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*Industrial R&D on Innovative Surface Treatments
for an Ecological Descaling of "Acciaierie Valbruna"
Stainless Steel Wire Rods in Replacement
of the Traditional Acid Etching*

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Contents

Acronym	8
Abstract.....	9
Introduction.....	11
1.1. Steel production	11
1.2. The Iron - Iron Carbide phase diagram.....	13
1.2.1. Cast Iron.....	14
1.3. Alloy types and application.....	15
1.4. Thermal treatment and scale formation.....	17
1.5. Cleaning of stainless steel.....	19
1.5.1. Descaling.....	19
1.5.2. Acid etching.....	20
1.5.2.1. Typical procedure of acid pickling stainless steel.....	22
1.5.2.2. Organic acid pickling solutions.....	23
1.6. Electrochemical etching and polishing.....	24
1.6.1. Benefits and disadvantages of electropolishing.....	25
1.6.2. Solutions for electropolishing stainless steel.....	26
2. Ionic liquids as new electrolytes.....	29
3. Passivation.....	33
3.1. Chemical passivation.....	33
3.2. The anodic passivation.....	34
3.2.1. Corrosion protection.....	35
4. Experimental part.....	37
4.1. The characterization of the scale layer.....	37
4.1.1. The characterization of thickness and anisotropy.....	38
4.1.2. Morphology and microstructural characterization.....	38
4.2. Characterization of the different steel types.....	40
4.3. Study of the effectiveness of pre-finish treatment.....	57
4.3.1. Study of the technique of high pressure rinsing.....	57
4.3.1.1. The effect of different pressure (100-800 bar).....	57
4.3.1.2. Study of the influence of the jet angle and different nozzle geometry.....	60
4.3.1.3. Study of the influence of adding the abrasive.....	62
4.3.2. Study of the effectiveness of “dry ice” -blasting (CO ₂ -blasting).....	64
4.3.3. Summary of the effectiveness pre-finish treatment.....	67

5.	Green Electropolishing	69
5.1.	The characterization of samples etched in the standard solution.....	69
5.2.	Study of the possibility of ionic liquids to electrochemically polishing of stainless steel.....	70
5.2.1.	<i>Ionic liquids as alternative electrolytes.</i>	71
5.2.2.	<i>Testing the new solutions consist of ionic liquids.</i>	71
5.3.	Study the other eutectics based on Choline Chloride.	78
5.3.1.	<i>Deviations of the eutectics and study the process parameters.</i>	79
5.3.2.	<i>The influence of ultrasound during the electropolishing.</i>	82
5.4.	Study of the contents of wastewater.	84
5.5.	Selecting the best solution.....	84
5.6.	Analysis of the applicability of the alternative solution.	88
5.6.1.	<i>The measurements of solution lifetime.</i>	88
5.6.2.	<i>Vapours analysis.</i>	90
5.6.3.	<i>Estimation of the process time.</i>	90
5.7.	Additional tests with Eutectic “O”.....	91
5.7.1.	<i>Electropolishing martensitic steel and steel doped with sulphur.</i>	91
5.7.2.	<i>Comparison of the electrolytes with carboxylic acid pure and technical grade.</i>	92
5.7.3.	<i>Study of the influence of preliminary treatment.</i>	94
5.8.	Optimization of the parameters of electropolishing in ionic liquids.....	95
5.8.1.	<i>Study of lower working temperatures.</i>	96
5.8.2.	<i>Study of the different ratios Choline Chloride – Carboxylic acid.</i>	98
5.8.3.	<i>Study of the influence of additives in Eutectic “O”</i>	99
5.8.4.	<i>Study of the influence of water on electropolishing process in ionic liquids</i>	101
5.8.5.	<i>Search of a new Choline chloride based ionic liquid for electropolishing.</i>	103
5.8.6.	<i>Summary of the ionic liquids mixtures, applicable to the electropolishing of the stainless steel.</i>	106
5.9.	Study of the recycling of ionic liquid.....	107
5.9.1.	<i>Study of the velocity of metal dissolving in fresh solution and recycled.</i>	109
5.10.	Study of the possibility to use AC power supply.....	110
6.	The first test in the construction of the new cleaning machine.....	113
6.1.	Experiments with samples in form of coils.....	113

6.2.	Testing the material for tank	115
6.3.	The construction of electrochemical plant for descaling stainless steel coils close to real conditions.....	118
6.3.1.	<i>Preparation of the solution and study of the process parameters. ..</i>	120
6.4.	The design of prototype for electropolishing of the wire rods in ionic liquid.....	122
7.	Study of the steel passivation after electropolishing.....	125
7.1.	Corrosion test in seawater.....	131
7.2.	Test on atmospheric corrosion for the wire rods.....	133
8.	Aqueous solution for descaling stainless steel.....	137
8.1.	Study of the possibility of electropolishing in aqueous electrolytes.....	137
8.1.1.	<i>Chemical etching of stainless steel.....</i>	137
8.1.2.	<i>Electrolytic cleaning in organic acids.....</i>	138
8.2.	Pulse reverse finishing.....	139
8.2.1.	<i>Pulse reverse electropolishing in aqueous solutions.....</i>	140
8.3.	Alternative solution for descaling stainless steel.....	143
8.3.1.	<i>Organic acid solution for electropolishing.....</i>	143
8.3.2.	<i>Inorganic acid solution for electropolishing.....</i>	145
8.4.	Study of the parameters for electropolishing stainless steel in inorganic acid solution.....	146
8.5.	Electropolishing of stainless steel coils in Solution “S”.....	148
8.5.1.	<i>Comparison of the applicability aqueous solutions for treatment stainless steel.....</i>	151
8.6.	Selecting the best parameters for electropolishing in alternative solution.....	152
9.	The design of technological demonstrator for the wire rods descaling.....	155
	Conclusions.....	159
	<i>List of figures.....</i>	163
	<i>List of tables.....</i>	169
	Bibliography.....	173

Acronym

AISI - American Iron and Steel Institute

ChCl – Choline Chloride

CA – Carboxylic Acid

DES – Deep Eutectic Solvents

EG – Ethylene Glycol

EP – Electrochemical Polishing

EDX – Energy Dispersive X-ray Spectroscopy

HPWR – High Pressure Water Rinsing

IL – Ionic Liquid

OV – Over Potential

PS – Power Supply

T – Temperature

Abstract

This work deals with an industrial research on ecological innovative descaling treatments for stainless steels, in substitution of the acid etching process: from the study and the research on samples, the most efficient techniques and their application to industrial purpose are explained.

The research has basically covered the study of two pre-finishing treatments (high pressure water blasting and “dry ice”-blasting) and two etching treatments (electropolishing with ionic liquids and in aqueous media).

In the field of stainless steels, the surface oxide of iron Fe (III) is combined with the multiple elements added to alloys in order to increase their characteristics (carbon, chromium, nickel and other). Moreover, the surface oxide is presented as a layer very tenacious and compact. In addition, heat treatment leads to the formation of a layer without chromium more readily attacked by oxygen from the atmosphere. Surface treatments are required to remove the surface oxide and recover the chromium layer.

The chemical pickling, that is one of the most common etching processes, depends on many factors, such as the size of the pieces, the type of plant, the type of alloy et al. In general, the traditional solutions contain from 10% to 20% by weight of nitric acid, and 1% to 5% by weight of hydrofluoric acid. The oxidizing environment is provided by nitric acid, which effectively removes the oxide surface, and is subsequently used without the hydrofluoric acid to restore the passive layer (passivation). From the environmental point of view, however, the use of this reagent is very costly:

- Air pollution: the formation of nitrogen oxides (NO_x) during the process causes fumes and vapours. These gases are harmful to health, highly polluting (production of acid rain) and extremely aggressive towards metals.

- Water pollution: the high concentration of nitrates and nitrites is one of the causes of eutrophication. In particular, nitrites may form carcinogenic compounds such as nitrosamines, which can enter the food chain through fish.

- Health and safety: hydrofluoric acid is highly corrosive and a poison. It should be handled with extreme attention, using protective equipment and safety precautions. Once absorbed into the blood through the skin, it reacts with blood calcium and may cause cardiac arrest. In addition, it combines with calcium and

magnesium of the bones. Since its action can be delayed for many hours, it can distribute throughout the body, causing the erosion of bones.

These features have shown how the study of alternative "green" treatments is crucial.

Introduction

1.1. Steel production

Today there are hundreds types of steels graded by different classifications: European standards, International Organization for Standardization (ISO), ASTM International and the Society of Automotive Engineers (SAE). Two of the most widely used series are 302 and 304 steels in equipment construction, such as vacuum systems. The grades range from steels, magnetic steels, to stainless steel. Construction irons and steels include buildings, bridges, heavy-duty equipment, vehicles, and "tin" cans.

As a very brief resume of iron and steel fabrication [1], major iron ores are the iron oxides, such as hematite, Fe_2O_3 ; magnetite, Fe_3O_4 ; siderite, FeOxH_2O and the pyrite, FeS_2 . The iron ores are initially kiln fired and roasted in a vertical blast furnace to obtain "pig iron" (4% carbon; 3% silicon; phosphorus and sulphur). The phosphorus makes it brittle when cold; the sulphur makes it brittle when hot.

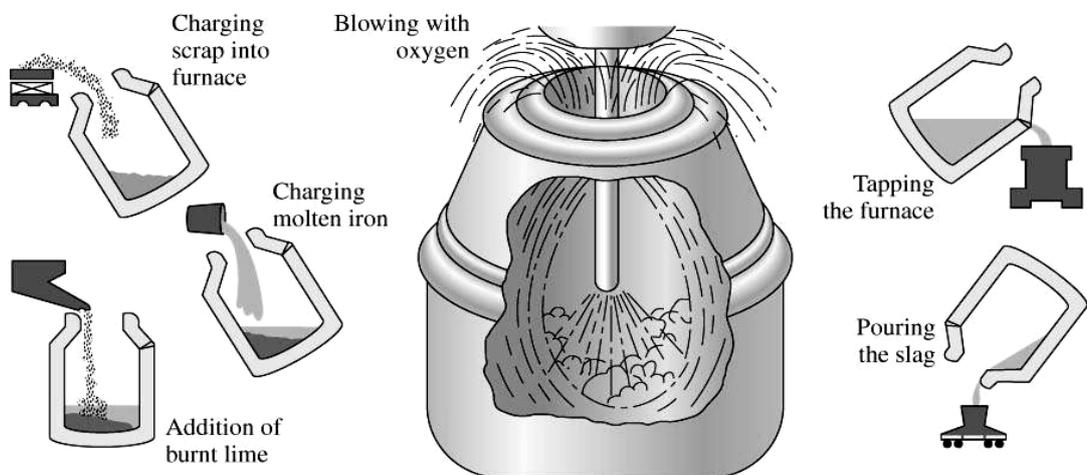


Figure.1.1: Production of the steel from the iron ore in basic-oxygen furnace [2].

Cast iron is made from the initial "pig iron" as white cast iron with a high cementite, Fe_3C content; and as grey cast iron with some cementite separation into iron and graphite. Wrought iron is made by removing the carbon with air blowing through the iron mass. Silicon iron (15% Si) is brittle but very acid resistant and used as holding vessels, crucibles, piping and linings in acid processing equipment. Manganese iron is tough. With 1-7% Mn used for machine tooling; with >7% Mn for heavy-duty equipment, such as rock crushers.

