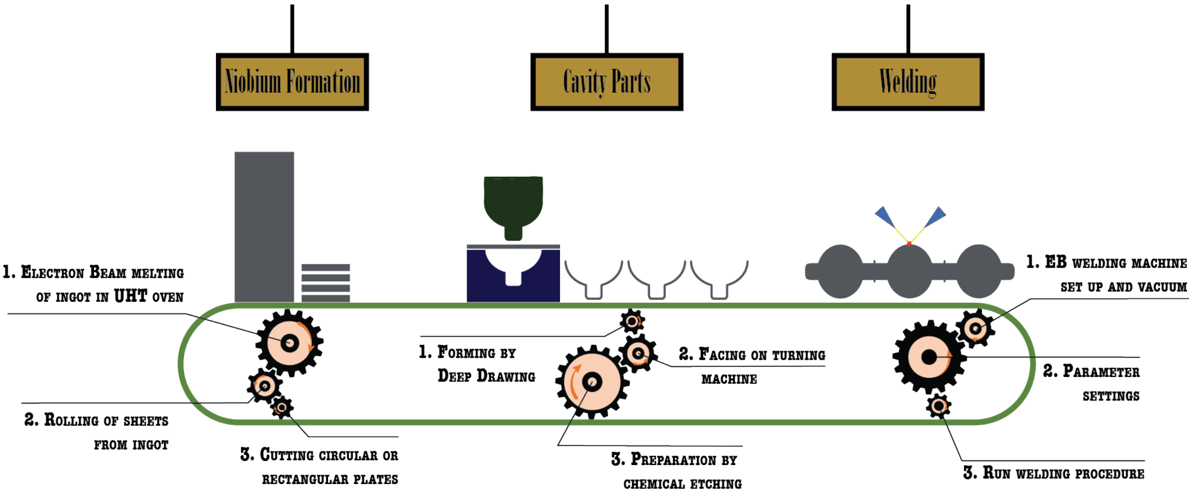

FIGURE 4.2 - INFOGRAPHIC SCHEME OF 9 CELL CAVITIES PRODUCTION

4.1.1 Fabrication of Niobium

First requirement of SRF cavities is that niobium of high purity is needed. Among the interstitially dissolved impurities, oxygen is dominant due to the high affinity of Nb for O_2 above 200°C. Interstitial atoms act as scattering centres for the unpaired electrons and reduce the RRR and the thermal conductivity. So the niobium ingot is highly purified by several melting steps in a high vacuum electron beam furnace. This procedure reduces the interstitial oxygen, nitrogen, and carbon contamination to a few ppm.

After forging and sheet rolling, the 2.8 mm thick Nb sheets are degreased, a 5 µm surface layer is removed by etching, and then the sheets are annealed for 1-2h at 700°C-800°C in a vacuum oven at a pressure of 10^{-5}-10^{-6} mbar to achieve full recrystallization and a uniform grain size of about 50 µm.

4.1.2 Cavity Forming

The 9-cell resonators are made from 2.8 mm thick sheet niobium by deep drawing of half-cells, followed by trimming and electron beam welding.

Deep drawing is a sheet metal forming process in which a sheet metal blank is radially drawn into a forming die by the mechanical action of a punch [Figure 4.3]

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[28] H. Padamsee - *RF Superconductivity Science, Technology and Applications*

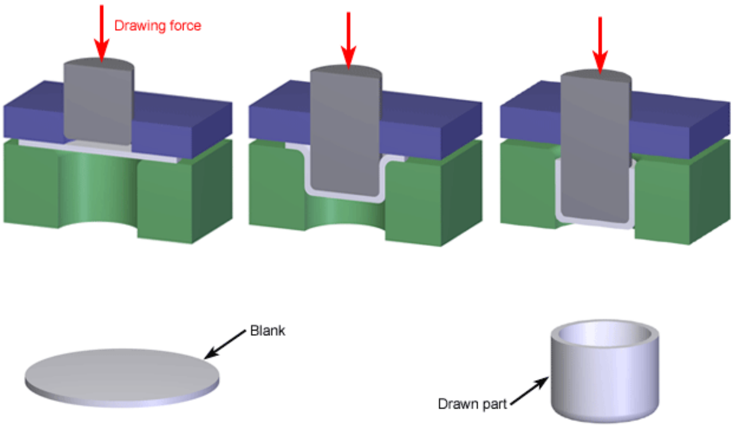

FIGURE 4.3 - DEEP DRAWING SCHEME

Lubricants are used to reduce friction between the working material and the punch and die. They also aid in removing the part from the punch.

4.1.3 Welding

Two cups are then joined at the iris with an EB weld to form a "dumbbell." Since niobium is a strong getter material for oxygen, it is important to carry out the EB welds in a sufficiently good vacuum.

The next step is the welding of the stiffening ring. After proper cleaning by a 30µm etching, the dumbbells are visually inspected. Defects and foreign material imprints from previous fabrication steps are removed by grinding. After the inspection and proper cleaning (a few µm etching followed by ultraclean water rinsing and clean room drying), eight dumbbells and two beam-pipe sections with attached end cups are stacked in a precise fixture to carry out the equator welds which are done from the outside. The completed cavity has both internal and external chemistry to further remove the damage layer from the fabrication steps of both welding and handling.

4.1.4 Disadvantages and limitation

The two primary issues with cavity fabrication are quality assurance on the niobium materials and on the electron beam welds. Niobium materials must be scanned to detect and eliminate surface defects, and then protected with care throughout the manufacturing process. Welds must have a smooth under bead and form no surface irregularities, in particular, sharp edges where the weld puddle meets the bulk material. Defects in the equator welds will limit the gradient by thermal quenches due to the high magnetic fields there. Thermal mapping of quench locations suggests that they are typically located at or near the equator region.

Cavity fabrication by electron-beam welding of deep-drawn half-cells is a delicate procedure, requiring intermediate cleaning steps and a careful choice of the weld parameters to achieve full penetration of the joints. First, two half cells are connected at the iris; the stiffening rings are welded in next. At this point weld shrinkage may lead to a slight distortion of the cell shape which needs to be corrected. Particularly critical are the equator welds, which are made from the outside, and a reliable method for obtaining a smooth weld seam at the inner cavity surface was required.

4.2 SEAMLESS CAVITIES

20,000 nine-cell resonators would be required for the ILC[29]. A great many physicists believe that a so huge amount of resonators could not be manufactural using the standard fabrication technique[30], and the bare bulk Niobium cavity costs roughly include material costs and fabrication costs. 500 tons of high purity Niobium will be need; the procedure of EB welding is very complicated as described in the previous section and long-time costs. For this reason, there is a trend to research on alternative fabrication technology[31]. At the same time the substitution of bulk Nb with sputtered niobium on a copper substrate is very attractive.

At the National Institute of Nuclear Physics in Legnaro (INFN-LNL) the well-known spinning technique has been adapted to form a fully seamless resonator without electron beam welding[32]. 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.

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[29] *International linear collider reference design report*, ILC global design effort and worldwide study, August 2007

[30] V. Palmieri, *Seamless Cavities: the most creative topic in RF Superconductivity*, 8th Workshop on RF Superconductivity, Abano Terme (Italy), October 1999.

[31] V. Palmieri, Advancements on spinning of seamless multi-cell reentrant cavities, Proc of the 11th Workshop on RF Superconductivity SRF2003.8-12 September 2003, Luebeck, Germany, TuP26.

[32] V. Palmieri, R. Preciso, V.L. Ruzinov, S.Yu. Stark, S. Gambalonga, *Forming of seamless high beta accelerating cavities By the spinning technique*, Nuclear Instruments and Methods in Physics Research A342 (1994) 353-356, North-Holland

Both 1.3 GHz niobium and copper cavities can be easily manufactured with high reproducibility and significant savings in manufacture costs.

