FUNDAMENTALS OF ELECTROCHEMISTRY - THE ELECTROLYTIC POLISHING OF METALS: APPLICATION TO COPPER AND NIOBIUM

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Abstract

In the surface polishing system electropolishing is a mandatory stem for the preparation of superconducting cavities both bulk niobium made and Niobium sputtered copper. Since the aim of this tutorial is to facilitate the approach of newcomers to the field, or to give an hint to experts in order to promote further investigation, the history of the electrolytic polishing is resumed from the beginning. Several explanation attempts are reported, and a few new techniques are recalled. Nevertheless it does not exist yet one extensive theory that applies to any polishing system, both metal and electrolyte. Ac-Impedance spectroscopy offers unique insight into such a complex phenomena that, although it is usually considered a simple classical problems, it can be intimately understood only by means of quantum-mechanics.

INTRODUCTION

The development of new forming techniques for the fabrication of seamless TESLA-type cavities requires good control of the Electro-Polishing process (EP). After mechanical forming the surface appears damaged and the internal surface layer must be removed. Within the sequence of surface finishing operations, electropolishing just follows mechanical polishing. It is well-known indeed that mechanical polishing produces an altered microstructure of the outermost layer. For both bulk Niobium cavities and for Niobium sputtered cavities, which thickness of Niobium or Copper has to be removed by electrolytic polishing, is not a trivial question.

The removal by electrolytic polishing of such an altered layer, should be strongly determined by the understanding of the nature of mechanically polished surfaces and of the mechanism by which they are produced. It is a common belief that polishing is a abrasive action in which surface asperities are cut away, so that a polished surface consists of a series of grooves as fine as the smaller is the scale of abrasive medium. A different "thought school" [1] proposes that asperities are not cut away during polishing, but they are smeared across the surface to fill the depressions and smooth the surface. Such a smeared layer, called Beilby layer, estimated thinner than 100 Å would be amorphous. The concept of the Beilby layer has been radically questioned by Samuels [2], proposing that a polished surface is crystalline but plastically deformed and moreover, that the severity of plastic deformation at the surface decreases progressively with increasing of fineness of polish.

In this context, even if the state of surface vary with the type of mechanical finish, it is instructive looking at experimental results already existing in literature about mechanically polished Copper surfaces. Turley and Samuels [3] for instance report the following microstructure for an OFHC Copper surface abraded by P1200 grade silicon carbide abrasive paper (fig. 1).
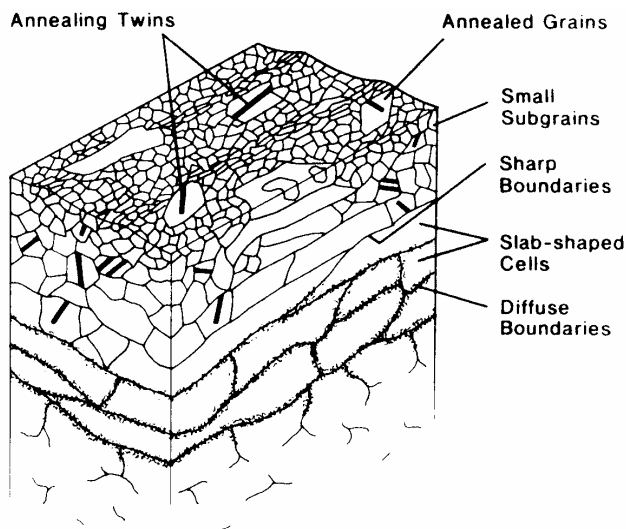

Fig. 1 - Schematic sketch of the structure observed for an abraded OFHC Copper surface.

The outermost layer for a depth of around 1500 Å is constituted by very small subgrains approximately equiaxed. The small subgrains have sharp boundaries and part of them got recrystallization due to plastic strain and/or to a local increase of temperature. Recrystallized grains were most identifiable by the presence of annealing twins. No evidence was found of the presence of an amorphous-like layer. At depths lower than 1500 Å, subgrains get larger up to when they are replaced by cells having a slab morphology and sharp boundaries. Getting deeper, the boundaries of the slab-shaped cells became diffuse. The plastically deformed layer matches smoothly the virgin structure of Copper, its thickness depending on the degree of polishing.

In the case of Niobium sputter-coated Copper cavities, it is not clear if we can tolerate an altered Copper superficial layer as the one of fig. 1 at the interface between Cu and Nb. From the point of view of thermal boundary, it is clear that such a layer should be removed. In fact it is well known that dislocations induced by plastic deformations can decrease thermal conductivity even of an order of magnitude. From the point of view of diffusion barrier of impurities from the bulk Copper to Niobium, the role of this layer is uncertain, since it should be investigated if a compact array of micrograins will allow impurities diffusing less or more efficiently than a layer of normal size grains. From the point of view of contamination trapped on the Copper surface, this altered layer should be removed. Indeed all the mechanically polished samples we have examined, display foreign inclusions such as Al, Ca, Mg, even after rinsing several times with deionized water.