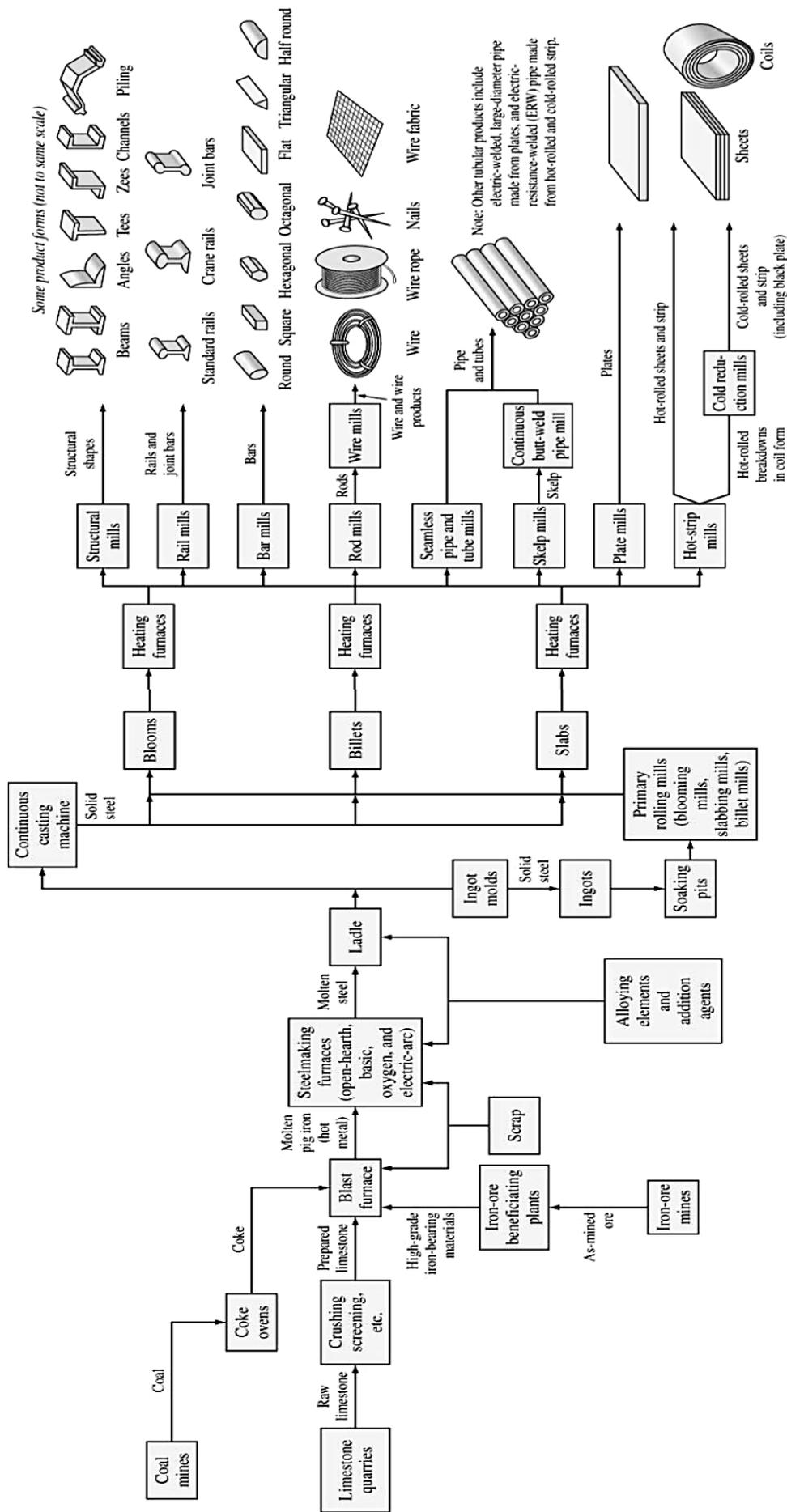


Figure 1.2: Flow diagram showing the principal process steps involved in converting raw materials into the major product forms, excluding coated products [3].

Nickel steel has a great tenacity and is a primary construction steel with 0.5% Ni, and for armour plate with 3-5% Ni. Tungsten steel holds a temper at high temperatures, such that it is used for lathe cutting tools, knives, and scalpels. Both molybdenum and cobalt steels are similar. Chromium steel with 12—15% Cr is corrosion resistant and used for tools, equipment and armour plate. With >18% Cr it is stainless steel.

1.2. The Iron - Iron Carbide phase diagram.

Figure 1.3 shows the equilibrium diagram for combinations of carbon in a solid solution of iron. The diagram shows iron and carbons combined to form Fe-Fe₃C at the 6.67% C end of the diagram. The left side of the diagram is pure iron combined with carbon, resulting in steel alloys. Three significant regions can be relative to the steel portion of the diagram. They are the eutectoid E, the hypoeutectoid A, and the hypereutectoid B. The right side of the pure iron line is carbon in combination with various forms of iron called α -iron (ferrite), γ -iron (austenite), and δ -iron. [4]

α -ferrite. This phase is an interstitial solid solution of carbon in BCC iron crystal lattice. Stable form of iron at room temperature. The maximum solubility of C is 0.022 wt %. Transforms to FCC γ -austenite at 912 °C.

γ -austenite. The interstitial solid solution of carbon in FCC iron. The maximum solubility of C is 2.14 wt %. Transforms to BCC δ -ferrite at 1395 °C. It is not stable below the eutectic temperature (727 °C) unless cooled rapidly.

δ -ferrite. The interstitial solid solution of carbon in BCC iron crystal lattice as α -ferrite but with a greater lattice constant. It is stable only at high temperature above 1394 °C. Melts at 1538 °C.

Fe₃C (iron carbide or cementite). This intermetallic compound is metastable, it remains as a compound indefinitely at room temperature, but decomposes (very slowly, within several years) into α -ferrite and carbon (graphite) at 650 - 700 °C. [5]

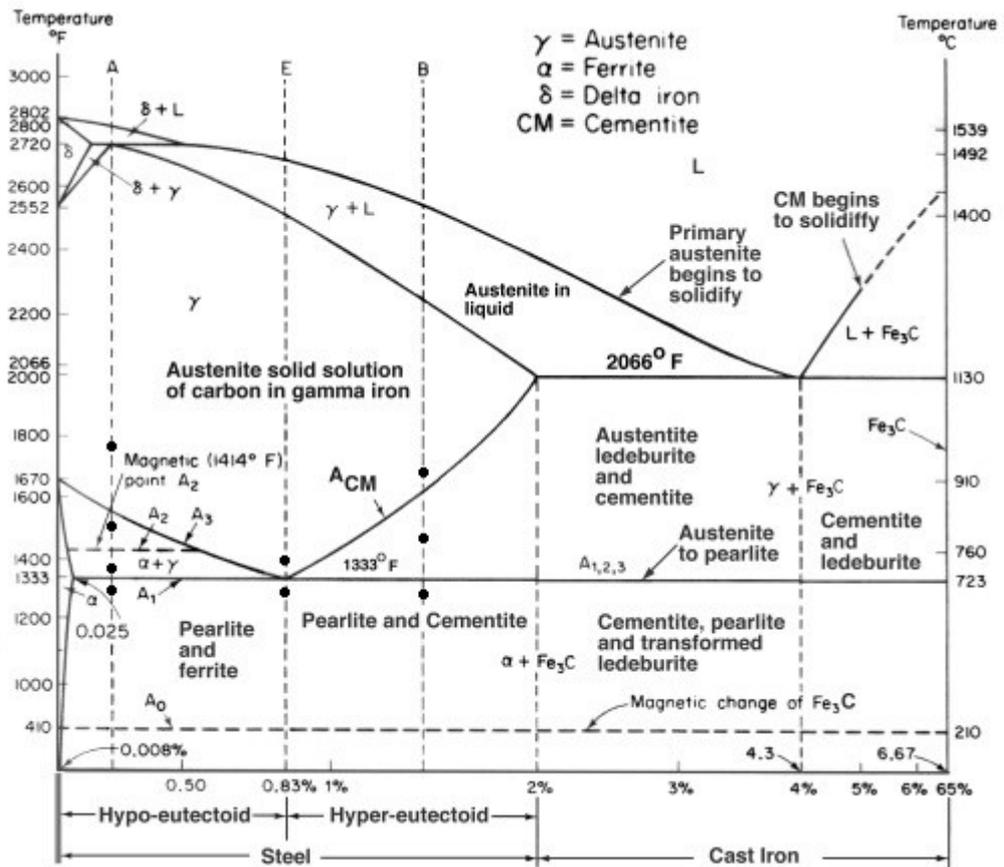


Figure 1.3: Fe-Fe₃C phase diagram. [4]

1.2.1. Cast Iron.

Cast irons are a family of ferrous alloys with a wide range of properties, and as their name implies, they are intended to be cast into the desired shape instead of being worked in the solid state. Unlike steels, which usually contain less than about 1% carbon, cast irons normally contain 2 to 4 %carbon and 1 to 3% silicon.

Cast irons make excellent casting alloys since they are easily melted, are very fluid in the liquid state, and do not form undesirable surface film when poured. The wide industrial use of cast irons is due mainly to their comparatively low cost and versatile engineering properties.

Four different kinds of cast irons can be differentiated from each other by the distribution of carbon in their microstructures: white, gray, malleable and ductile iron. [5]

White cast iron. These contain less Si or C than grey cast irons and undergo faster cooling. This results in cementite forming in favour of graphite. Again the name 'white' has little to do with the ordinary appearance of the alloy,

but rather refers to the fracture surface. White cast irons are much more brittle than grey cast irons, and so their fracture surfaces are reflective, leading to their classification as 'white'.

Gray Cast Iron. Usually contain more carbon or silicon than white cast irons, and require a lower cooling rate. They are called 'grey' cast irons not because of their colour, but due to the appearance of a fractured surface. Grey cast irons are quite ductile and have unreflective fracture surfaces. Gray cast iron has good machinability at hardness levels that have good wear resistance, resistance to galling under restricted lubrication, and excellent vibration damping capacity.

Ductile iron is a family of cast graphitic irons that possess high strength, ductility and resistance to shock. Annealed cast ductile iron can be bent, twisted or deformed without fracturing. Its strength, toughness and ductility duplicate many grades of steel and far exceed those of standard gray irons. Yet it possesses the advantages of design flexibility and low cost casting procedures similar to gray iron.

Malleable cast iron is produced from white cast iron, which is made from hot liquid iron with certain chemical components. The white cast iron needs to be treated by malleablizing, such as graphitizing or oxidation and decarbonization, and then its metallographic structures or chemical components will be changed, so can become into malleable cast iron. [6]

1.3. Alloy types and application.

Stainless steel is not a single alloy: the name applies to a group of iron-based alloys containing a minimum 10.5% chromium. Other elements are added to improve the corrosion resistance and heat-resisting properties, enhance mechanical properties, and/or improve fabricating characteristics.

There are over 50 stainless steel grades that were originally recognized (AISI). A steel corrosion resistance, weldability, mechanical properties are largely determined by metal microstructure (see figure 1.4). This is determined by the steel chemical composition. As per EN 10088, stainless steels can be divided into the following, basic, microstructure-dependent groups:

- Martensitic.
- Ferritic.
- Austenitic.

- Austenitic-ferritic (duplex). [7]

As they are normally added to increase corrosion resistance, the various alloying elements have a large impact on the ease with which a stainless steel can be pickled (pickleability). It is the proportions of the different alloys that have a significant effect on the pickleability of stainless steel. Consequently, the higher the alloy content (i.e. the corrosion resistance), the more difficult it is to pickle the steel.