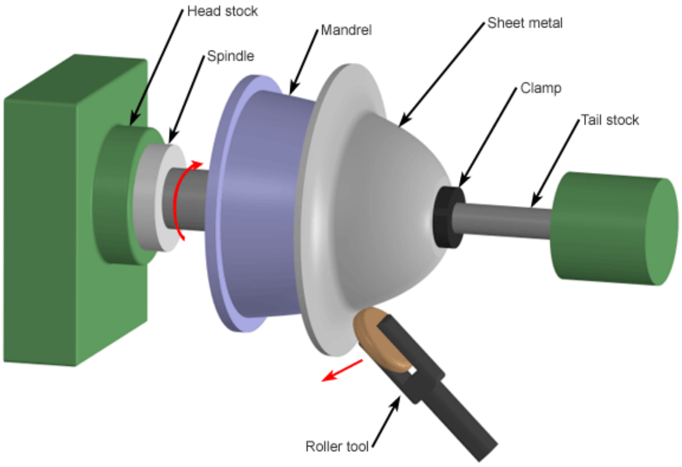

FIGURE 4.4 - SPINNING METHOD

Spinning of a seamless mono-cell resonator from a circular blank is depicted on Figure 4.4. The process is mainly divided in four steps[33]:

A. a circular disk of 400 mm diameter and 3 mm thickness is first 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.

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[33] P. Kneisel, V. Palmieri, K. Saito, “*Development of Seamless Niobium Cavities for Accelerator Application*”, Proceedings of the 1999 IEEE Particle Accelerator Conference. 29 Mar - 2 Apr 1999, New York, New York. 18th IEEE Particle Accelerator Conference, p.943-945

4.3 6 GHZ CAVITIES

The R.F. characterization of samples is a useful diagnostic tool to accurately investigate local properties of superconducting materials. However, the most common limitation of such a system, consists often in the difficulty of scaling the measured results to the real resonator. Using 1.3/1.5 GHz resonant structures cavities is obviously the most direct way, but would be too onerous both for the material cost and the cryogenic expense. Instead, the micro-cavities that completely equal in shape to the real scale model would be the best and most direct way for measuring material R.F. properties.

Using the spinning technique, it becomes feasible to produce small scale resonators in little time, negligible cost and in large quantity.

In INFN-LNL, large number of 6 GHz cavities made of Niobium, Cooper, Lead, even Iron [Figure 4.5] 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.

FIGURE 4.5 – FROM LEFT: NB, NB, CU, FE, PB

4.3.1 Advantages of 6 GHz cavities

6 GHz cavities are made from the remaining material of larger cavities fabrication using spinning technology, they don’t need welding (even for flanges) and finally 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.

With a tool 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 tests real cavities. It is also possible to study new thin film superconducting materials grown for example by sputtering or thermal diffusion.

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

- no welding
- short fabrication 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

4.3.2 Drawback

The die has exactly the same shape of the cavity interior, composed of three collapsible mandrels is used to guide the material when spinning.

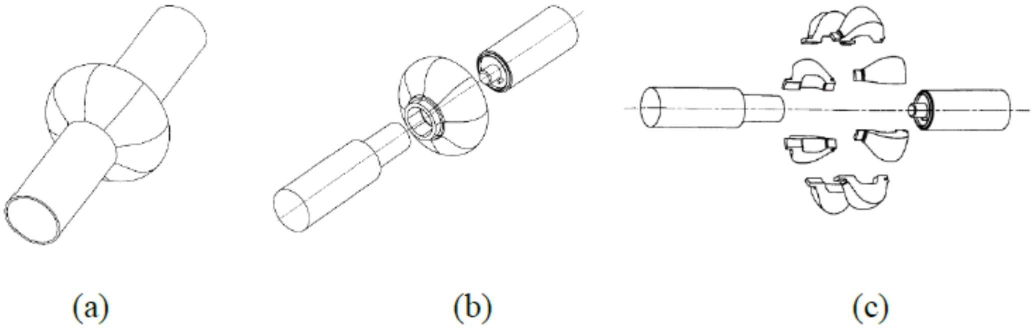

FIGURE 4.6 - SCHEME OF MANDREL USE TO SPINNING CAVITIES

Originally the central mandrel was Nylon shell, which composed of eight sectors [Figure 4.6(c)], locked together by the two steel cylinders. Pure motor oil is used as the lubricant between the die and resonator.

The main problem with this system is the evident vertical scratches [see Figure 4.7] were extruded in the inner surface of the cavity due to the using central mandrel.

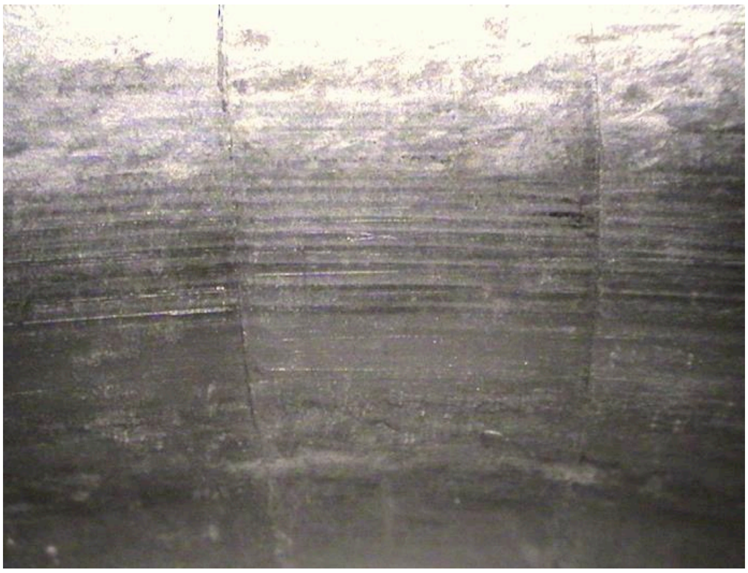

FIGURE 4.7 - VERTICAL SCRATCHES DUE TO THE MANDREL SECTORS IN A NB CAVITY.

4.3.3 Development of new mandrel

A possible solution to this problem is to use a low melting point alloy. The one actually used is called ONION'S and is a special alloy made of Pb:Bi:Sn that melt at 138°C[34]. The alloy ingot is melted in a preformed crucible [Figure 4.8], extracted, processed with precision lathe and then used as mandrel to spin the cavity.

FIGURE 4.8 - MOLTEN ALLOY POURED INTO THE MOLD

In order to remove the alloy from inside [Figure 4.9 (a)], it is melt at 140°C. Since Nb, or Cu OFHC are used, we have to prevent the oxidation, so oil is employed as heating bath. Not all oils can however be used, for example silicone fluids are absolutely to be avoided since irreparably contamination of the surface of the cavity and may also be trapped in the alloy ONION'S degrading its characteristics. So the choice of the oil to use in these preliminary tests was: olive oil and seeds oil. They both are cheap, with a smoke point up to 160°C and a density between 0,91 – 0,93 g/cm^3. Furthermore, they are not toxics, and easily removable.