It can be uncertain which technique to utilize for removing this damaged layer, but there is no doubt that it must be removed. Electropolishing is only one of the possible techniques that can be used. In the following indeed we report the polishing system including all the possibilities one has in order to clean a surface:

1. Abrasive cleaning, Grinding and Mechanical Polishing
2. Solvent cleaning: Chlorofluorocarbons and Liquid CO_2
3. Semi-acqueous cleaners: Terpenes; Alcohols; Ketones; Esters; Amines
4. Ultrasonic and Megasonic Cleaning
5. Saponifiers, Soaps and detergents
6. Wipe-clean
7. Supercritical Fluids
8. Chemical Etching
9. Electrochemical Polishing
10. Electroless Electrolytic Cleaning
11. Deburring: Laser Vaporization, Thermal Pulse Flash Deburring
12. Strippable Coatings
13. Outgassing
14. Reactive Cleaning: Anodic Oxidation and Subsequent Removal of the Oxide
15. Ozone Cleaning
16. Hydrogen Cleaning
17. Reactive Plasma Cleaning And Etching
18. Plasma Cleaning
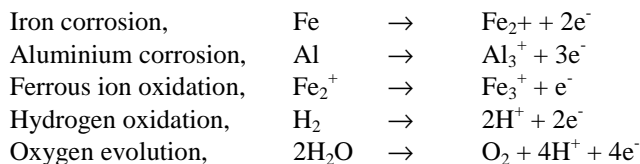19. Sputter Cleaning
20. Ion Beam Cleaning

Electropolishing however is a base necessary process. After having removed 100 – 200 microns or even more from the surface, one can even adopt any other techniques from the above list, for instance supercritical fluid cleaning.
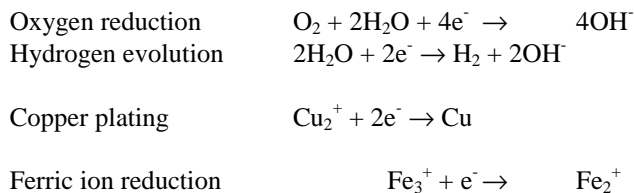
THE ELECTROLYTICAL POLISHING

In order to better understand the following, we wish to recall a few basic electrochemistry concepts. In an electrolytic cell we can have anodic reactions and cathodic reactions.

Anodic reactions are all the oxidation reactions and in general all reaction that produce electrons. Examples are the reactions as:

Iron corrosion,	Fe	$\rightarrow$	$Fe_2{+} + 2e^-$
Aluminium corrosion,	Al	$\rightarrow$	$Al_3^+ + 3e^-$
Ferrous ion oxidation,	Fe_2^+	$\rightarrow$	$Fe_3^+ + e^-$
Hydrogen oxidation,	H_2	$\rightarrow$	$2H^+ + 2e^-$
Oxygen evolution,	$2H_2O$	$\rightarrow$	$O_2 + 4H^+ + 4e^-$

Cathodic Reactions are all the reduction reactions and in general all reaction that consume electrons. Examples are the reactions as:

Oxygen reduction $\quad O_2 + 2H_2O + 4e^- \rightarrow \quad 4OH^-$

Hydrogen evolution $\quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Copper plating $\quad\quad Cu_2^+ + 2e^- \rightarrow Cu$

Ferric ion reduction $\quad\quad Fe_3^+ + e^- \rightarrow \quad Fe_2^+$

Anodic reactions in electrolytic polishing depend mainly on the nature of the dissolving metal, the electrolyte composition, the temperature, the current density and the degree of agitation.

The following reactions may take place:
1) Transfer of metal ions into the solution
$$Me = Me_2^+ + 2e^-$$
2) Formation of oxide layers:
$$Me + 2OH^- = MeO + H_2O + 2e^-$$
3) Evolution of oxygen:
$$4OH^- = O_2 + 2H_2O + 4e^-$$
4) Oxidation of various components of the solution.

The electrolytes used in electropolishing should satisfy a number of requirements, for instance:
1) the electrolyte should contain complex ions;
2) the electrolyte should contain anions with large radii and a small charge,
e.g., ClO_4^-, $H_2PO_4^-$, $H_3P_2O_7^-$, …
3) a viscous liquid layer should be formed on the anode during the process.

Electropolishing history starts in 1912 with a patent issued by the Imperial German Government for the finishing of Silver in a cyanide solution. It seems probable that the bright silver surface found at that time was not the effect of a dedicated investigation, but as for many scientific discoveries, it was achieved by accident, just due to the unintentional inversion of electrical contacts.

No advancement was made until 1935, when Copper was successfully electropolished. Then in 1936 and 1937 Charles Faust electropolished Stainless Steel. During World War II, both Allied and Axis scientists yielded a substantial number of new EP formulas. Data produced in this period were published in hundreds of papers during the immediate post-war and dozens of paper were registered in that same period.