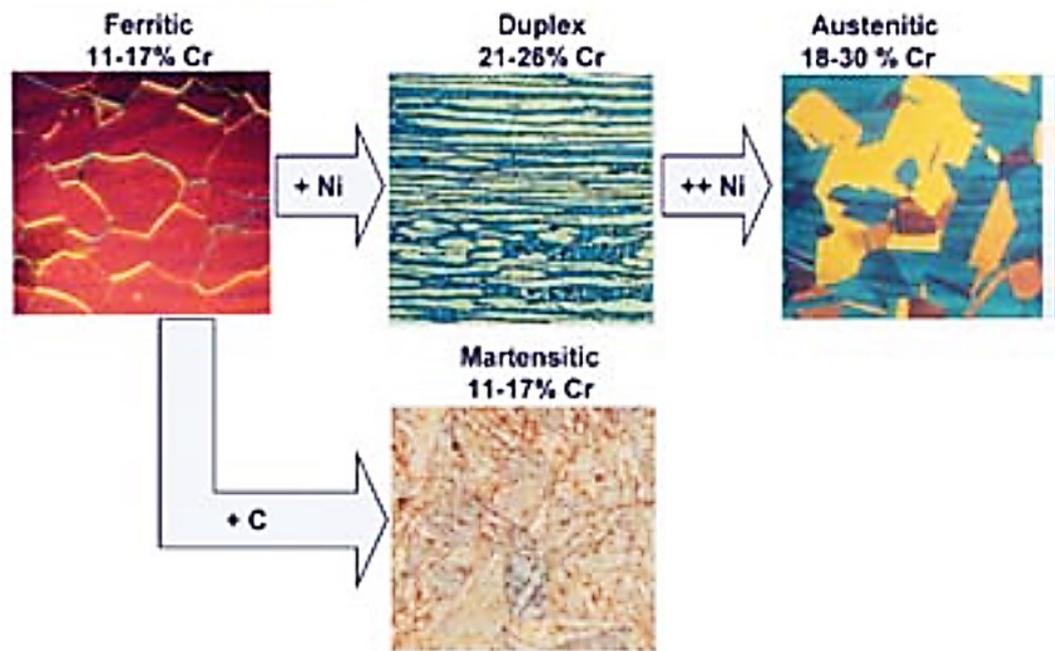


Figure 1.4: Typical microstructures of different stainless steel grades. [7]

The most basic grades are the iron-carbon-chromium alloys. These fall into two groups – martensitic and ferritic.

Martensitic stainless steels generally contain only from 11 to 17% of chromium and have a higher carbon content than the ferritic grades. The steels in this group are characterised by high strength and limited corrosion resistance. They are mainly used where hardness, strength and good wear resistance are required (e.g. turbine blades, razor blades and cutlery).

Ferritic stainless steels are more corrosion resistant than the martensitic grades, but less resistant than the austenitic grades. The most common of these steels contain either 12% or 17% of chromium – 12% of steels are used mostly in structural applications and automotive applications (exhaust systems) while 17% steels are used for catalytic converters, housewares, boilers, washing machines and internal building structures.

This lower resistance means they are “easier” to pickle. In other words, to avoid the risk of overpickling, they need a shorter pickling time or a less aggressive pickling agent. The addition of nickel to the austenitic and austenitic-ferritic steels further improves their corrosion resistance.

Austenitic is the most widely used type of stainless steel. It has a nickel content of at least 7%. This gives it non-magnetic properties, good ductility and good weldability. Austenitic steels can also be used throughout a wide range of service temperatures. Applications for which austenitic stainless steels are used include housewares; containers; industrial piping; tanks; building structures. This type of stainless steel dominates the market.

Austenitic-ferritic (duplex) stainless steels have a ferritic and austenitic lattice structure (hence duplex). To give a partly austenitic lattice structure, this steel has some nickel content. The duplex structure delivers both strength and ductility. Duplex steels are mostly used in the petrochemical, paper, pulp and shipbuilding industries.

1.4. Thermal treatment and scale formation.

After stainless steel is formed, most types must go through an annealing step. Annealing is a heat treatment in which the steel is heated and cooled under controlled conditions to relieve internal stresses and soften the metal. Some steels are heat treated for higher strength. However, such a heat treatment, known as age hardening, requires careful control for even small changes from the recommended temperature, time, or cooling rate that can seriously affect the properties. Lower aging temperatures produce high strength with low fracture toughness, while higher-temperature aging produces a lower strength, tougher material.

Though the heating rate to reach the aging temperature (482 to 537 °C) does not affect the properties, the cooling rate does. A post-aging quenching (rapid cooling) treatment can increase the toughness without a significant loss in strength. Such a process involves water quenching of the material in a 1.6 °C ice-water bath for a minimum of two hours.

The type of heat treatment depends on the type of steel. Austenitic steels are heated to above 1037 °C for a time depending on the dimensions. Water quenching is used for thick sections, whereas air-cooling or air blasting are used for thin sections. If cooled too slowly, carbide precipitation can occur. This build up can be

eliminated by thermal stabilization. In this method, the steel is held for several hours at 815 to 871 °C. Cleaning part surfaces of contaminants before heat treatment is sometimes also necessary to achieve proper heat treatment.

Hot rolling is a metalworking process that occurs at a temperature above the recrystallization temperature of the material. The starting material is usually semi-finished casting products such as slabs, blooms, or billets. The cast microstructure is broken down and deformed during processing and the deformed grains recrystallize, which maintains an equiaxed microstructure (a structure in which the grains have approximately the same dimensions in all directions) and prevents the steel from work hardening. [8]



Figure 1.5: The hot rolled rod coil.

After these processing steps, the surface has dark non-uniform appearance called “scale”. Scaling should be distinguished from rusting, which involves the formation of hydrated oxides. Scale usually is an iron oxides consisting of iron (II) oxide (FeO), iron (III) oxide (Fe₂O₃), and iron (II, III) oxide (Fe₃O₄, magnetite). It is usually less than 1 mm thick and initially adheres to the steel surface. The surface chromium has been lost during the high temperature processing steps, and without removal of the scale, stainless steel would not provide the expected level of corrosion resistance.

1.5. Cleaning of stainless steel.

Stainless steels need to be cleaned not only for aesthetic considerations but to preserve corrosion resistance. Stainless steel is protected from corrosion by a thin layer of chromium oxide. Oxygen from the atmosphere combines with the chromium in stainless steel and form the passive chromium oxide film that protects from further corrosion. Any contamination of the surface by dirt, or other material, hinders this passivation process and traps corrosive agents, reducing corrosion protection. Thus, some form of the cleaning is necessary to preserve the appearance and integrity of the surface. Stainless steels are easily cleaned by many different methods.

In selecting a metal cleaning process, many factors must be considered, including:

- 1) the nature of the scale to be removed;
- 2) the substrate to be cleaned;
- 3) the degree of cleanliness required;
- 4) the environment impact of the cleaning process;
- 5) the cost consideration;
- 6) the total surface area to be cleaned;
- 7) effects of previous processes;
- 8) rust inhibition requirements;
- 9) materials handling factor;
- 10) the surface requirements of subsequent operations, such as phosphate conversion coating, painting, or plating. [9]

1.5.1. Descaling.

Descaling is the removal of heavy, tightly adhering oxide films resulting from hot-forming operations, thermal treatments (such as annealing or hardening), or welding. [9] Since most stainless steel products received from the producing mill have been etched, descaling is required only because of subsequent manufacturing operations. There are basic methods used for removing rust and scale from metal parts:

- abrasive blasting (dry or wet);
- tumbling (dry or wet);

- brushing;
- acid etching (or pickling);
- salt bath descaling;
- alkaline descaling;
- electrochemical polishing (or etching). [9]

Abrasive blasting is defined as an operation in which materials are cleaned by the abrasive action of any metal shot or mineral particulate propelled within a gas or liquid. Blasting cannot be considered as a complete cleaning procedure in itself.

Tumbling is often the least expensive process for removing rust and scale from metal parts. Size and shape of parts are the primary limitations of the process.

Etching in hot, strong solutions of acids is used for complete removal of scale from mill products and fabricated parts.

Electrolytic etching, although more expensive than usual pickling, can remove scale twice as fast and may prove economical where the time is limited.

Salt bath descaling is an effective means of removing or conditioning scale on stainless steels. Several types of salt baths either reduce or oxidize the scale. Various baths operate within a temperature range of 400 to 525 °C.

Alkaline descaling or alkaline derusting is used to remove rust, light scale, and carbon smut. Alkaline descaling is more costly and slower in its action than acid pickling, but no metal is lost using the alkaline method, because chemical action stops when the rust or scale is removed. Alkaline descaling also allows complete freedom from hydrogen embrittlement.

Electrochemical polishing. A less commonly used polishing technique is electrolytic polishing. Electrolytic polishing, known as anodic dissolution. In electropolishing, the metal is removed ion by ion from the surface of the metal object being polished.

1.5.2. Acid etching.

When planning an acid etching operation, it is necessary to know the type of stainless steel and its metallurgical and physical condition. Since the various stainless steels have different alloy compositions, they behave differently when exposed to etching acids. In addition, stainless steel parts that have been sensitized by welding or thermal treatment, or parts in a highly stressed condition, may be more susceptible to corrosive attack and thus require

special attention [10].



Figure 1.6: Mixed-acid etching line. [8]

The most commonly acids used for pickling stainless steels are nitric (HNO_3), hydrofluoric (HF), sulphuric (H_2SO_4) and hydrochloric (HCl).

Nitric acid is oxidizing, whereas the others are reducing. Nitric acid tends to promote and preserve the corrosion-resistant qualities of stainless steels; it does not act to destroy the microscopically thin oxide surface film that gives stainless steels their corrosion resistance. Its oxidizing behaviour accounts for the fact that when alone or in solution with water, nitric acid will not dissolve and remove oxide scale from stainless steels.

Other acids accomplish descaling by reducing the oxides of which scale is composed. At the same time, they also reduce the protective oxide film on stainless steel and thus lay the underlying metal open to corrosive attack.

Because of the inherent characteristics of oxidizing and reducing acids, mixtures of the two acid types are used for pickling stainless steels. The most frequently used solution is a combination of nitric and hydrofluoric acids. They combine the scale-removing feature of the reducing acid constituent and the base metal protecting or passivating action of the nitric. By changing the relative proportions of these two acids in an aqueous solution, a wide range of strengths

is obtainable, which can still be further manipulated by varying temperatures.

Solutions of sulphuric acid find their main use as a preliminary step in descaling. Sulphuric acid provides a quick initial attack on scale deposits, and it is always followed by the much more controllable nitric/hydrofluoric treatment.

Hydrochloric acid solutions behave similarly to sulphuric acid mixtures. Since the action of hydrochloric acid on both oxide scale and base metal is exceedingly rapid, it must be used with extreme caution. Unlike sulphuric acid, however, hydrochloric acid produces ferric chloride that is an active pitting agent. As the salt content builds up in the bath, pitting becomes quite rapid. For that reason, solutions can be used but for a short time and should be discarded as soon as any tendency toward pitting attack becomes apparent.

Hydrofluoric acid is never used alone. Because of the hazards connected with its handling, users should observe strict safety precautions [8].

1.5.2.1. Typical procedure of acid pickling stainless steel.

Mixtures of nitric and hydrochloric acids in water are the most effective and most widely used solutions for pickling the chromium-nickel stainless steel. The solutions can vary from 5 to 25 % of nitric acid and from 0,5 to 3 % of hydrofluoric (both by volume). For light scale, 12-15% nitric and 1 % of hydrofluoric is satisfactory. For the heavier oxides, the amount of hydrofluoric acid is higher, 2-3%. Bath temperature ranges from 50 to 60 °C. As higher the temperature is, as faster is the descaling, but because of acid evaporation, it is better to avoid higher temperature. The immersion time is from 10 to 15 minutes. The rinsing in water should follow pickling to remove any acid residues and after drying.

The sulphuric acid solution can be used as a preliminary step for this use 8-10% solution of concentrated sulphuric acid in water at 65-70 °C. Immerse for 5 minutes, rinse quickly with clean hot water, and after immerse in nitric/hydrofluoric acid bath and follow the procedure as previously described.