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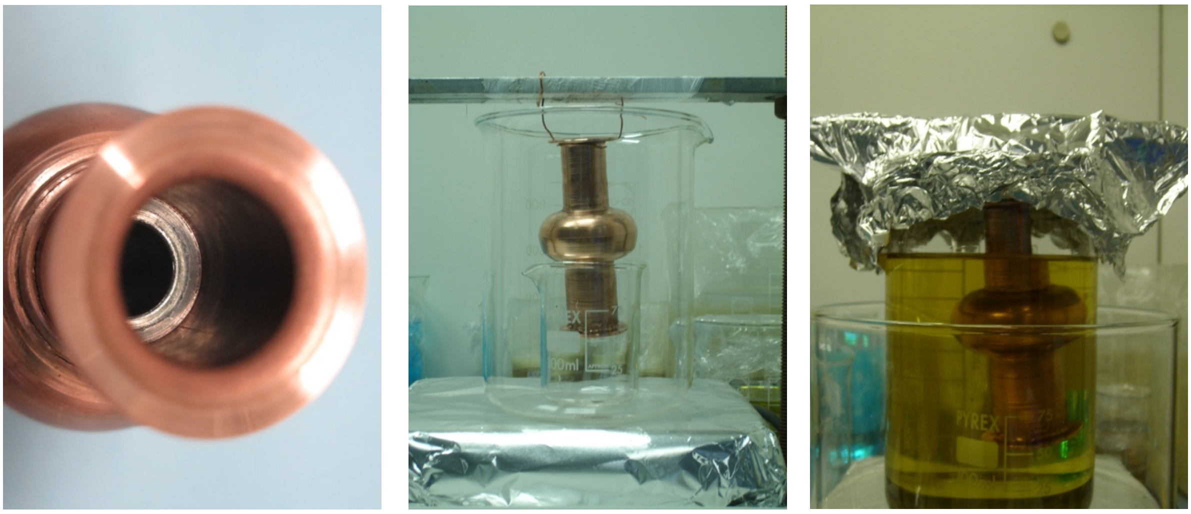
[34] William B. Jensen, *Onion's Fusible Alloy*, J. Chem. Educ., 2010, 87, 1050-1051



(a) (b) (c)

Figure 4.9 – (a) view of the mold inside the cavity; (b) simple extraction apparatus formed by two baker placed on a hot plate and (c) filled with oil.

Figure 4.10 – once melted, it was impossible to remove the alloy from the baker. So it was melted again inside the glass (left) and, after that, a teflon sheet was placed around the inner walls of the baker and left cool down. With this trick it was tossible to extract the alloy from the baker (right)

To quickly recover the ONION bar, another way to melt the mold was investigated.

A stainless steel melting pot was connected to a heater band powered by a Variac [Figure 4.11].

Increasing the current circulating inside the heater there is the possibility to control the temperature of the system. Unfortunately, there was not the ability to connect the Variac to an automatic control system that regulates the current loop as function of the temperature of the thermo band. In addition to this, the high coefficient of thermal diffusion of the steel has made it very difficult to evaluate the temperature of the oil bath inside the cavity. In fact, once it reaches 140°C the potentiometer has been turned off, but probably the outer walls of the steel cylinder were much hotter and continued to heat the oil to a temperature of about 190-200°C.

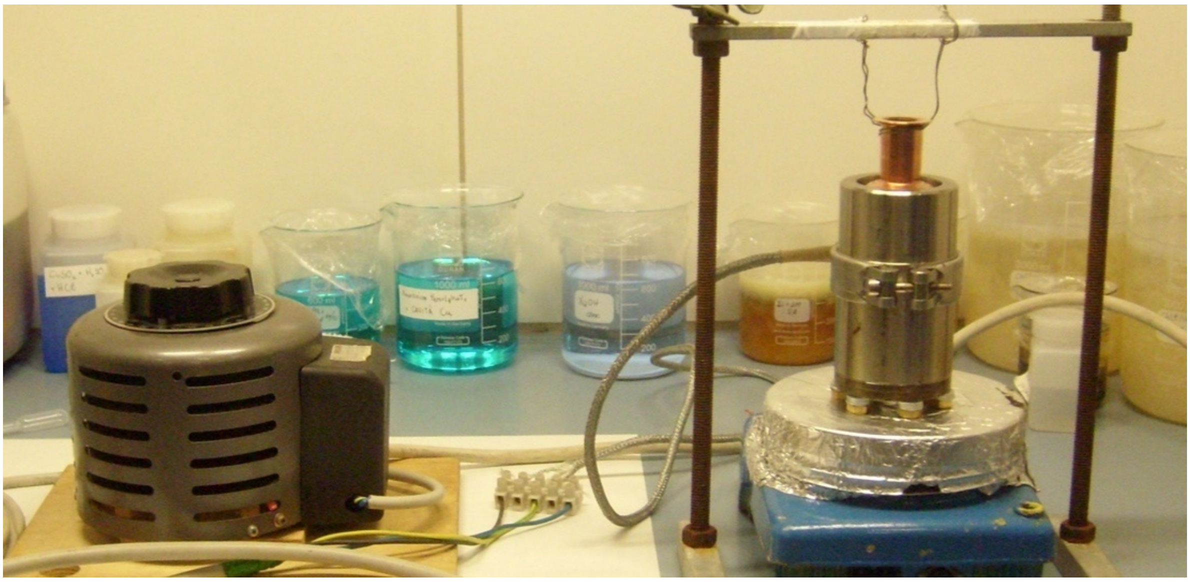
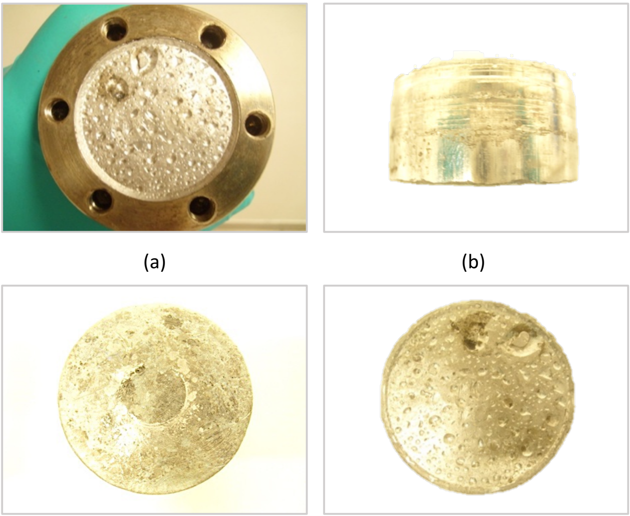


Figure 4.11

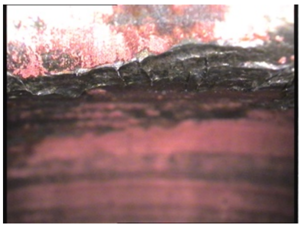


(a) (b)

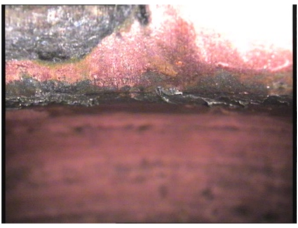
(c) (d)

Figure 4.12 – Once solidified the alloy was removed from the cylinder by an hydraulic press. On the bottom is clearly visible a “bubble texture” (a-d) probably due to the high temperature reached. (b) Lateral view. (c) Top view.

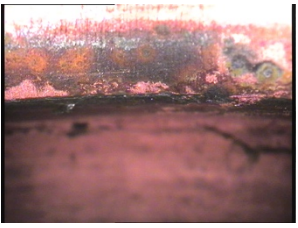
To see what had happened inside the cavity a dental camera was used. Below is clearly visible that the alloy diffused inside the copper as suspected.



down 0°

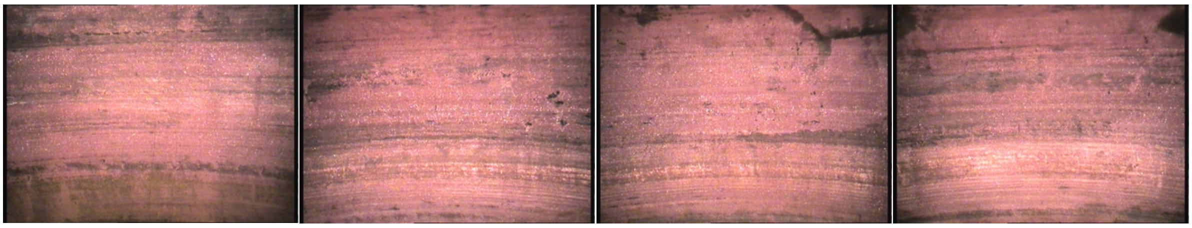


down 90°

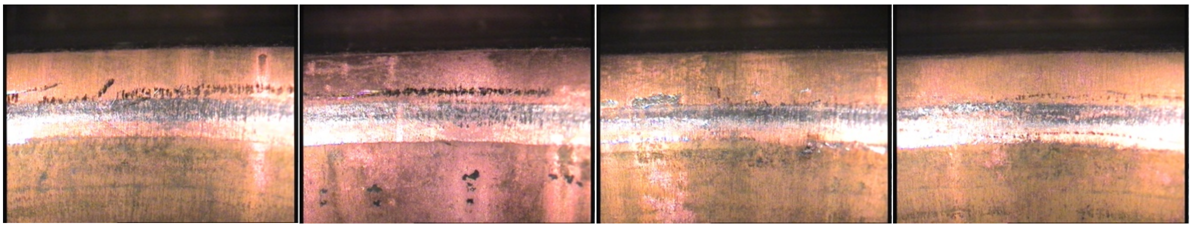


down 180°

down 270°



CENTER 0° CENTER 90° CENTER 180° CENTER 270°



UP 0° UP 90° UP 180° UP 270°

It is then returned to a system constituted by an oil bath heated by a heating plate controlled by a thermocouple. Instead of the steel cylinder, heavy and difficult to handle, especially if covered with oil, was used directly the aluminium mold of the mandrel [Figure 4.13].