Important work has been prepared around the end of the late thirties by Jacquet [4], that first investigated the electropolishing of Copper in phosphoric acid by observing

the I-V Characteristics. He found that, depending of the voltage applied, it is possible to obtain pitting, polishing or gas evolution, as shown in fig. 2.
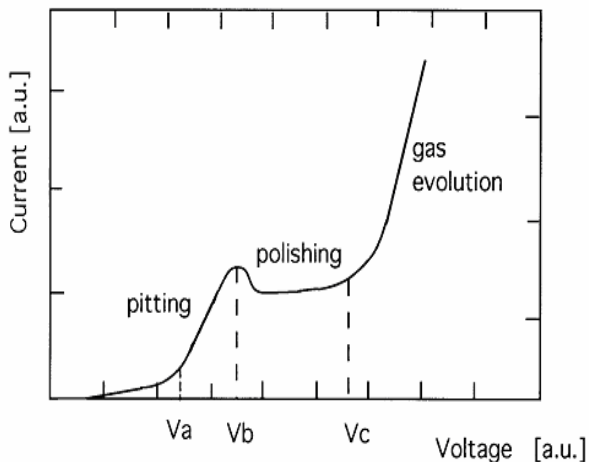

Fig. 2 - Current density vs. voltage for Copper electropolishing in phosphoric acid

In particular he found that up to the point V_B, the surface conserves its mechanically worked appearance and shows some signs of pitting. Fluctuations in both voltage and current and a simultaneous drop in current density are found just after V_B. Over the horizontal range $(V_B - V_C)$, the current density remains constant although the voltage increases; A polishing effect is observed between V_B and V_C, but the best results are obtained near point V_C. The first bubbles of gaseous oxygen appear on the anode at a voltage corresponding to point V_C. A well polished surface is obtained over section V_C, at higher voltages, the dissolution of metal is accompanied by evolution of oxygen, but there is some pitting as a result of contact with oxygen bubbles trapped on the surface. At potentials much higher than V_C the quality of polishing improves, since the oxygen bubbles cannot be trapped on the surface and there is no pitting. A solid, brown film is formed on the anode surface for voltages between V_A and V_B, the film adheres to the metal but is destroyed at higher current densities.

The thin layer of electrolyte in the vicinity of the anode assumes a bluish color. Moderate agitation of the solution reduces the thickness of the bluish layer while voltage drops. Vigorous agitation reduces the thickness to a few tenth of a mm and voltage drops even more. Jacquet assumed that a relationship exists between the formation of the viscous layer in the electrolyte and the polishing effect. According to Jacquet, the process should be controlled by maintaining a constant voltage rather than a constant current density; in this case it is not necessary to calculate the total surface area of the sample to be polished. Rigorously speaking, it would be not possible to control the electropolishing process solely on the basis of voltage or current density measurements,

The Applied Voltage V is a function of the anode and cathode potentials, the Voltage Drop in the electrolyte ($I\ R_{electr}$) and the voltage drops in the conductors and contacts ($I\ R_{Conduct}$), i.e.

$$V = (V_{anode} - V_{cathode}) + I\ R_{electrol} + I\ R_{Conduct}$$

Thus V depends on the electrode potentials, the electrolyte concentration, the anode and cathode surfaces, the arrangement of electrodes in the bath and the shape and size of the bath. Hence, the "applied voltage" used by Jacquet as a control parameter would not always correspond to the optimum polishing conditions. The electropolishing process could be controlled on the basis of the anode potential through the use of a special non-polarizing auxiliary reference probe (for example a saturated calomel third electrode). On the other hand. the potentials of the anode and of the auxiliary electrode do not remain constant - they change as a function of the time of electrolysis and the composition of the electrolyte. For this reason, the reading of the auxiliary electrode should be corrected from time to time.

A reference electrode commonly use a Saturated Calomel Electrode (SCE) as a third electrode. The use of SCE is of great help, however great attention must be paid to its correct use. Properties may degrade with time (and misuse). One indeed should perform comparative checks (should not be more than 1 to 2 mV difference); current should not pass through the reference electrode (e.g. do not connect to working or counter electrode); last the SCE should be not allowed to dry out.

By using a reference electrode, one can adopt two different measurement methods: the Potential control and the Current control.

In Potential control regime (fig.3), electrodes are connected to the corresponding terminals on potentiostat. The potentiostat controls potential. A counter-electrode (Secondary Electrode) provides current path into solution, while a Reference Electrode is the connection for potential measurement that by a detects potential close to the metal surface by a Luggin Probe.
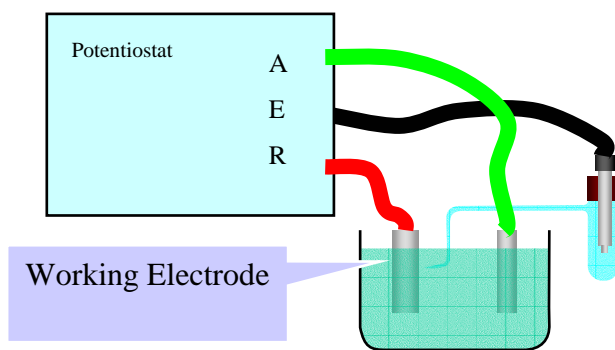