To avoid the hazardous hydrofluoric acid, it may be replaced with hydrochloric acid. Hydrochloric acid is extremely corrosive to stainless steel, so we need to be very accurate in immersion time and acid concentration. Nitric/hydrochloric acid solution is good for one-time-use job when you need to clean a single piece. Hydrochloric acid promotes the formation of ferritic chloride

in the bath; therefore, these solutions must be limited to a short time use if pitting attack is to be avoided.

Table 1.1: The etching solutions for stainless steel. [11]

№	Solution	Conditions
1	Sulphuric acid, 400 - 450 g/l Hydrochloric acid, 250 - 300 g/l SAS, 3 - 5 g/l	Time, 60 min Temperature, 15 - 30 °C
2	Nitric acid, 220 – 240 g/l Sodium fluoride, 20 – 25 g/l Sodium chloride, 20 – 25 g/l	Time, 60 min Temperature, 15 - 30 °C
3	Sulphuric acid, 80 – 110 g/l Nitric acid, 70 – 80 g/l Hydrofluoric acid, 15 – 50 g/l	Time, 10 - 60 min Temperature, 15 - 30 °C

1.5.2.2. Organic acid pickling solutions.

Organic acid chelates can be used to clean light oxides or scales and free iron particles from stainless steel surfaces. The organic compounds combine acid solution activity with passivant and buffering properties. Light scale residues can be solubilized in dilute solutions of ammonium citrate. Treatments of this type are satisfactory for final cleaning of fabrications for the food and chemical industry. A concentration of 3 to 5 % organic acid is preferred, and this solution is adjusted with ammonium hydroxide to a pH of between 3 and 4. An operating temperature of 80 °C will produce good cleaning within acceptable time cycles.

The iron particles may contaminate stainless steel surfaces because of shot blasting or machining. This free iron decreases the corrosion resistance. The ammonium citrate combined with anionic or non-ionic wetting agents are effective in removing these metal particles. An operating temperature of 80 °C and concentrations of 2 to 5 %.

Glycolic acid, formic acid, etc. are used in many equipment cleaning operations including pharmaceutical processing equipment, whiskey storage tanks, steam generators, and nuclear reactors. In addition to their ability to combine with many other chemical compounds, the advantages of using acids of this type for these applications include the low corrosion rate experienced, ability

to hold iron in solution, and safe handling properties. A number of manufacturers of these compounds have detailed descriptive literature of specific formulations that may be employed for cleaning stainless steel surfaces. [10]

1.6. Electrochemical etching and polishing.

Electrochemical polishing of metal is one of the anodic metal processing, which results in the dissolution of the metal surface layer. The formation of a new surface layer with a lower micro-roughness, the smoothing of surface relief that does not contain cracks, foreign inclusions, hidden defects. This process utilizes a reducing acid environment in conjunction with substantial DC. It smooths the surface and leaves a shiny appearance. Moreover, more importantly it acquires better performances such as increased endurance limit, durability, fatigue resistance, elastic limit, and corrosion resistance. It is often used in applications where extreme cleanliness is necessary, for example in the pharmaceutical, semiconductor and dairy industries.

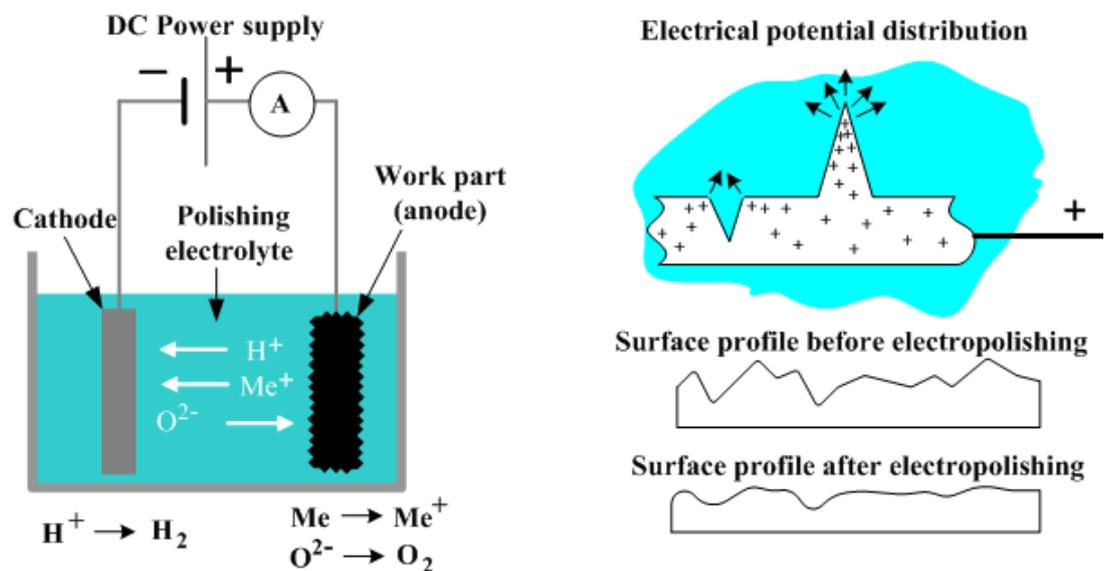
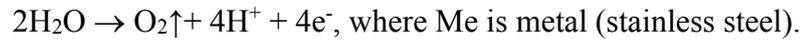
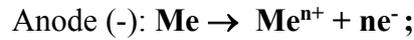
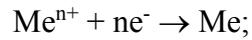


Figure 1.7: Typical electropolishing setup and surface profiles.

A typical electropolishing installation is similar in appearance to an electroplating line (see figure 1.7). The tank fabricated from plastic or steel with lining is used to hold the chemical bath. A lead, copper or stainless steel cathode immerses into the bath and connect to the negative (-) side of the power supply. The

working pieces are coupled to the positive (+) side. During the electropolishing, the metal is dissolved from the anodic electrode, passing in the solution and forms soluble salt of the metal.



All components of stainless steel – iron, chromium and nickel – undergo this reaction simultaneously, producing a controlled smoothing of the surface. Some metallic ions are deposited on the cathodes, which require regular cleaning. Several side reactions also occur, creating by-products that must be controlled to produce the highest possible quality of electropolishing.

1.6.1. Benefits and disadvantages of electropolishing.

Benefits of electropolishing:

- bright appearance;
- absence of abrasive scratches;
- improved fatigue strength due to stress relieving and defects free surface;
- lower coefficient of friction due to smoother surface (reduced microasperities);
- better corrosion resistance;
- allows processing fragile and delicate parts.

Disadvantages of electropolishing:

- rough surface defects cannot be removed;
- electropolishing multiphase alloys may cause roughening due to selective dissolution of different phases.

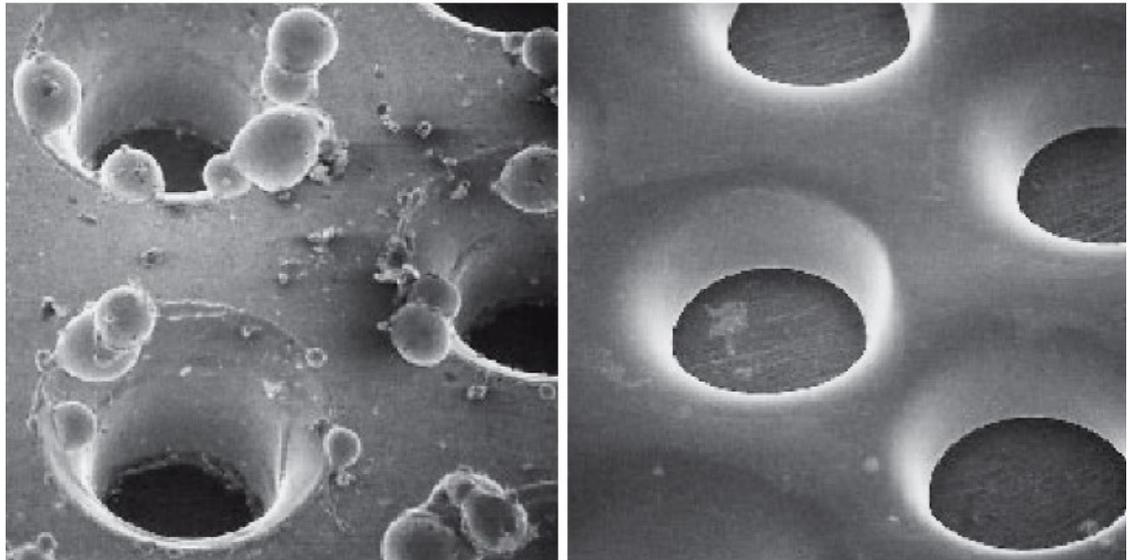


Figure 1.8: A microscopic view of the same surface before and after electropolishing shows that the process produce clean metallic surface. [12]

The result can be reproducible with a high degree of precision, so components with tight tolerance can also be treated safely. On figure 1.8, we can see that electrochemical polishing produces the clean surface.

1.6.2. Solutions for electropolishing stainless steel.

Practically speaking, three major process steps are necessary to electropolish most metal surfaces successfully:

1. Metal preparation and cleaning.
2. Electropolish (electropolish drag-out rinse).
3. Post-treatment (rinse, 30% by volume of nitric acid, rinse, deionized hot water rinse).

The metal preparation consists of alkaline cleaning or degreasing and pickling (usually used before deposition to remove oxides). The purpose of cleaning in alkaline is to remove oils, grease, fingerprints and other parts after mechanical work.

A typical electropolishing solution consists of mixture of 96% sulphuric acid and 85% orthophosphoric acid. The operating conditions are following current density 5 -25 A/dm²; temperature 40 – 75 °C; time 2 – 20 min; cathode material – stainless steel, copper, or lead. [11]

There are organic electropolishing baths, inorganic baths, and organic/inorganic baths. Some typical formulas are shown in table 1.2.

Table 1.2: The literature recipes for electropolishing steel.

№	Solution	Conditions
1	Citric acid, 55% Sulphuric acid, 15%	Current density minimum, 10 A/m ² Temperature, 90 °C
2	Lactic acid, 33% Phosphoric acid, 40% Sulphuric acid, 13,5%	Current density, 7,5-30 A/m ² Temperature, 70-100 °C
3	Phosphoric acid, 56% Chromic acid, 12%	Current density, 10-100 A/m ² Temperature, 25- 80 °C

In rinsing, we should remember that electropolishing solution is viscous and does not mix readily with water. It should be controlled the quality of rinsing and avoided that solution drying on the metallic parts causing rusting and corrosion during the storage.

In the case of creating the film of sulphates and phosphates that are difficult to remove by water rinsing only, the nitric acid post-treatment should be carried out. The residual nitric acid solution can be removed with cold water rinsing because it is more soluble in water. The last step is drying that should be done in order to evaporate residual moisture and prevent staining during the storage or use.

2. Ionic liquids as new electrolytes.

Ionic liquids (or deep eutectic solvents) is a type of ionic solvent with special properties composed of a mixture that forms a eutectic with a melting point much lower than either the individual components (see figure 2.1).