The disadvantage of this apparatus is that it was necessary to use a 4 Lt baker, as it was the only one with a diameter sufficient to allow to insert the mold.

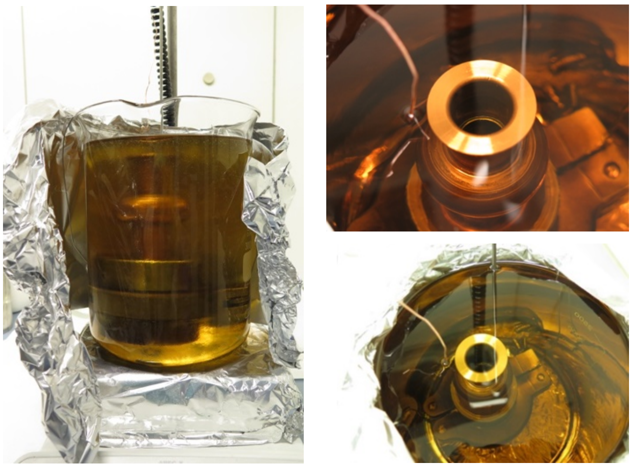


FIGURE 4.13 – EXPERIMENTAL SET UP TO MELT THE ALLOY DIRECTLY INTO THE SPINDLE MOLD

FIGURE 4.14 - RESIDUES OF ALLOY REMAINED AT THE BASE OF THE MENISCUS

On the other hand such a large amount of oil is difficult to thermalize, and consequently will have significant temperature differences inside.

This has made it difficult to melt the alloy rapidly and the result is shown in [Figure 4.14].

To improve the thermalization of the bath, it was tried to raise the support in which melt the alloy, in order to be able to insert a magnetic stir bar to mix the oil.

To do this it was decided to go back to using a glass backer in which blend the onion, because the glass, being lighter than stainless steel, it was easier to keep it suspended without complicated supports.

In Figure 4.15 all the components are showed:

- HEATING PLATE – used to heat the oil
- THERMOCOUPLE – used to control the temperature of the oil
- ALUMINIUM FOIL – used to reduce the heat dispersion
- THE INNER BACKER – used to collect the melt alloy
- THE STIRRER – used to mix the bath

Both the backer that the cavity has been supported with a copper wire.

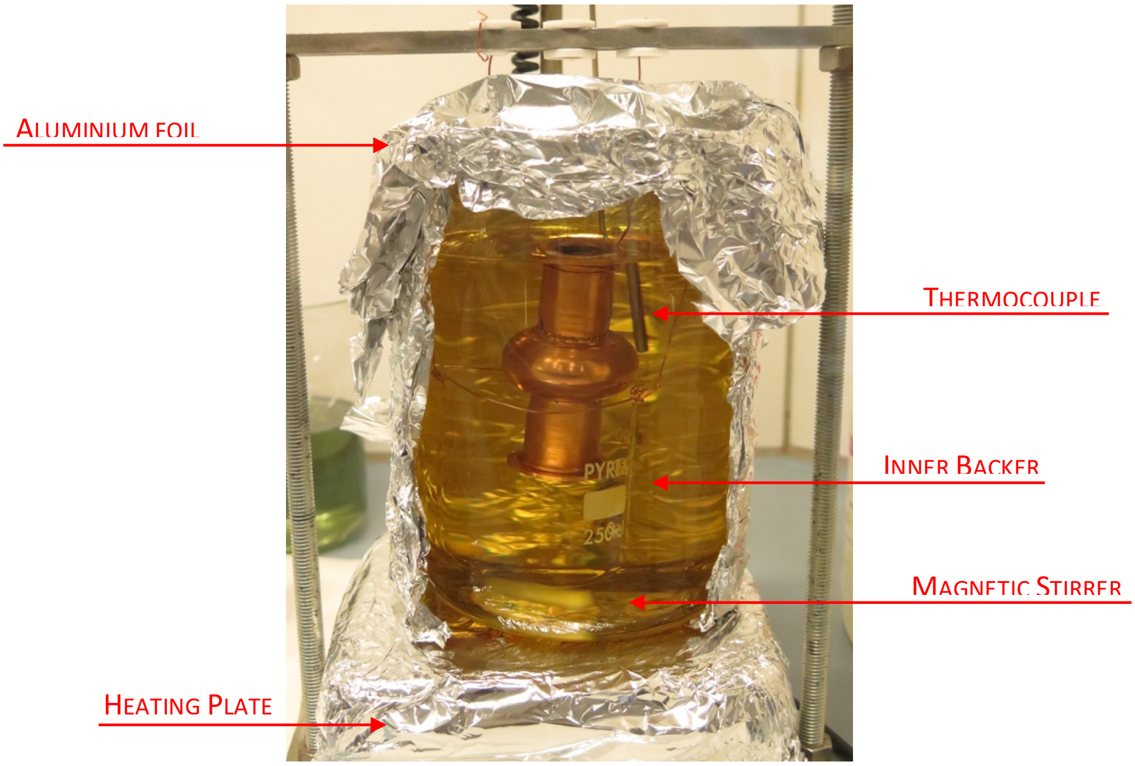


Figure 4.15 – Experimental apparatus with glass backer suspended and stirrer

The result was very good. In particular, this configuration gave some advantages:

- throughout the melting process was visible from beginning to end;
- a total of six cavities were processed one after the other;
- the temperature was maintained almost constant throughout the process time;
- after the oil has reached the temperature of 150 °C (about 1h 30 min) the time necessary to melt the alloy inside each cavity is at most 15 min from the immersion.