Fig. 3 - The Potential Control circuit in electrolytic polishing

In Current control regime, instead the Reference Electrode is not connected to potentiostat, but it is only used to monitor potential,
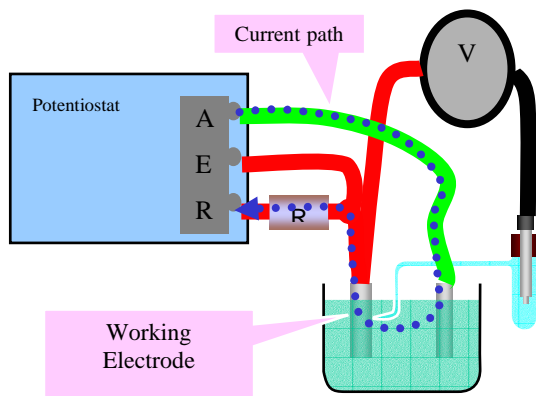
Fig. 4 - The Current Control circuit in electrolytic polishing

MECHANISM OF THE ELECTROPOLISHING PROCESS

Several hypotheses exist for explaining the mechanism of electropolishing of Copper in phosphoric acid solutions. All of them concern with the existence of the thin bluish viscous layer of electrolyte forming in proximity of the anode.

The simplest explanation is the one proposed by Jacquet [5]. When a current passes across the electrolyte, the anodic film has higher viscosity and higher electrical resistivity than the bulk of the electrolyte. The thickness of such a film on a rough surface (fig. 5) differs from site to site: above protrusions the film is thinner than above valleys. Hence protrusions dissolve more rapidly than wells.

According to Elmore instead the cause of the surface levelling is related to the diffusion of anodic dissolution products from the anode through the film [6]. The dissolution rate is again higher from protrusions than from wells.

The "viscous film" theory of Jacquet and the diffusion theory of Elmore have much in common. In fact, a viscous film really forms on the anode surface and diffusion and convection processes really occur at different rates on projections and crevices. Jacquet attributes the leveling of rough surfaces to differences in the degree of "insulation" of peaks and crevices, Elmore believes that the effect is associated with differences in the concentration gradients of metal ions. However, the presence of a viscous, high-resistivity film on the anode surface (as in the case of Cu EP in H3PO4) is not in all cases essential for high quality polishing. Moreover, Jacquet and Elmore theories do not answer to the question of metal oxidation during EP, and do not explain the anodic polarization curves. In other words, they do not reveal the mechanism of anodic polishing, since they are mainly based on the influence of single factors.

Simple geometrical considerations are the basis of Baumann and Ginsberg analysis, noticing that Jacquet model does not apply in case of both vigorous agitation of the electrolyte and voltages much higher than the *plateau*. Electric field has higher intensity at corners,

edges and protuberances than at wells, cavities and craters. Surface levelling occurs as a result of greater dissolution probability of peaks [7].
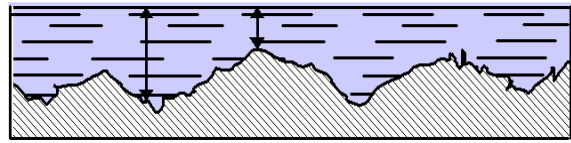

Fig. 5 - The Copper anode coated by the viscous liquid film

Vozdvizhenskii [8] regarded the anodic dissolution in terms of a "reversed electrolytic crystallization" which depends on the texture of the metal. Mechanical working of metals produces a micro-rough surface with deformed crystal sites, that are the ones preferentially dissolved upon anodic polarization of the metal. The electrolytic polishing causes levelling of the initial roughness, but also leads to the appearance of a new surface roughness as a result of the anodic etching. Vozdvizhenskii's model is considered incomplete by Shigolev [9] since under optimum polishing conditions the surface layers of a metal can be dissolved uniformly regardless of surface texture. The effect of gas evolution and grain orientation on the electropolishing has been studied by Dmitriev [10].

Elmore's model was criticized by Edwards that assumed that electropolishing processes are governed by the diffusion of anionic acceptors as $(H_2PO_4)^-$, $(HPO_4)^{2-}$, and $(PO_4)^{3-}$ to the anode surface [11].

The Copper dissolution reaction is written as

$$Cu + s_A \cdot A^{m-} \rightarrow (CuA_{sA})^{2-s_A{}^m} + 2e^-$$
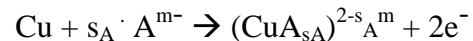
The process has a threshold given by a critical concentration of acceptor ions. The polishing rate is determined by the mobility of the acceptor toward the anode. The acceptor concentration gradient is higher on peaks rather in valleys. It is just the threshold hypotheses to help us in understanding intuitively the nature of the plateau in the I-V characteristic. Below V_b the viscous layer is not yet completely formed: the layer is becoming thicker and thicker up to a saturation value that is V_b. In the meanwhile the rate of diffusion of anions increases with voltage. The two effects are in competition and the negative part of the characteristic would correspond to a region where the viscous film is still growing but it has already became too thick for allowing tunneling of anions. A subsequent increasing in voltage increases the anodic potential, but, up to V_c, current does not change. Current will begin to increase again versus voltage as soon acceptors will have enough energy to tunnel the viscous film. At this specific voltage value, V_c, we have the highest resistivity and also the best polishing effect.