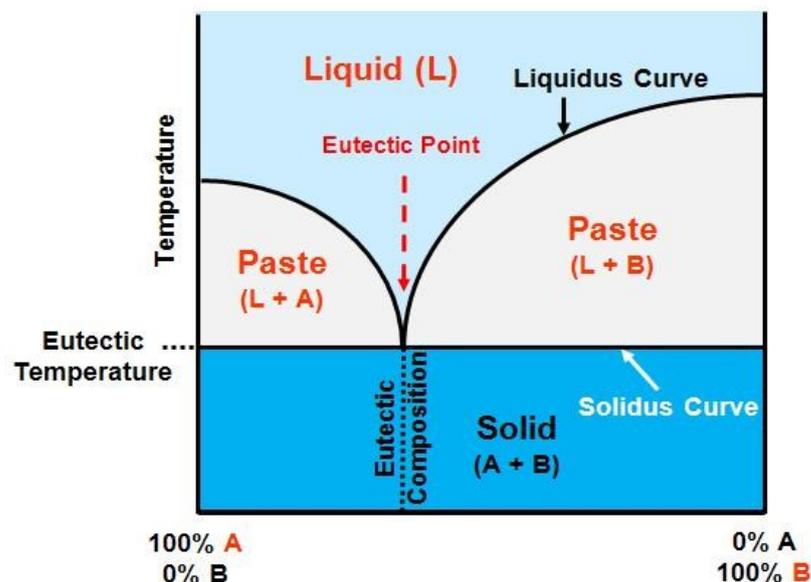


Figure 2.1: Eutectic phase diagram.

The first generation of eutectic solvents were based on mixtures of quaternary ammonium salts with hydrogen bond donors such as amines and carboxylic acids. There are four types of eutectic solvents [13]:

- I. Quaternary ammonium salt + metal chloride;
- II. Quaternary ammonium salt + metal chloride hydrate;
- III. Quaternary ammonium salt + hydrogen bond donor;
- IV. Metal chloride hydrate + hydrogen bond donor.

Abbott et al. [14] have shown a new process for electropolishing the steel using the choline chloride based eutectic. The operating conditions are similar to the existing acid based solutions and represent simple drop-in replacement technology. It has been shown [15] that the electropolishing mechanism is fundamentally different in an ionic liquid compared to an acidic solution. No passivating layer is formed on the electrode in an ionic liquid and this decreases the ohmic resistance of the cell. The corrosion tests show that the result is equivalent to the current technology.

It was shown [16] that an eutectic mixture of choline chloride with urea gave a liquid with a freezing point of 12 °C. This fluid was found to have interesting solvent properties that are similar to ambient temperature ionic liquids, and a wide variety of solutes was found to exhibit high solubility. It is not limited to amides, but can be applied to a wide variety of other hydrogen bond donors such as acids, amines and alcohols [17]. The figure 2.2 displays the freezing points of mixtures of the carboxylic acids with choline chloride as a function of the composition.

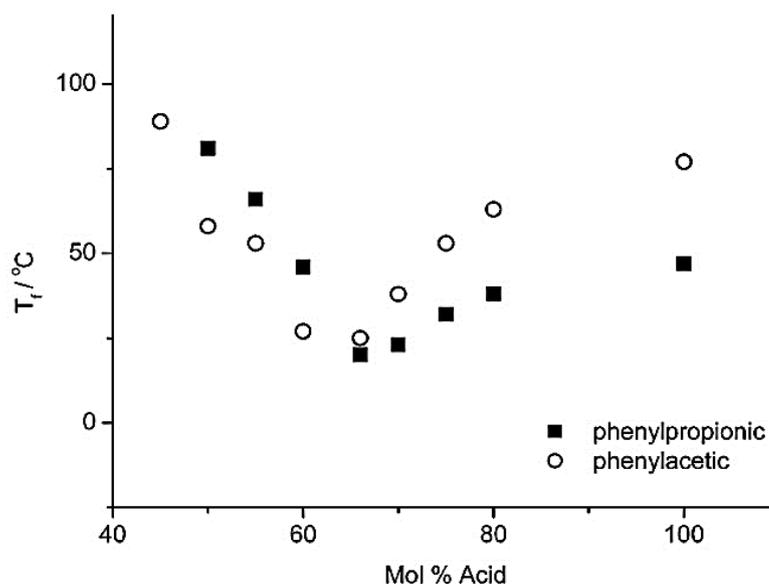


Figure 2.2: Freezing point of choline chloride with phenylpropionic and phenylacetic acids as function of composition.

In reference [18] three kinds of ionic liquids are described: acidic, neutral and basic. Typical ionic liquid anions can be described as neutral in the acid/base sense. These ions exhibit weak electrostatic interactions with the cation and thus give advantageously low melting points and viscosities. Ionic liquids formed from these anions typically show good thermal and electrochemical stability and thus are often utilized as inert solvents in a wide range of applications. For example, hexafluorophosphate, bis (trifluoromethanesulfonyl) amide, tetrafluoroborate, methanesulfonate, tricyanomethide and p-toluenesulfonate. The examples of acidic ionic liquids are those based on the protic ammonium, pyrrolidinium and imidazolium ions, of which many are known. There is a number of ionic liquid forming anions that can be classified as basic. These include the lactate, formate, acetate (and carboxylates generally) anion.

The most of electrochemical processes based on aqueous solutions (acidic or basic). The advantages of using aqueous solutions are:

- Cost;
- Non-flammable;
- High solubility of the electrolytes;
- Good throwing power;
- High conductivity.

For this and other reasons, the water will remain the main component of the metal finishing industry. There are also some disadvantages in using aqueous solutions:

- Limited potential window;
- Gas evolution and as result hydrogen embrittlement;
- Passivation of the metals during the process;
- Necessity of surface active substances and complexing agents.

As it is told [19], the ionic liquids are the salts with weak interaction between the ions and this allows them to become liquid at room temperature, below 100 °C. Ionic liquids are a good solvent for a wide range of organic and inorganic compounds, which makes them an attractive solvent alternative for environmentally friendly processes.

Among the advantages of using ionic liquids, there are the following:

- The cost of ionic liquids is higher than aqueous electrolytes, but higher conductivity and efficiency will provide energy savings compared with aqueous one.
- In electropolishing, we use strongly acidic aqueous solutions, which create large quantities of the corrosive effluent solutions saturated with metal ions; while, in the ionic liquid electrolytes, the metallic precipitation can be separate and recycle.
- The possibility to replace the hazardous and toxic materials currently used in water, such as chromium (VI), high corrosive and caustic electrolyte.
- Since these are non-aqueous solutions, there is negligible hydrogen evolution and thus less problems in using cathodic materials.

These properties of ionic liquids could provide better health and safety standards for employees in the workplace, i.e. elimination of hazardous vapours, elimination of highly corrosive acidic/alkaline solutions, reduce the use of toxic chemicals.

Current aqueous treatment solutions have a strongly negative impact on the environment, which obliges the treatment of wastewater and the dumping of the ultimate waste in landfill. [20]

A.P. Abbott et al. [21] had successfully demonstrated the electropolishing of type 316 stainless steel in a ChCl: EG mixture. The dissolution mechanism is shown to be different to that found in aqueous acid solutions. The dissolution of the oxide film is slower than in aqueous solutions and this can lead to pitting at low current densities. The polishing mechanism is found to be anisotropic and micro-roughness can be reduced to less than 100 nm. The electropolishing liquid is non-corrosive and is air and moisture stable. Figure 2.3 shows an AFM image of the interface between an electropolished region and a region where the surface was protected with an acrylic resin.

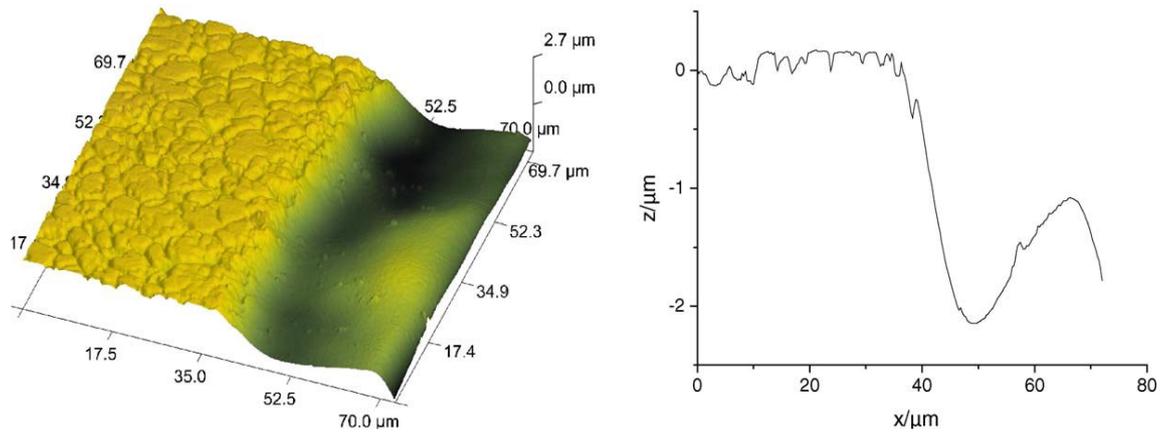


Figure 2.3: Atomic force microscopy images (3D left and 2D right) of stainless steel 316 grade Hull cell plate etched in 1 ChCl:2 EG mixture at 7.0V for 10 min at 45°C showing the boundary between a region protected with acrylic resin and a polished region. [21]

3. Passivation.

Passivation of stainless steels is a surface cleaning operation conducted with solutions of nitric acid in water, which has the effect of eliminating surface contamination that may cause discoloration or superficial corrosive attack in service. Typical contamination includes iron from cutting tools and contaminated sandblast materials. [22]

This layer of chromium oxide is passive (chemically inert), tenacious (strongly attached to the surface of SS) and self-renewing (see figure 3.1). The self-renewing property of the film means that if the film is removed or damaged (as it happens when the surface is machined or scratched), the film forms again by itself! All that is required is oxygen that is present in the air. This is what makes stainless steel special.

The passivating value of electro-polishing methods is frequently a subject of inquiry. These processes actually remove metal of uniform thickness and in doing so they also dislodge foreign materials. The iron and nickel are removed from the surface to a depth of some 20-30 angstroms. The result is a dense film of chromium oxyhydroxide across the metal surface. Thus the electropolishing provides the most dense and durable passive film.

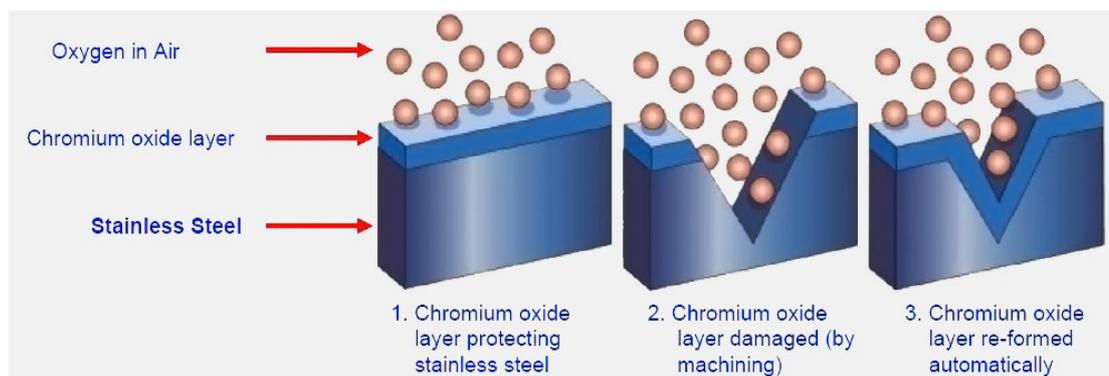


Figure 3.1: Self-repair mechanism of stainless steel. [7]

3.1. Chemical passivation.

Protective oxide films form on clean stainless surfaces in the presence of oxygen in normal air. Their effect is to make the material passive, which is to say that the material is placed in a condition of maximum corrosion resistance.

Experience indicates that the speed of oxide formation is accelerated by the oxidizing behaviour of nitric acid. For example, a 30 percent solution of that acid is known to produce more rapid passivation than usual air.

There is a certain latitude in solution strengths, operating temperature and immersion time in acid baths. However, any solution can be applicable to all grades. For all chromium-nickel stainless steel including the precipitation hardening alloys nitric acid passivating solutions usually contain from 20 to 40% nitric acid, the temperature range is from ambient temperature up to 60 °C for periods of 30 to 60 minutes.