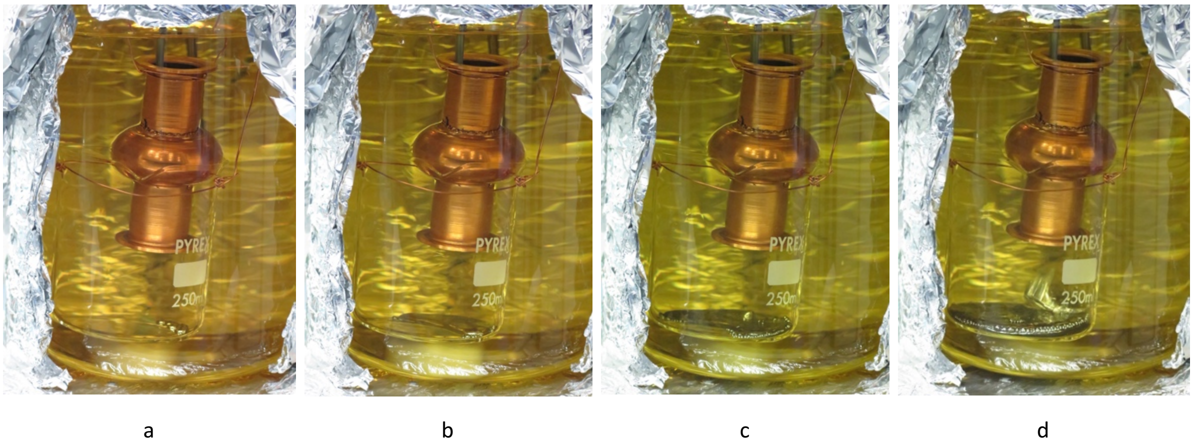

a b c d

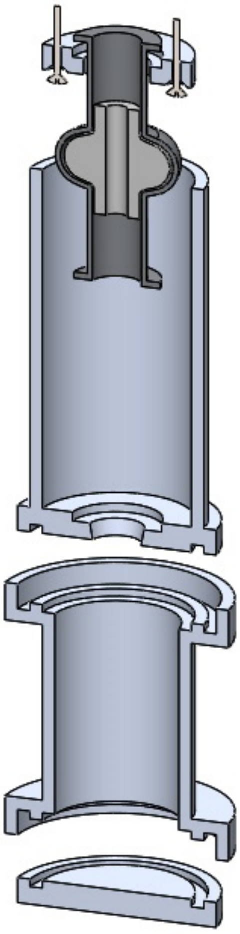
Figure 4.16 – Sequence of alloy melting

FIGURE 4.17 – ONION'S EXTRACTED FROM 6 CAVITIES

RESUMING TAB	
OIL TEMPERATURE	*150 °C*
TIME NEEDED TO REACH THE OIL TEMPERATURE	*90 min*
TIME NEEDED TO MELT ONE CAVITY	*10 min*
TIME NEEDED TO MELT SIX CAVITIES	*70 min*
TOTAL TIME OF PROCESS	*2h 1/2*
TIME NEEDED TO COOL DOWN THE OIL BATH	*2h*
TOTAL TIME REQUIRED FOR THE SET UP, THE PROCESS, THE EXTRACTION AND FOR THE CLEANING OF THE INSTRUMENTATION	*6h*

ADVANTAGES	**DISADVANTAGES**
• Process is visible • Ease of process of different cavity • Good control of the temperature	• Security risks due to handling glass (cutting hazard) containing hot oil (danger of burns) • Instability of the internal baker • Difficulty in handling the internal baker once extracted, because it extremely slippery by oil • The glass baker had to be broken to extract the alloy

4.3.3.1 Further improvements

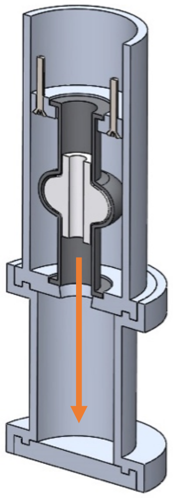


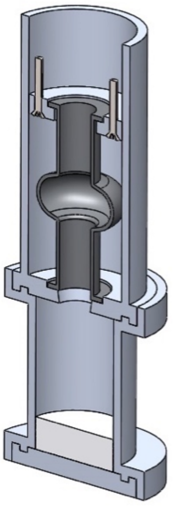
To avoid problems due to the handling glass bakers filled with oil at temperature up 150°C, and, at the same time allow a faster heating and cooling cycle, a new system has been designed.

It is made by 4 components:

1. Lower cap
2. Collecting mold
3. Heating chamber
4. Hook for cavity extraction

Adding to the heating bands a thermocouple, and checking and back driving the system with LabVIEW you should get a better temperature control.





Material: aluminium. Excellent heat exchanger, inhert to the alloy.

Security: easy to mount/unmount. There is no risk of rupture and oil spillage. Sealing is guaranteed by a clamp (not showed). The high density of both oil and alloy, not allow them to escape from the "tooth" specially made.

Serial operation: possibility to process more than one cavity per time.

Better thermal uniformity adding a stirrer.

Smoke point

Another upgrade could be to use different oils, with different smoke points and different viscosity.

The smoke point of an oil or fat is the temperature at which, under defined conditions, enough volatile compounds emerge when a bluish smoke becomes clearly visible from the oil. At this temperature, volatile compounds, such as free fatty acids, and short-chain degradation products of oxidation come up from the oil. These volatile compounds degrade in air to give soot. The smoke point indicates the temperature limit up to which that cooking oil can be used.

The smoke point correlates with the amount of free fatty acid in an oil. It varies widely, depending on origin and refinement. The smoke point of an oil does tend to increase as free fatty acid content decreases and degree of refinement increases. Heating the oil produces free fatty acid and as this heating time increases, more free fatty acids are produced, thereby decreasing smoke point. It is one reason not to use the same oil to deep fry more than twice. Considerably above the temperature of the smoke point is the flash point, the point at which the vapours from the oil can first ignite when mixed with air.
The following Table 4.1 presents smoke points of various fats:

		Temperature
Avocado oil		270°C
Safflower oil	Refined	266°C
Rice bran oil		254°C
Mustard oil		254°C
Ghee (Indian Clarified Butter)		252°C
Tea seed oil		252°C
Canola oil (Rapeseed)	High Oleic	246°C
Soybean oil	Refined	238°C
Palm oil	Fractionated	235°C
Sunflower oil	Semi refined	232°C
Corn oil	Refined	232°C
Peanut oil	Refined	232°C
Sesame oil	Semi refined	232°C
Sunflower oil	Refined	227°C
Cottonseed oil		216°C
Olive oil	Virgin	210°C
Coconut oil	Dry Refined	204°C
Castor oil	Refined	200°C
Olive oil	Refined or light-tasting	199° - 243°C

TABLE 4.1 – SMOKE POINT OF VARIOUS OILS ABOVE 200 °C

4.4 COPPER CAVITIES SURFACE TREATMENTS

Copper cavities need a peculiar attention to surface treatment because it has been proved that a reduction in roughness allows for a consistent reduction in film defect density. In many cases niobium film seems to replicate the copper substrate morphology as the result of an hetero epitaxial growth mechanism, which favours the growth of some niobium planes parallel to particular copper planes for which there is a good lattice match[35].

Generally, the copper cavities undergo the following sequence of surface treatments (if not else specified) and processes:

I. MECHANICAL BRUSHING or CHEMICAL STRIPPING of the previous coating
II. From 1h to 2h of Ammonium Persulphate CHEMICAL ETCHING
III. HIGH PRESSURE WATER RINSING (HPWR) – several minutes @ 100 bar
IV. ELECTROPOLISHING
V. CHEMICAL POLISHING with SUBU for 10 min
VI. PASSIVATION in Sulfamic Acid for 10 min
VII. HPWR – several minutes @ 100 bar

In some cases washing in ultrasonic bath were tried, mainly to remove the chemistry residuals.

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[35] S. Calatroni, C. Benvenuti, M. Hakovirta, H. Neupert, M. Prada, A.-M. Valente, *CERN studies on niobium-coated 1.5GHz copper cavities*, Proceedings of the 10th Workshop on RF Superconductivity, KEK, Tsukuba, Japan, 2001

5. TECHNOLOGICAL TRANSFER FROM RESEARCH APPLICATIONS TO INDUSTRY

The know-how acquired in the copper treatments for CUPID experiment (see section 2) and for the treatment of 6 GHz cavities (see section 3) was transferred to the resolution of an industrial problem***: cleaning of anodes for X-ray tubes without using phosphor-chromic baths***.

Producing a radiogenic tube requires great technological capability, and at the same time, handcrafted ability. That's why C.E.I. flanks the most modern plants with the expert hands of technicians.

The high vacuum level of the radiogenic tube requires special cleaning conditions, which are obtained in the controlled atmosphere of the assembly chamber.

Some process phases require high temperatures, under controlled conditions, to guarantee high-precision welding with perfect sealing.

Strict controls give the C.E.I. tube the utmost reliability: no component can continue along the production process if it does not satisfy the limits imposed by the Research & Development department.

Only after the final inspection, which simulates the actual operating conditions of the radiogenic tube, are the tubes ready for delivery[36].

5.1 THEORY ABOUT X-RAY TUBES.

An X-ray tube is a vacuum tube that converts electrical input power into X-rays.

The availability of this controllable source of X-rays created the field of radiography, the imaging of partly opaque objects with penetrating radiation. In contrast to other sources of ionizing radiation, X-rays are only produced as long as the X-ray tube is energized. X-ray tubes are also used in CT scanners, airport luggage scanners, X-ray crystallography, material and structure analysis, and for industrial inspection.