Some theories [12] explain the limiting-current plateau by means of a salt-film mechanism: the solubility limit is exceeded by the surface concentration of the metal ions that are produced from the dissolution reaction, and a salt film is precipitated. According Vidal and West [13], however, a salt-film mechanism is inappropriate for high rate dissolution of Copper in concentrated phosphoric acid, while it is

considered valid a water-acceptor mechanism. In reality the problem is complex. Apparently, the source of the mass-transfer limitation depends on both the metal and the electrolyte. The role of electrolyte has been tested by the addition of controlled amounts of water or cupric salts. The addition of water causes an increase in current density, while the addition of the cupric salt leads to a decrease. These experimental evidences however are difficult to interpret unambiguously. For example, changes in water content affect the electrolyte viscosity and the water diffusion coefficient. Additionally, the dissociation of phosphoric acid is higher with water addition. Since protons hydrate strongly, it is possible that not all the added water is available for solvation of the copper-ion products. Finally, the addition of large amounts of water may change the mechanism of dissolution. For example the solubility of cupric phosphate is dramatically smaller in pure water than in concentrated phosphoric acid. The decrease in current density with the addiction of copper salts is superficially consistent with a salt-precipitation mechanism. Nevertheless, much of the observed drop in current can be explained by changes in the transport properties of the electrolyte. Cupric ions are probably hydrated by five to six water molecules. Thus the addition of a cupric salt may also change the bulk concentration of water [13]. Therefore steady state measurements with modified electrolytes are unable to distinguish between an acceptor and a salt-film mechanism, and the only technique that complement steady state observations is the ac-impedance spectroscopy. By ac-admittance studies indeed already Glarum and Marshall [14] reported results that supported the acceptor mechanism, concluding that the region depleted of water behaves as a thin viscous film with a space charge.

Based on acceptor hypothesis, the first quantitative mathematical description of electropolishing theory has been proposed by Wagner [15] in 1954 on the basis of simple considerations. He hypothesizes a surface roughness described at the time **t** by a sine-wave profile with a wavelength, **a**, and an amplitude, **b** (fig. 6). If an "ideal electropolishing process" is considered then the metal ions are consumed immediately upon arrival to the outside of the hydrodynamic polishing layer of thickness δ
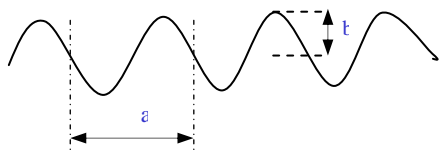
Fig. 6 – Schematization of surface roughness according Wagner

The displacement **u** for a decrease from b_0 (at time t = 0) to **b** (time t) is given by:

$$u = a\rho/2\pi \,.\, \ln b_0/b \quad \text{for} \quad b << a, \ a << \delta$$

where ρ is the density of the metal. The theory finds good agreement with experimental results, by predicting a linear plot for $\Delta m/A$ vs $\ln b_0/b$.

It must be said that there is not yet one theory of electropolishing that is universally valid, however many authors believe that EP is accompanied by the formation of passive films on the anode. Modern explanations of the electrolytic polishing of metals are based on the modern concepts of anodic passivity of metals. During the process the metal does not assume a steady stable passivation state, because of chemical dissolution of a passivating oxide film in the electrolyte. Surface levelling takes place because the passivation of wells is more stable and it inhibits etching. Peaks are instead dissolved more rapidly.

Together with the observation of the I-V characteristic, both the anodic and cathodic polarization curves are monitored. The anodic polarization curve versus current density has a thoroughly similar behaviour of curves obtained in the case of anodic passivation processes. According to this the sharp step in anodic polarization corresponds to a transition of the metal from an active to a passive state. Anodic polarization curves are quite similar to curves obtained in the case of anodic passivation processes as shown in fig. 7. It is worthwhile to notice that different plotting of Polarization Curves can be adopted for identifying anodic and cathodic regions. Log-i plots instead than linear-*i* plots represent as straight lines exponential behaviours, while 90 degree rotated plots are quite usual too.
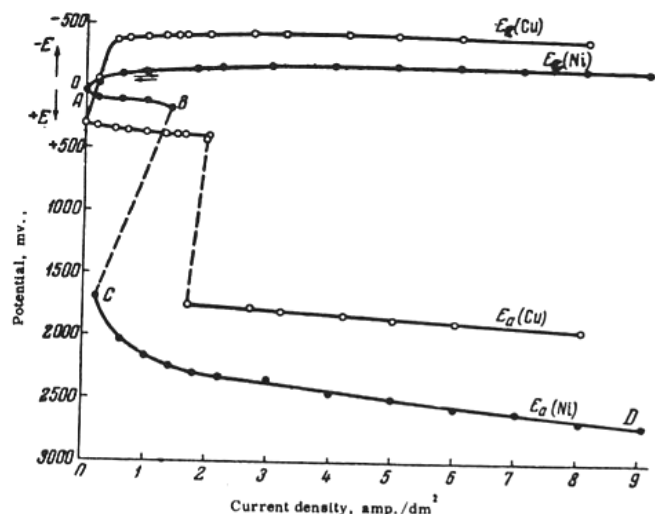
Fig. 7 - Anodic and Cathodic polarization curves for Ni in H_2SO_4 at 40° and Cu in H_3PO_4 at 20° C