A passivation solution, recently widely advertised, is the use of chelating agents. It is claimed that these comprise extremely versatile, highly active compounds, which complex and remove a variety of metallic ions that would otherwise adversely affect the corrosion resistance of the alloy. The function of chelates is explained in that way that, the ring structure is formed around a contaminant metallic ion that is removed and strongly held. It cannot work as a metallic element any longer and is removed by the chelating agent [8]. Commonly used chelates are polyfunctional organic carboxylic acids, with salts containing hydroxyl and amine constituents.

Hydrogen peroxide is a strong chemical oxidant that decomposes into water and oxygen in the presence of a catalytic quantity of any transition metal (e.g., iron, copper, nickel, etc.). This ability of peroxides, to produce oxygen used to the passivation of a surface. Usually, hydrogen peroxide adds in the treatment solution to provide uniform cleaning and partially passivation.

3.2. The anodic passivation.

Passivity: a condition of corrosion resistance due to the formation of thin surface films under highly oxidizing conditions at high anodic polarization. Anodic passivation or anodizing is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal parts. The process is called anodizing because the part to be treated forms the anode electrode of an electrical circuit. Anodizing increases corrosion resistance and wear resistance.

For anodising the steel are using following solutions: 5% $K_2Cr_2O_7$ at 40 – 55 °C during 10 – 15 minutes, current density - 3÷5 A/dm². After rinsing, the details are placed in bath with sodium hydroxide 350 – 600 g/l at 65 – 80 °C for 10

– 30 minutes, current density is $3\div 5 \text{ A/dm}^2$. For details with simple profile usually used solution: CrO_3 - $150\div 250 \text{ g/l}$; HBF_4 - $1\div 2 \text{ g/l}$; temperature - $40\div 50 \text{ }^\circ\text{C}$; current density - $5\div 10 \text{ A/dm}^2$, time - $10\div 15$ minutes. [11]

3.2.1. Corrosion protection.

Anodic protection parameters can be obtained from anodic polarization measurements. Measurements of current-potential relations under carefully controlled conditions can yield information on corrosion rates, coatings and films, passivity, pitting tendencies and other important data. The specimen potential is scanned slowly in the positive direction and therefore acts as an anode such that it corrodes or forms an oxide coating. These measurements are used to determine corrosion characteristics of metals in aqueous environments. Investigations such as passivation tendencies and effects of inhibitors or oxidizers on metals are easily performed with this technique.

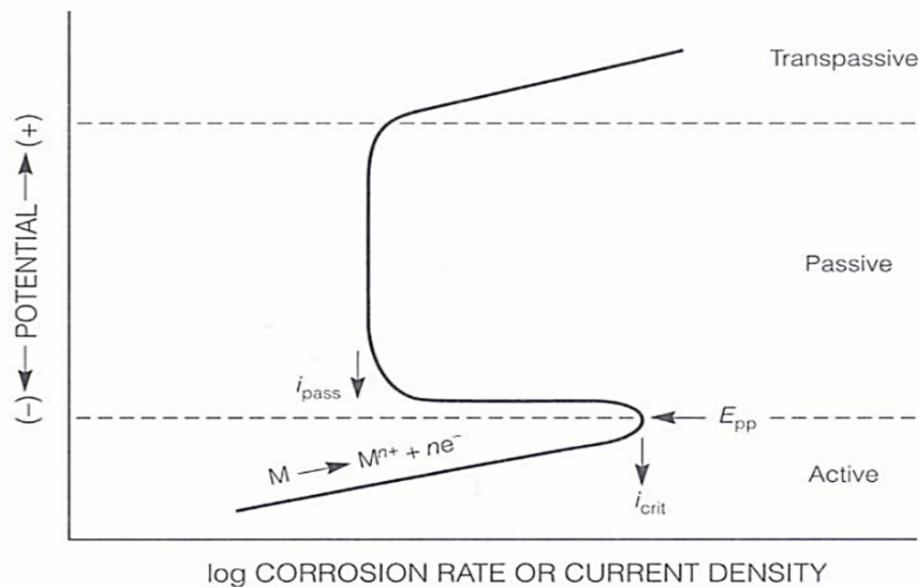


Figure 3.2: The anodic polarization curve.

The anodic polarization curve for an active-passive metal consists of three regions (see figure3.2):

1. Active region:

– i increases with E until E_{pp} (primary passive potential);

– i_{crit} the maximum current.

2. Passive region:

– above E_{pp} , the passive film forms and the corrosion current density drops to

i_{pass} ;

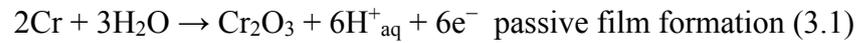
– i_{pass} is very small in the passive state.

3. Transpassive region:

– the protective anodic film is damaged and may break down completely;

– i is proportional to E in the transpassive region.

For chromium, the anodic dissolution produces divalent chromium ions in the active state and the passivation occurs forming an extremely thin, trivalent chromium oxide film on the metal surface.



The transpassive dissolution of metallic chromium is the oxidative dissolution of trivalent chromic oxide into soluble hexavalent chromate ions in acidic solution. Hence, the anodic transpassive dissolution proceeds through the formation of a chromic oxide film on the metal surface. [22]

4. Experimental part.

4.1. The characterization of the scale layer.

The microscope used is a Philips XL-30, which as an electron source uses a filament of Tungsten (W). Scanning electron microscopy (SEM) is a method for high-resolution imaging of surfaces. The SEM uses electrons for imaging, much as a light microscope uses visible light. The advantages of SEM over light microscopy include much higher magnification ($>100,000\times$) and greater depth of field up to 100 times that of light microscopy. Qualitative and quantitative chemical analysis information is also obtained using an energy dispersive x-ray spectrometer (EDS) with the SEM. The SEM generates a beam of incident electrons in an electron column above the sample chamber. The electrons are produced by a thermal emission source, such as a heated tungsten filament, or by a field emission cathode. The energy of the incident electrons can be as low as 100 eV or as high as 30 keV depending on the evaluation objectives. The electrons are focused into a small beam by a series of electromagnetic lenses in the SEM column. Scanning coils near the end of the column direct the position of the focused beam onto the sample surface. The electron beam is scanned in a raster pattern over the surface for imaging. The beam can also be focused at a single point or scanned along a line for x-ray analysis. The beam can be focused to a final probe diameter as small as about 10 Å. The incident electrons cause electrons to be emitted from the sample due to elastic and inelastic scattering events within the sample's surface and near-surface material. High-energy electrons that are ejected by an elastic collision of an incident electron, typically with a sample atom's nucleus, are referred to as backscattered electrons. The energy of backscattered electrons will be comparable to that of the incident electrons. Emitted lower-energy electrons resulting from inelastic scattering are called secondary electrons. Secondary electrons can be formed by collisions with the nucleus where substantial energy loss occurs or by the ejection of loosely bound electrons from the sample atoms. The energy of secondary electrons is typically 50 eV or less. [23]

4.1.1. The characterization of thickness and anisotropy.

To calculate the thickness of scale some pictures of a raw square bar 50x12 austenitic and martensitic steel were analysed by electron microscope. The thicknesses were measured on both sides of the bar, to clarify the difference in thickness. The high thickness ranging from 20 μm to 50 μm for the austenitic bar and from 70 to 100 μm in the martensitic bar. On the figures, 4.1 and 4.2 are the SEM micrographs.

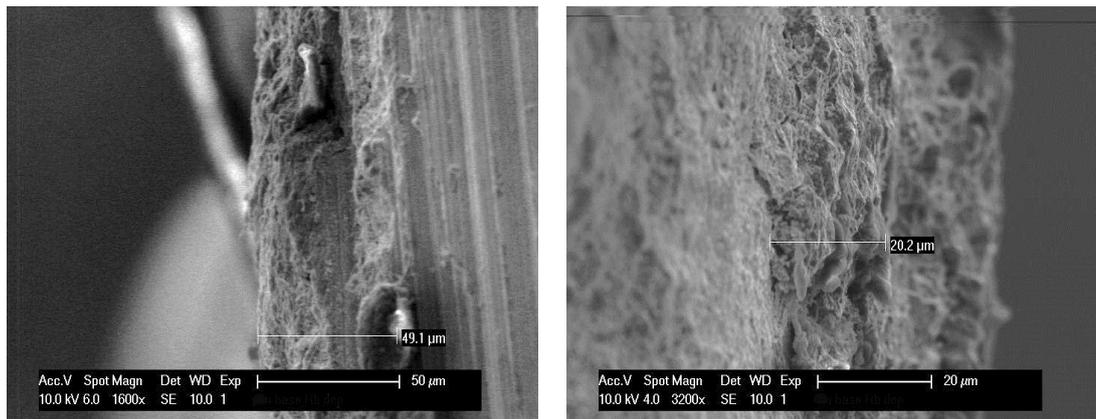


Figure 4.1: SEM micrographs of the austenitic bar from both side.

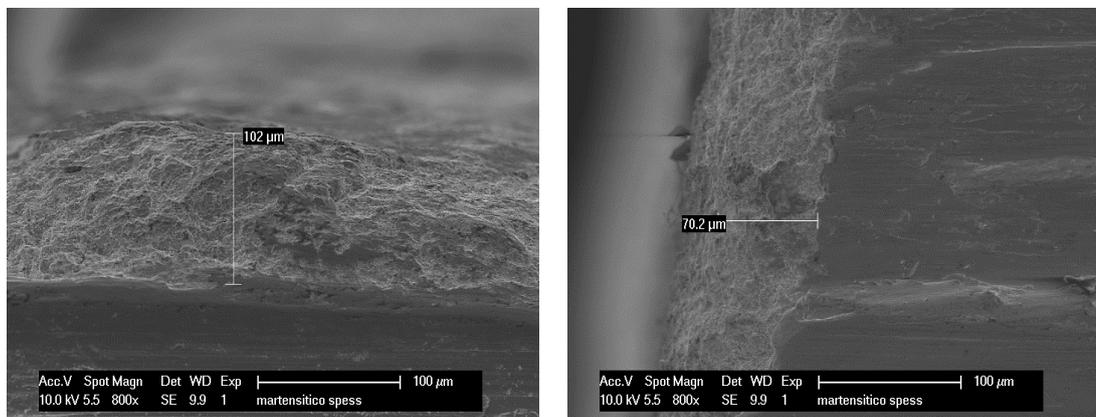


Figure 4.2: SEM micrographs of the martensitic bar from both side.

4.1.2. Morphology and microstructural characterization.

After examination of the samples, we saw the different morphology due to the presence of scale and its partial and total removal in the process of blasting and chemical cleaning. The EDX shows a different amount of chromium, nickel and oxygen, depending on the cleaning and passivation. Particularly, the amount of

carbon, chromium, nickel and oxygen is maximum in the rough while it decreases in the sandblasted and chemical etched samples.