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[36] http://www.cei-xray.it/azienda/index.html

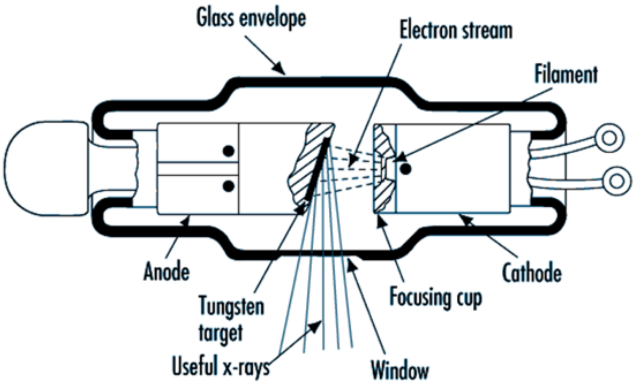

FIGURE 5.1 – SCHEME OF A STATIONARY X-RAY TUBE

As with any vacuum tube, there is a cathode, which emits electrons into the vacuum and an anode to collect the electrons, thus establishing a flow of electrical current, known as the beam, through the tube. A high voltage power source, for example 30 to 150 kilovolts (kV), is connected across cathode and anode to accelerate the electrons. The X-ray spectrum depends on the anode material and the accelerating voltage.

Electrons from the cathode collide with the anode material, usually tungsten, molybdenum or copper, and accelerate other electrons, ions and nuclei within the anode material. About 1% of the energy generated is emitted/radiated, usually perpendicular to the path of the electron beam, as X-rays. The rest of the energy is released as heat. Over time, tungsten will be deposited from the target onto the interior surface of the tube, including the glass surface. This will slowly darken the tube and was thought to degrade the quality of the X-ray beam, but research has suggested there is no effect. Eventually, the tungsten deposit may become sufficiently conductive that at high enough voltages, arcing occurs. The arc will jump from the cathode to the tungsten deposit, and then to the anode. This arcing causes an effect called "crazing" on the interior glass of the X-ray window. As time goes on, the tube becomes unstable even at lower voltages, and must be replaced. At this point, the tube assembly is removed from the X-ray system, and replaced with a new tube assembly. The old tube assembly is shipped to a company that reloads it with a new X-ray tube.

The X-ray photon-generating effect is generally called the bremsstrahlung effect.

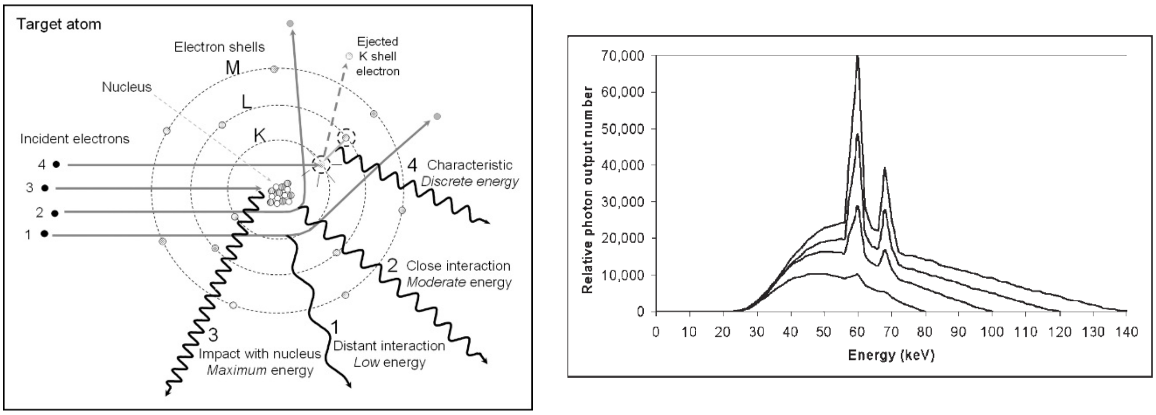

Figure 5.2 – **(left)** X-ray production by energy conversion. Events 1, 2, and 3 depict incident electrons interacting in the vicinity of the target nucleus, resulting in bremsstrahlung production caused by the deceleration and change of momentum, with the emission of a continuous energy spectrum of x-ray photons. Event 4 demonstrates characteristic radiation emission, where an incident electron with energy greater than the K-shell binding energy collides with and ejects the inner electron creating an instable vacancy. An outer shell electron transitions to the inner shell and emits an x-ray with energy equal to the difference in binding energies of the outer electron shell and K shell that are "characteristic" of tungsten. **(right)** Bremsstrahlung and characteristic radiation spectra are shown for a tungsten anode with x-ray tube operation at 80, 100, 120, and 140 kV and equal tube current[37].

The range of photonic energies emitted by the system can be adjusted by changing the applied voltage, and installing aluminium filters of varying thicknesses. Aluminium filters are installed in the path of the X-ray beam to remove "soft" (non-penetrating) radiation. The number of emitted X-ray photons, or dose, are adjusted by controlling the current flow and exposure time. The tube current and exposure time affect the dose and therefore the contrast of the image.

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[37] *X-Ray Imaging Physics for Nuclear Medicine Technologists*. Part 1: Basic Principles of X-Ray Production.

5.2 C.E.I. ANODES

FIGURE 5.3 – ANODE SAMPLE MODEL REALIZED AND RENDERED WITH SOLIDWORKS ®

Anodes have shapes and dimensions specific for each application, but we can sketch 4 constitutive parts:

A. Tungsten target
B. Copper cylinder
C. Kovar ring
D. Glass

5.2.1 Tungsten

Tungsten is a hard steel-grey metal that is often brittle and hard to work. If made very pure, tungsten retains its hardness (which exceeds that of many steels), and becomes malleable enough that it can be worked easily. It is worked by forging, drawing, or extruding. Tungsten objects are also commonly formed by sintering.

Of all metals in pure form, tungsten has **the highest** melting point (3422 °C) and tensile strength, and the lowest vapour pressure and coefficient of thermal expansion.

Thermal Expansion	Thermal Conductivity	Electric Resistivity	Melting Point	Heat of Fusion	Molar Heat Capacity
4.5 µm/(m·K)	173 W·(m·K)	52.8 nΩ·m	3695 K	35.3 KJ/mol	27.27 J/(mol·K)

TABLE 5.1 – PHYSICAL PROPERTIES OF TUNGSTEN

5.2.2 Copper

The copper has the function of heat exchanger, in order to remove the heat from the tungsten tablet.

The copper used is Cu OFHC (see section 1.3)

5.2.3 Kovar®

Kovar®, an iron-nickel-cobalt alloy, has low thermal expansion similar to high-borosilicate glass and is frequently used for glass-metal seals especially for the application in x-ray tubes or glass lasers. It can bond to glass via the intermediate oxide layer of nickel(II) oxide and cobalt(II) oxide; the proportion of iron oxide is low due to its reduction with cobalt. The bond strength is highly dependent on the oxide layer thickness and character. The presence of cobalt makes the oxide layer easier to melt and dissolve in the molten glass. A grey, grey-blue or grey-brown colour indicates a good seal. A metallic colour indicates lack of oxide, while black colour indicates overly oxidized metal, in both cases leading to a weak joint.
Given in percentages of weight[38].

Fe	Ni	Co	C	Si	Mn
balance	29%	17%	< 0.01%	0.2%	0.3%

The one utilized by C.E.I. is dilver P1® [39]

5.2.4 Borosilicate glass

Borosilicate glass is a type of glass with silica and boron trioxide as the main glass-forming constituents. Borosilicate glasses are known for having very low coefficients of thermal expansion (~3 × 10^{-6} K^{-1} at 20 °C), making them resistant to thermal shock, more so than any other common glass. Such glass is less subject to thermal stress and is commonly used for the construction of reagent bottles.
In addition to quartz, sodium carbonate and aluminium oxide traditionally used in glassmaking, boron is used in the manufacture of borosilicate glass. The composition of low-expansion borosilicate glass, such as those laboratory glasses mentioned above, is approximately 80% silica, 13% boric oxide, 4% sodium oxide and 2–3% aluminium oxide. Though more difficult to make than traditional glass due to the high melting temperature required (Corning conducted a major revamp of their operations to manufacture it), it is economical to produce. Its superior durability, chemical and heat resistance finds excellent use in chemical laboratory equipment, cookware, lighting and, in certain cases, windows.