Hoar and Rothwell [16], then Kojima and Tobias[17], proposed that electropolishing occurs due to the formation of a solid copper-oxide film. An oxide film has been detected by Poncet et al. by the electroluminescence technique [18-21]. The growth of a double junction of semiconductor n-doped and p-doped Cu_2O and CuO Oxides has been observed during electropolishing on the Copper anode surface (fig. 8).
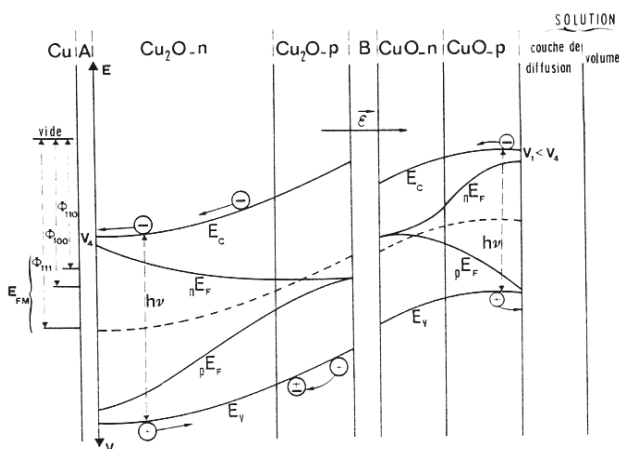
Fig. 8 – Scheme and energetic band of the n-p double junction of CuO and Cu₂O oxides detected by Poncet et al.

The observation of a semiconductor junction is a very important consideration for a deep understanding of the electropolishing process, since the presence of a semiconductor n-p junction is the key for a quantum mechanical explanation of electropolishing based on tunneling. On the other hand it is worthwhile to underline two considerations: the former is that no classical mechanism, if not quantum tunneling, can explain a negative slope in a I-V characteristics; the latter is displayed in fig. 9, that reports the I-V characteristics in a tunnel diode. The curve is extraordinarily similar to the electropolishing polarization curve, and if, "the same equations have the same solutions", there is a no-zero probability that the Physics under both phenomena is the same.
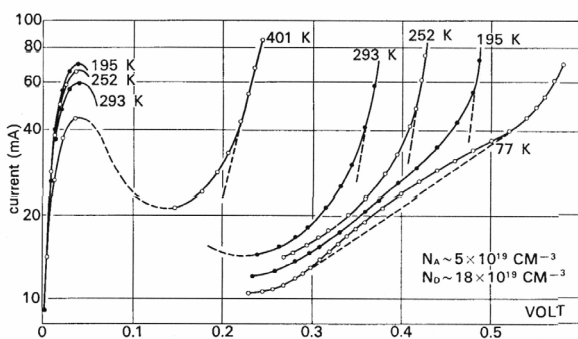

Fig. 9 - Semilog plots of current-voltage characteristics in a tunnel diode, where $N_A \sim 5 \times 10^{19}\,cm^{-3}$ and $N_D \sim 1.8 \times 10^{19}\,cm^{-3}$ [22]

THE SEARCH FOR BEST ELECTRO-POLISHING CONDITIONS AND FOR NEW ELECTROLYTES

In this paragraph we will not get into the detail of the problem cavity electropolishing, that has been already covered in detail by many other papers [23-26]. We will rather discuss general methods that by a deeper understanding of the process improve the probability of success. This techniques, Even if referred in the following to Copper or Niobium, the following techniques are thoroughly general. They are indeed of direct industrial applicability, very successful for a variety of metals and in a plethora of applications, such as: the electropolishing of gold without cyanides, the electropolishing of magnesium, aluminium and alloys for spectacles; the cleaning of titanium for dental implant, prothesis and cardiac valves, the electropolishing of stainless steel and cast iron for general mechanical applications, and of other alloys for electronic applications.

If the plateau region in the I-V characteristics gives the best polishing conditions, it is important to look at the effect that process parameters have on the plateau. The four most important parameters are the electrolyte Temperature, Acid Concentration, Viscosity and Stirring. The temperature does not affect the plateau voltage range, but only the current density; the same holds for acid concentration, the plateau voltage remains unchanged, while the current density increases; the current density is inversely proportional to Viscosity; while stirring increases almost linearly the current density. It must be kept into account however, that often much attention must be paid to the stirring effectiveness, especially when electropolishing tricky shape surfaces. A too strong stirring, for instance applied by ultrasounds, damages the surface rather than polishing.

Great care must be paid for stable and controlled EP conditions, and this is sometime impossible for multi-phase/elements materials. On the way of searching for better polishing conditions, one skilful method, proposed by Lee [27], consists in the manipulation of film build-up conditions in micro-EP. Electropolishing can be broken down in 2 different processes: Macro-EP and Micro-EP respectively acting on Macro-roughness and Micro-roughness.

According to Lee, periodic cycles of macro-EP and micro-EP must be alternated by a right balancement of film dissolution and film creation. Rapid oscillations from low current regimes (where there is a film build-up) to high current regimes (where there is film removal) will simultaneously apply both macro-EP and micro-EP to the surface.