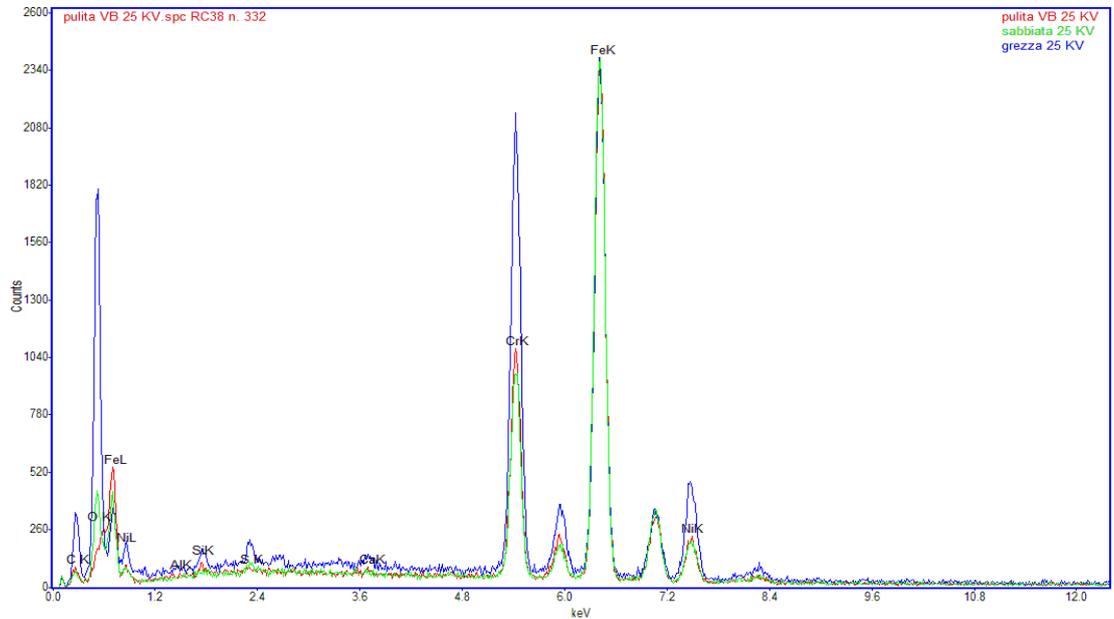


Figure 4.3: EDX spectroscopy - rough surface - sandblasted - cleaned with standard chemical etching.

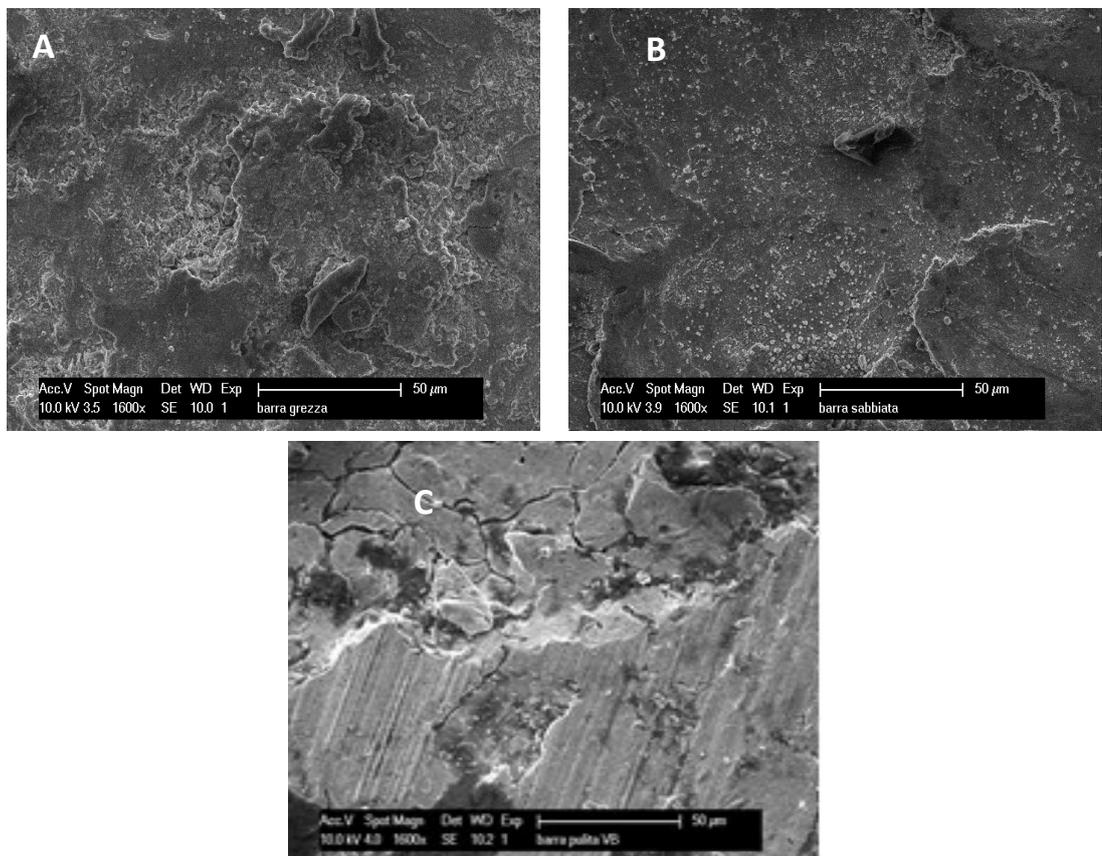


Figure 4.4: SEM micrograph rough surface (A), sandblasted (B), cleaned with standard chemical etching (C).

4.2. Characterization of the different steel types.

We characterized the samples with scale from typical steel fabrication by scanning electron microscope to observe differences in the surface morphology (see table 4.1)

Table 4.1: Samples used for the characterization of the scale surface layer.

Type	Material	Finish	Source
Bar	AISI 304	raw	Bar 8x15
AISL 50	AISI 304	sandblasted	Bar 8x15
AU1882/P 51	AISI 303 (doped with sulphur)	sandblasted	Bar 6x13
VAL 1C	AISI 410 (martens.)	sandblasted	square 50x40
Rod		raw	rod
Hexagonal bar		raw	Hexagonal bar
Squared bar		raw	Squared bar
Wire rod		raw	Wire rod diam. 21 mm

The SEM micrographs characterize the surface and shows difference in the surface morphology. The micrographs presented in three magnifications (100x, 400x, 1600x), while the surface EDX spectrum shows, which elements compose the outer layers of the sample. The study allowed us to determine that the scale always form a very compact and adherent layer with no visible cracks. Therefore, it is necessary to study a treatment that removes the scale uniformly, avoiding inclusion that mainly attack the underlying steel.

Raw bar. On the figures 4.5, 4.6 are presented SEM and EDX analysis of raw steel bar.

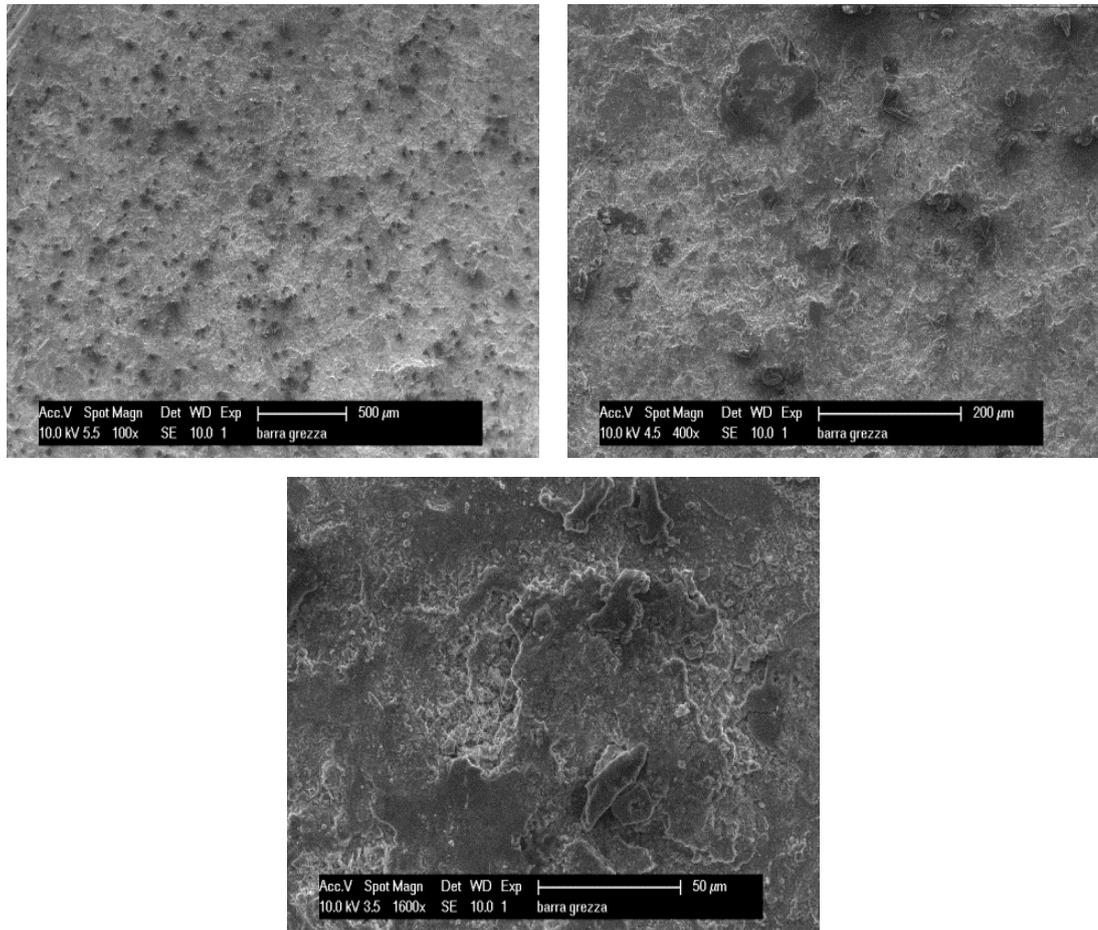


Figure 4.5: SEM micrographs of the raw bar, arranged with increasing magnification.

In the layer of scale, also have presented the same elements as in the substrate, such as chromium, nickel, and sulphur. The morphology of the layer is compact and has various structures of different heights. The layer of scale is very adherent to the surface, which appears uniform colour in photos SEM, and the composition remains constant in all areas.

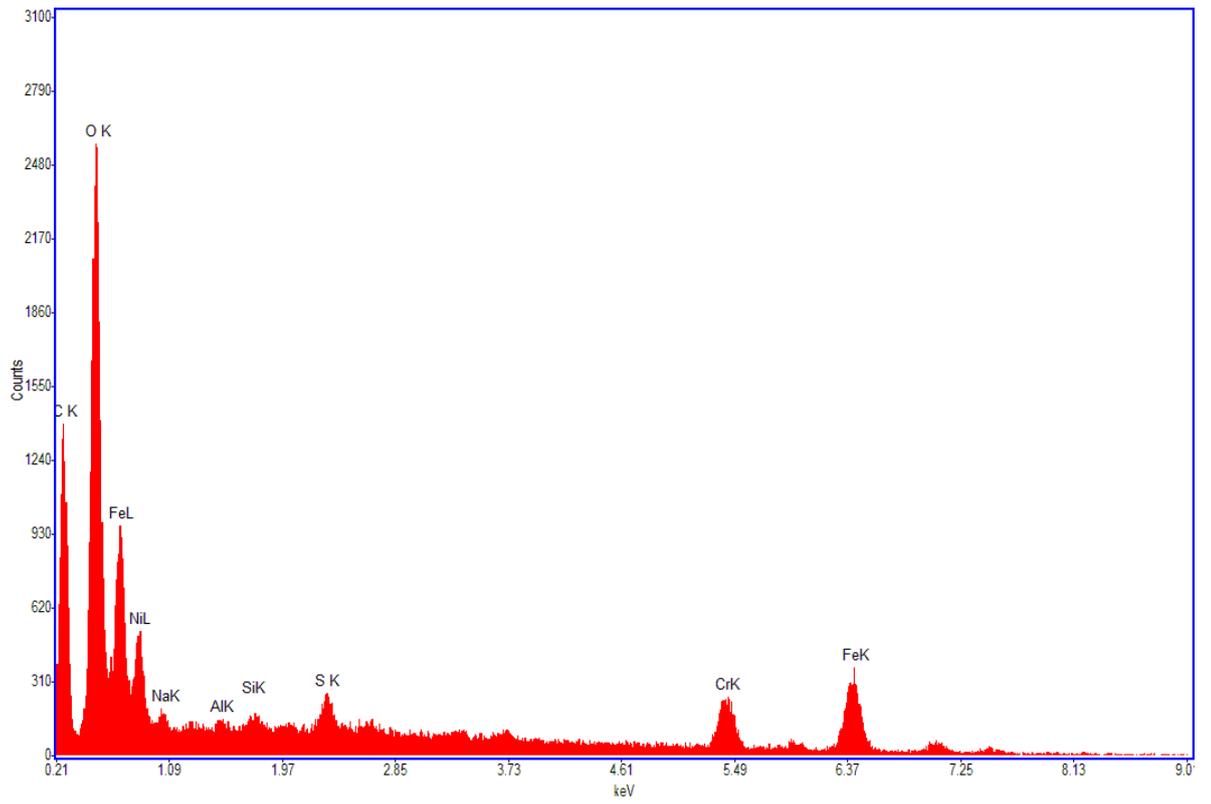


Figure 4.6: EDX spectrum of the raw bar.