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[38] http://www.espimetals.com/index.php/technical-data/99-Kovar

[39] http://www.aperam.com/alloysandspecialities/fileadmin/pdf/Aperam/datasheets/STRIPS_DP1.pdf

5.3 ACTUAL PROCESS

The process actually followed in C.E.I. is essentially made of 14 steps:

a. Fusion of the copper cylinder on tungsten tablet

b. Passivation of copper in Nitric Acid – HNO_3

c. Decarbonisation of dilver® ring

d. Cutting and cleaning of glass

e. Machining of copper and dilver®

f. Brazing of copper and dilver® with silver wire (under vacuum)

g. Sanding of dilver® preliminary to the welding with the glass

h. Welding between glass by direct oxidation of kovar

i. Turning and sanding of oxidized anode

j. Lapping tungsten pad

k. Electropolishing with Phosphoric-Chromic bath

l. Washing in basic soapy solution

m. Multiple rinsing with pure water

n. Cleaning with solvent in US

The main problem in this process is the presence of the CHROMIUM TRIOXIDE (step k). Chromium trioxide is highly toxic, corrosive, and carcinogenic[40]. It is the main example of hexavalent chromium, an environmental hazard. The related chromium(III) derivatives are not particularly dangerous; thus, reductants are used to destroy chromium(VI) samples.

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[40] http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=IT&language=EN-generic&productNumber=27083&brand=FLUKA&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Ffluka%2F27083%3Flang=it

5.4 CERASTI SOLUTION ©

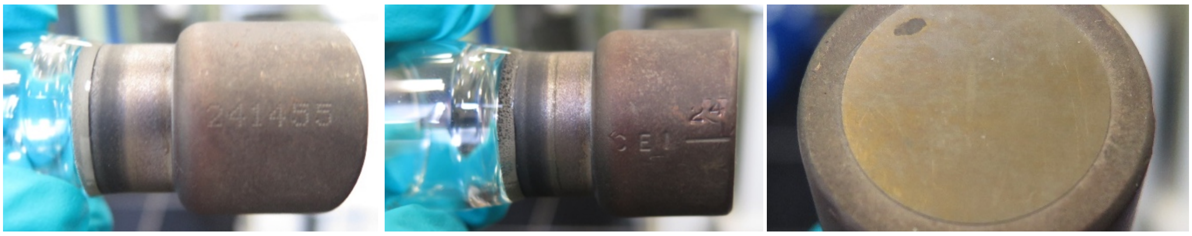
Problem: remove from the process sequence the electrochromic bath, replacing it with a safety one.

Objective: obtain a bright copper surface and a clean ring of kovar, without affecting the characteristics of the x-ray tube.

During the R&D several recipes have been tested and below is presented only the final result of work.

Starting point

After the welding of kovar and glass, the anode looks like Figure 5.4.
A hard mixed oxide layer is firmly adherent to the surface of both the copper and the kovar. Moreover, the tungsten cap is oxidised.



side 1 side 2 top

FIGURE 5.4 – INITIAL CONDITION OF THE ANODE

5.4.1 Step 1 – descaling

To remove this thick oxide layer a soft hydrochloric acid solution was used.

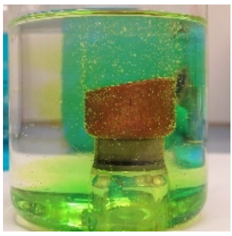
Recipe: *HC/PX*

Type: *descaling*

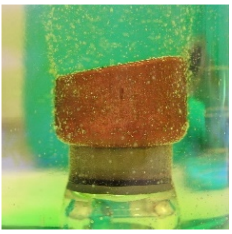
Composition:		H_2O demi	…	100 ml
	Hydrochloric Acid 37%	HCl	…	50 ml
	Hydrogen Peroxide 30 %	H_2O_2	…	4 ml
Time:	20 min			
Temperature:	Room Temperature			
Discussion:	The reaction is slightly exothermic. At the end the solution was 50°C. No agitation required. Rinse in demi water, wash in US, rinse with alcohol, dry with N_2			

TABLE 5.2 – RECIPE HC/PX

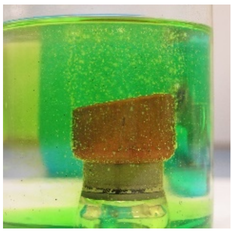
PROCESS



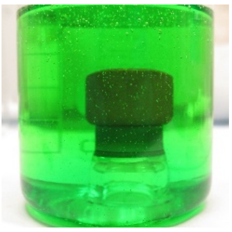
5 min



10 min

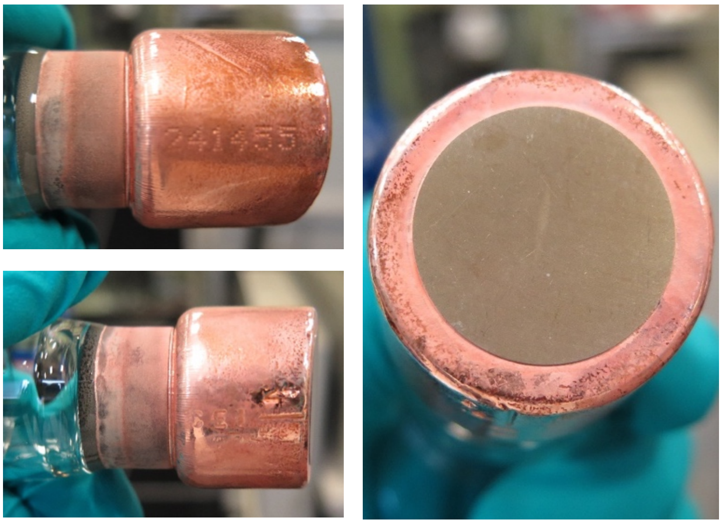


15 min



20 min

FINAL RESULT



5.4.2 *Step 2 - microetching*

After the descaling, the kovar seemed to be plated by a thin layer of copper.

To remove this layer, the standard solution of AMMONIUM PERSULFATE was used.

Recipe: *AP*	**Ref**: section 2.2.2	
Type: *microetching*		
Composition:	Ammonium Persulfate	$(NH_4)_2S_2O_8$ … 20 g/L
Time:	25 min	
Temperature:	Room Temperature	

TABLE 5.1 – RECIPE AP

PROCESS

FIGURE 5.5 - THE AMMONIUM PERSULFATE SOLUTION TURNS BLUE DUE TO THE DISSOLUTION OF COPPER

FINAL RESULT

FIGURE 5.6 - THE COPPER LAYER HAS BEEN REMOVED, BUT THE KOVAR PRESENT TWO DIFFERENT COLOURS, AND THE SURFACE OF THE ANODE IS NOT SMOOTH AND SHINY. BESIDES ALSO THE TUNGSTEN IS NOT CLEANED.

5.4.3 Step 3 - polishing

The third step is to shiny the copper using the SUBU5 recipe.