The author and his co-workers have proposed one useful technique that makes very easy to find automatically the optimum Electropolishing conditions. The technique is reported elsewhere [28], but, in brief, it consists in locking the minimum of the differential conductance found by numerically derivating the Polarization curve. The idea is that since the viscous layer has higher viscosity and greater electrical resistivity respect to the bulk of the electrolyte, by finding the minimum of the differential conductivity of the I-V characteristics, one automatically obtains the right electropolishing voltage. Computer control helps in finding this ideal working point and constantly tuning the process following the evolution of this point. The method has been further sophisticated by the use of flux gate magnetometry [29]. The magnetic flux linked to the magnetometer placed in proximity of the anode is plotted versus voltage. The H-V characteristics so detected is, units apart, totally similar to the I-V characteristics. Then the analogical derivative of the magnetic signal automatically gives the above mentioned minimum.

The method suitably applies to whatever metal (Copper, Niobium, Magnesium, Aluminium, Titanium and his alloys,

Gold alloys, and many technical alloys), and the operator does even not need to know the electrolyte he his using. This approach has permitted the author to easily find many new electrolytes [30], as for example the one for Niobium already reported in reference [28]: HF + OXALIC ACID + BORIC ACID + H_3PO_4; 30% HF, 15% H_3PO_4, 30 gr/lt Oxalic acid, 10 gr/lt Boric acid.

The search for new electrolytes for Niobium will certainly become a must whenever a cavity mass production will be launched. The ruling criteria for new electrolytes selection are manifold: i) Saving the same finishing quality standards, acids should be less aggressive and more easy to handle than the ones commonly used; ii) Costs must be kept low both when purchasing and when exhausting the electrolyte; iii) Moreover higher throwing-power is needed in order to save on electricity consumes.

In the same way it is possible to find the moderators to add in the electrolytes, in order to improve surface leveling. Normally alcohols are mixed to acids in order to both get a more bright finishing and for enlarging the plateau region over a wider voltage range. For copper electropolishing, for example, standard recipes mix phosphoric acid either with Butanol or with Glycerol. It is well-known, however that, 2-butyn-1,4-diol and glycerol work better than Butanol for the double or triple OH group (fig. 10).
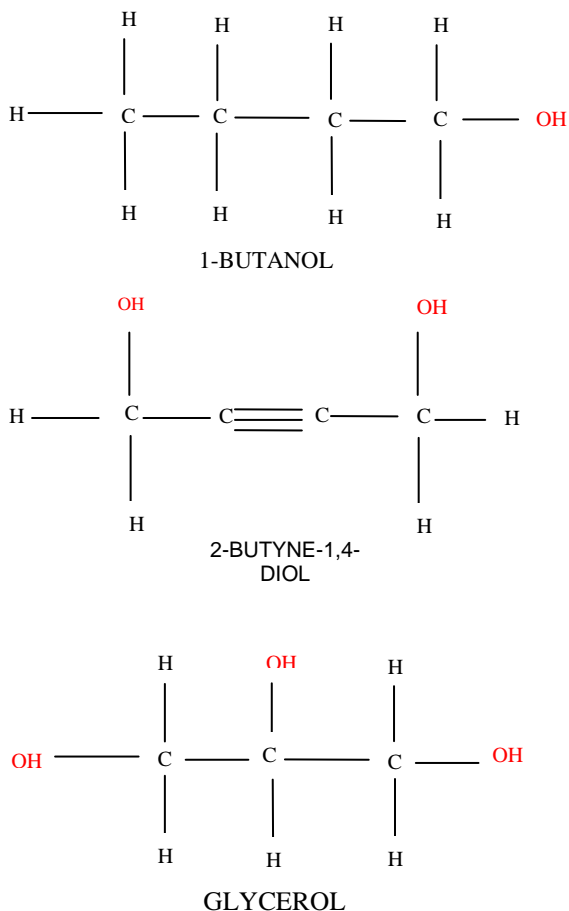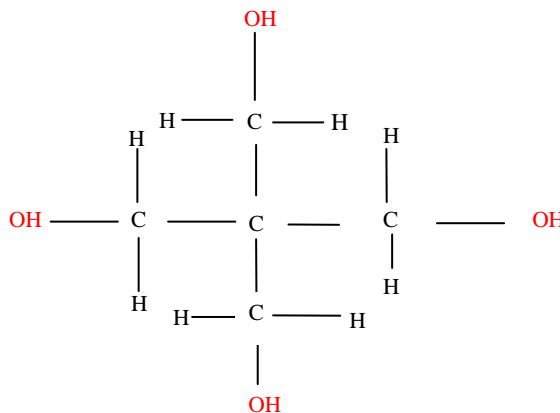
Fig.10 - Butanol, 2-Butyne-1,4-diol and glycerol molecule.

It is not commonly known instead, that Tetrakis(Hydroxymethyl)Methane better known as Pentaerythritol (fig. 11) works even better. The OH groups indeed work as many hooks, making the molecules linking to each other in a kind of bidimensional lattice that works as a viscous film on the anodic surface.

Fig. 11 – Molecule of Tetrakis(Hydroxymethyl)Methane also known as Pentaerythritol.

Alcoholic moderators should be added also to the standard HF + H_2SO_4 EP recipe, but in reality, the problem that deserves more investigation is the possibility to get rid of hydrofluoric acid.

Actually HF-free electrolytes for Niobium already exist, but they are not less harmful than Hydrofluoric acid. In order to avoid the hydrogen gettering during electropolishing, Schober and Sorajic introduced an hydrogen free electrolyte for Nb, by extrapolating what previously proposed by Epelboin [31]. The electrolyte consists of 0.05 mole/liter $Mg(ClO_4)_2$ in CH3OH, the EP Voltage is between 50 and 70 V, but what is most important is that the bath temperature must be kept not higher than -5°C. Since the electrolyte does not contain a hydrogen radical, no intake of hydrogen is possible.

Perchloric acid has been largely used as constituent of electropolishing baths for its peculiar properties, that can be resumed in the following: i) easy dissolution in non aqueous media; ii) powerful dissolution action of metals and alloys; iii) remarkable solubility of numerous metallic perchlorates in acid milieu. Perchloric acid is really the acid that is able to electropolish almost every metal, however, many explosions caused by perchloric acid solutions have been brought to notice in technical literature [32]. Polishing baths perchloric acid-based can be divided into two main classes: a) Strong solutions, containing perchloric acid mixed with anhydride or with acetic acid; b) Less concentrated solutions containing perchloric acid mixed with ethylic acid, acetic acid or acetic anhydride. It is important to notice to the reader that some authors maintains that ethyl perchlorate is as dangerous as Nitroglycerin. Mixes containing less than 55% in weight of perchloric acid cannot explode, unfortunately they are the

less interesting for the EP use. As displayed in fig. 12, the convenient polishing baths are just located in the flammable field.
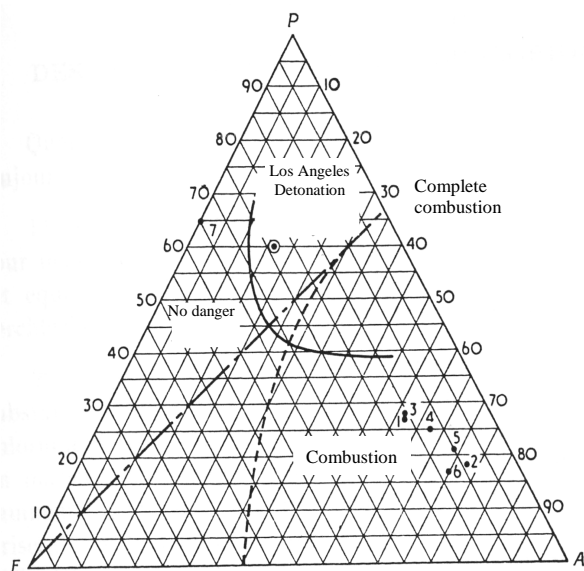

Fig. 12 – The triangular diagram of Perchloric acid, Acetic acid and Ethanol. The no-danger region is rather reduced in comparison of that in which there is combustion.

AC-IMPEDANCE SPECTROSCOPY

Whenever you deal with a problem in which it is needed to measure a resistance, try always to measure the ac-impedance. It will be like for your sight passing from back/white to colours. Impedance spectroscopy is a powerful and efficient method to investigate properties of electrolytes [33]. This technique permits to separate in the frequency domain the contributes of different phenomena due both to the electrolyte and to the electrode, like:

- transport properties of the reacting species in the bulk of the electrolyte often associated with chemical reactions.
- Adsorbtion of reacting species on the electrode.
- Chemical and elecectrochemical interfacial reactions often occurring in several monoelectronic steps.

In 1947, Randles [34] proposed to represent the processes inside the galvanic cell by means of a simple equivalent circuit made of capacities and resistances (fig. 13), with the same properties as a metal-solution interface.
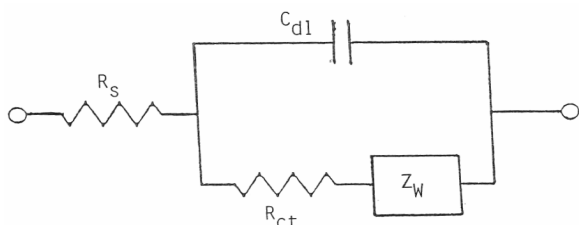

Fig. 13 – The Randles cyrcuit

The double layer capacity (C_{dl}) is in parallel with interface resistance (R_{ct}) and Warburg impedance (Z_W) relative to ions diffusion process. This parallel RC circuit is in series with solution resistance (Rs). An applied continuos current can flow only through the resistive branch of circuit, whereas an AC current can flow also through the capacitor that contributes to total impedance with $1/(2\pi f\, C_{dl})$ where f is the frequency of applied signal. By impedance techniques, the electromigration through the passive layer can be distinguished from diffusional transport, and the R_{sol}, C_{dl} and R_{ct} can be estimated [35].

CONCLUSIONS

Although electropolishing is a well-established technique both in research than in industry, it is still a phenomena not fully understood and that extends its roots into quantum-mechanics. Moreover it does not exist yet an universal theory that extensively describes the process. In this framework AC-impedance spectroscopy is definitely the most powerful method for investigating electrolytic cells, and in particular the problem of Niobium electropolishing that, nevertheless mastered for superconducting cavity preparation, still deserves a lot of investigation.

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