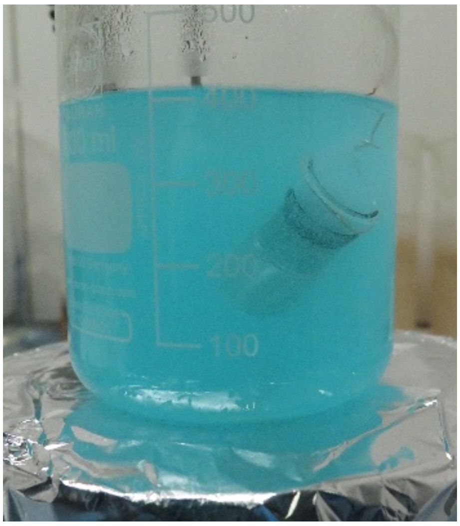
Recipe: *SUBU5* **Ref**: see section

Type: *Chemical Polishing*

Composition:				
		H_2O demi	…	1000 ml
	Ammonium Citrate	$HOC(CO_2H)(CH_2CO_2NH_4)_2$	…	1 g
	Sulfamic Acid	H_2NSO_3H	…	5 g
	Butanol	C_4H_9OH	…	50 ml
	Hydrogen Peroxide 30 %	H_2O_2	…	50 ml
Time:	10 min			
Temperature:	72 °C			

Discussion: Passivation in Sulfamic Acid 20 g/L

TABLE 5.3 – RECIPE SUBU5



PROCESS

FIGURE 5.7 – ANODE DURING SUBU

FINAL RESULT

FIGURE 5.8 – ANODE AFTER SUBU TREATMENT.

5.4.4 Step 4 – etching

The last challenge is to obtain shiny and uniform Kovar surface. To do this, a solution of Nitric/Acetic Acid was used.

Recipe: *NIT*	**Ref**:			
Type: *etching*				
Composition:		H_2O demi	…	20 ml
	Acetic Acid Glacial 99.9%	CH_2COOH	…	100 ml
	Nitric Acid 65%	HNO_3	…	50 ml
	Hydrochloric Acid 37%	HCl	…	2 ml
Time:	6 min			
Temperature:	Room Temperature			
Discussion:	Vigorous agitation. Rinse in demi water, wash in US, rinse with alcohol, dry with N_2			

TABLE 5.4 – RECIPE NIT

PROCESS

FIGURE 5.9 – SOLUTION OF NITRIC/ACETIC ACID USED TO ETCH THE KOVAR. THE INTENSE GREEN COLOUR MEANS A HUGE DISSOLUTION OF COPPER

FINAL RESULT

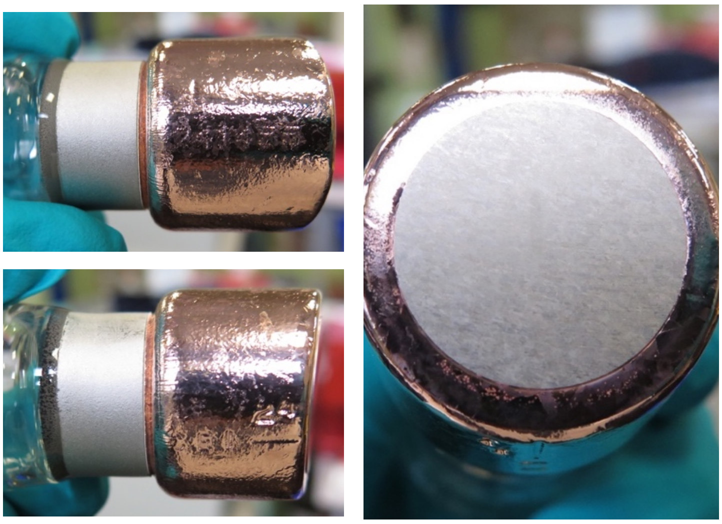


FIGURE 5.10 – ANODE AFTER ETCHING. KOVAR RESULTS UNIFORM BUT WITH A MATTE SURFACE

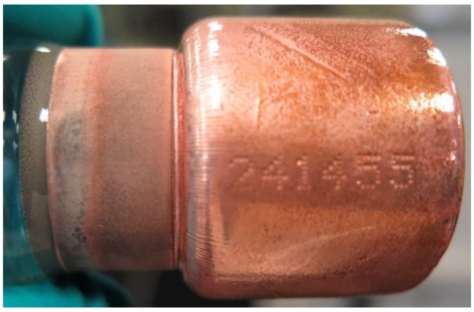
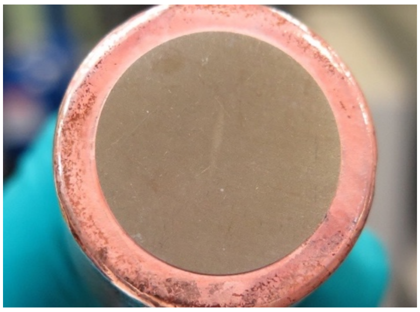
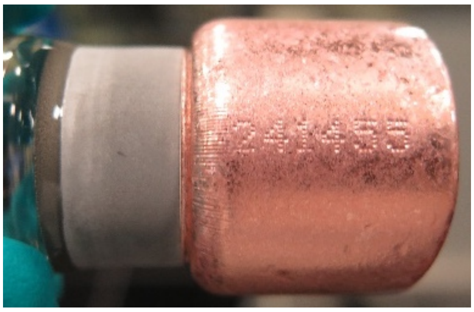
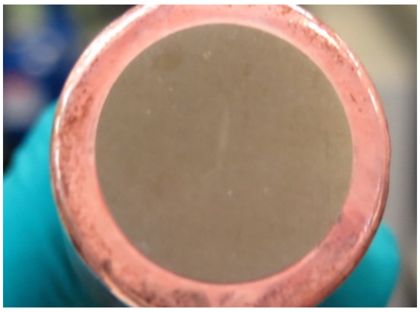
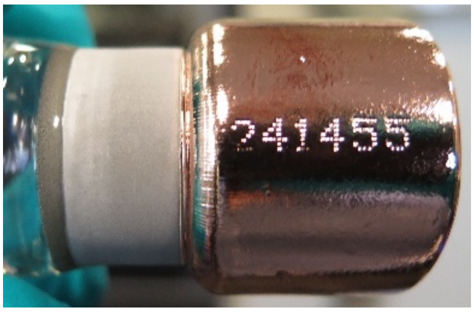
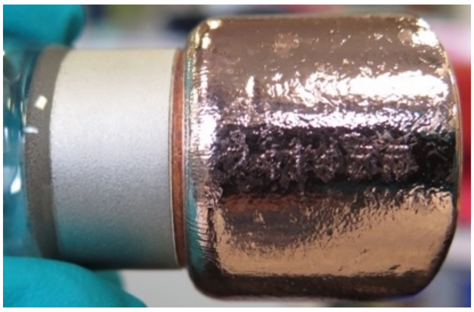
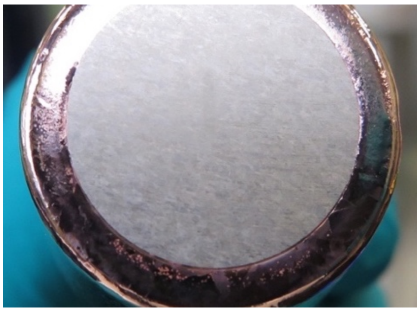
	FINAL RESULTS	
	On Kovar/Copper	On Tungsten
Initial Conditions		
Treatment 1 Hydrochloric/Peroxide		
Treatment 2 Ammonium Persulfate		
Treatment 3 Subu5		
Treatment 4 Nitric/Acetic		

Table 5.2 – Sequence of Treatments

As is clearly seen from the table, the series of chemical treatments proposed has allowed to obtain a uniform clean kovar, a bright copper surface and a tungsten pad free of oxides.

6. CONCLUSIONS

A. A total of **268** pieces of Cu OFHC were ultra clean with the procedure established for the CUPID project remaining on schedule.

A stroke of genius has avoided a possible contamination due to the presence of traces of ^{210}Po in the EP solution.

This protocol has been extremely effective in ultra cleaning of copper and can easily be used in all those areas that require a particularly copper cleansing boost.

B. It has been found a method to effectively (and in relatively short times) melt the ONION'S alloy from the inside of the 6GHz spun seamless cavity.

C. It has been developed a chemical treatment for polishing anodes made of Copper/Tungsten/Kovar for X-ray tubes, which can effectively replace the electrochemical bath based on Cr VI. Furthermore, once optimized it can substitute even other steps of the process.

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