50 AISL sandblasted. On figures 4.7 and 4.8 are SEM and EDX analysis of steel AISL, sandblasted.

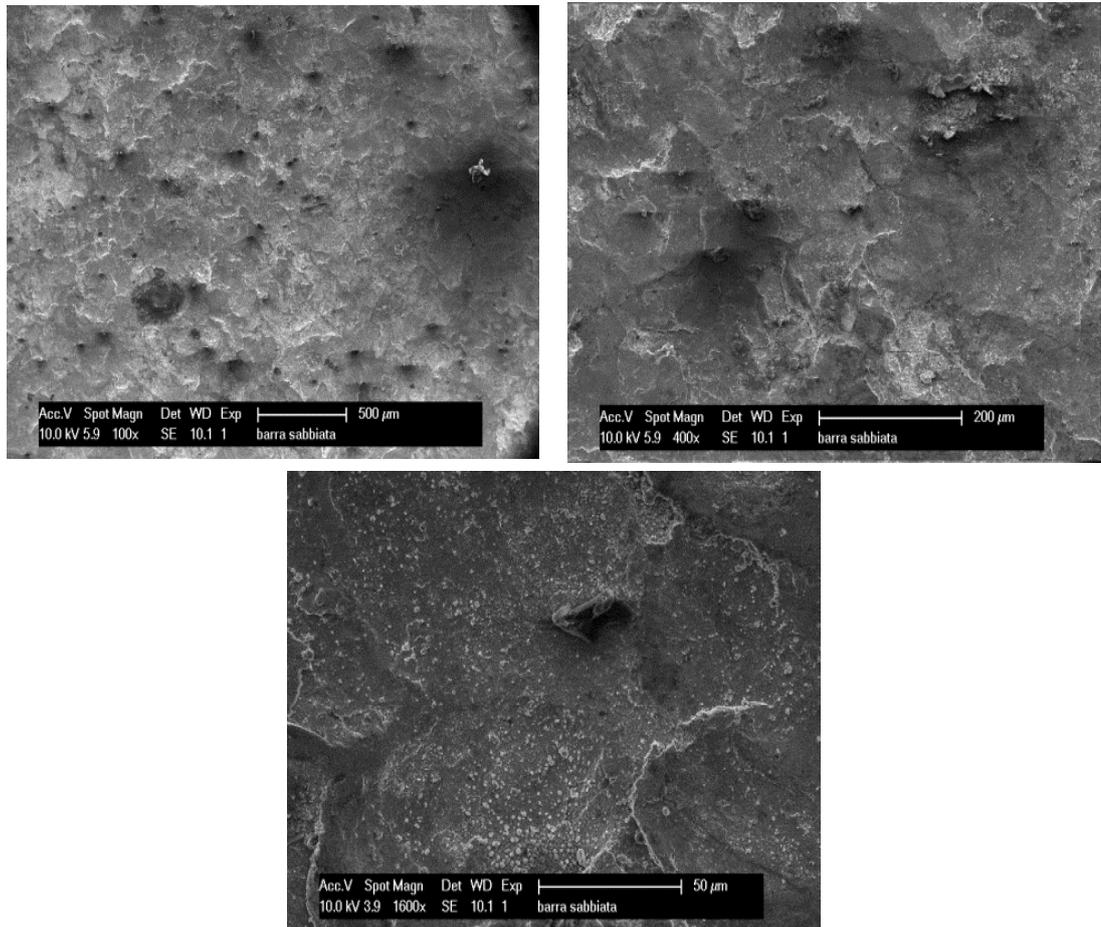


Figure 4.7: SEM micrographs of the bar 50 AISL sandblasted, arranged with increasing magnification.

The sandblasting on the rough bar reveals that the scale follows the roughness profile of the underlying metal: its crystal structure is very similar to steel below, giving rise to a compact and adherent layer. The elemental analysis detects chromium and sulphur with traces of nickel.

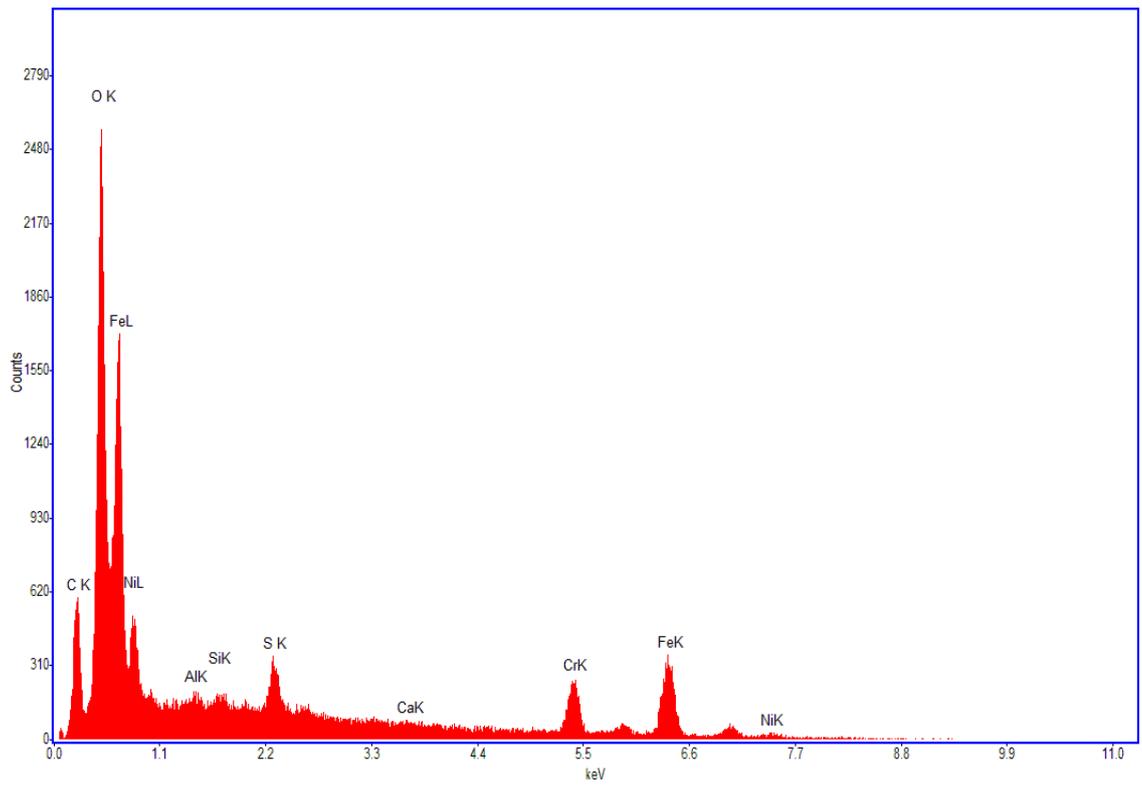


Figure 4.8: EDAX spectrum of the bar 50 AISL sandblasted.

AU 1882 / P 51 doped with sulphur. On figures 4.9 and 4.10 are SEM and EDX analysis of steel AU 1882 / P 51 (doped with sulphur).

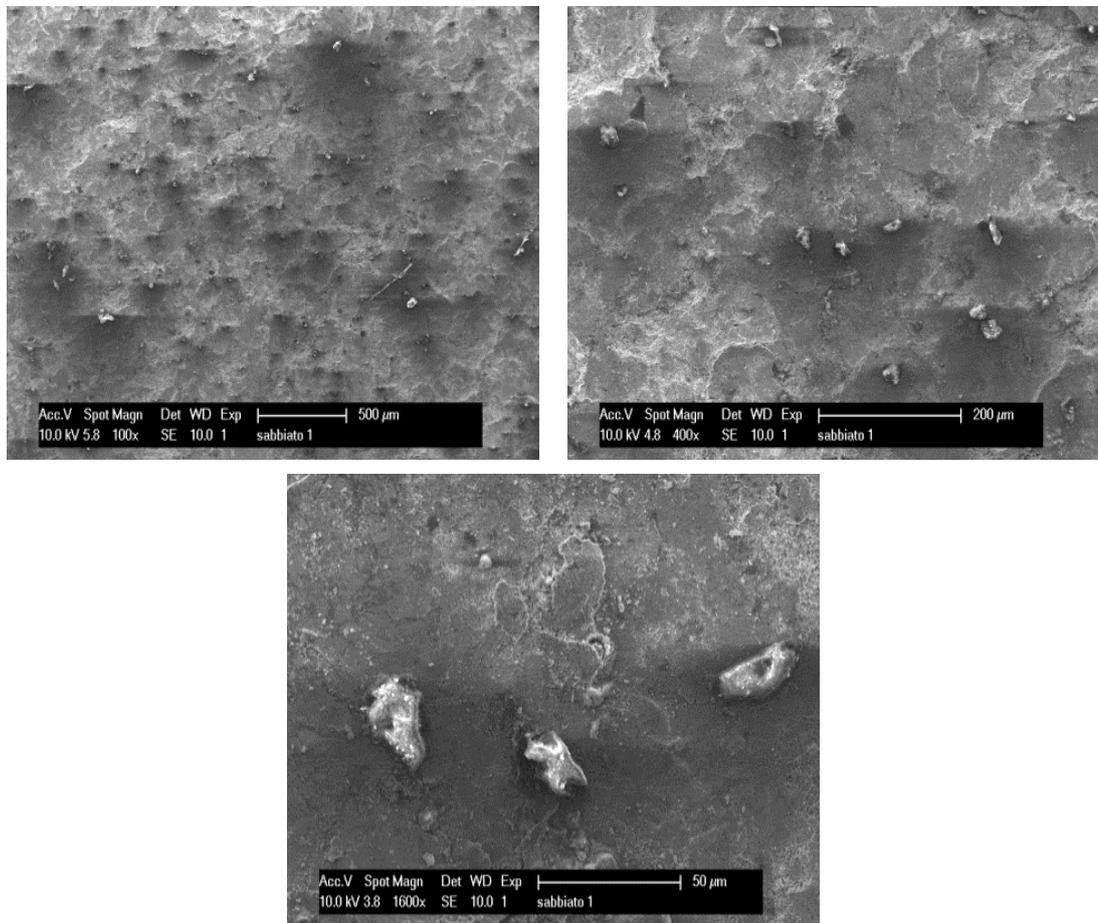


Figure 4.9: SEM micrographs of the bar AU 1882 / P 51 (doped with sulphur), arranged with increasing magnification.

The bar, doped with sulphur, presents a series of small inclusions in the steel insert. The layer appears compact, with no apparent porosity. The elemental analysis shows the presence of nickel, silicon and chromium.

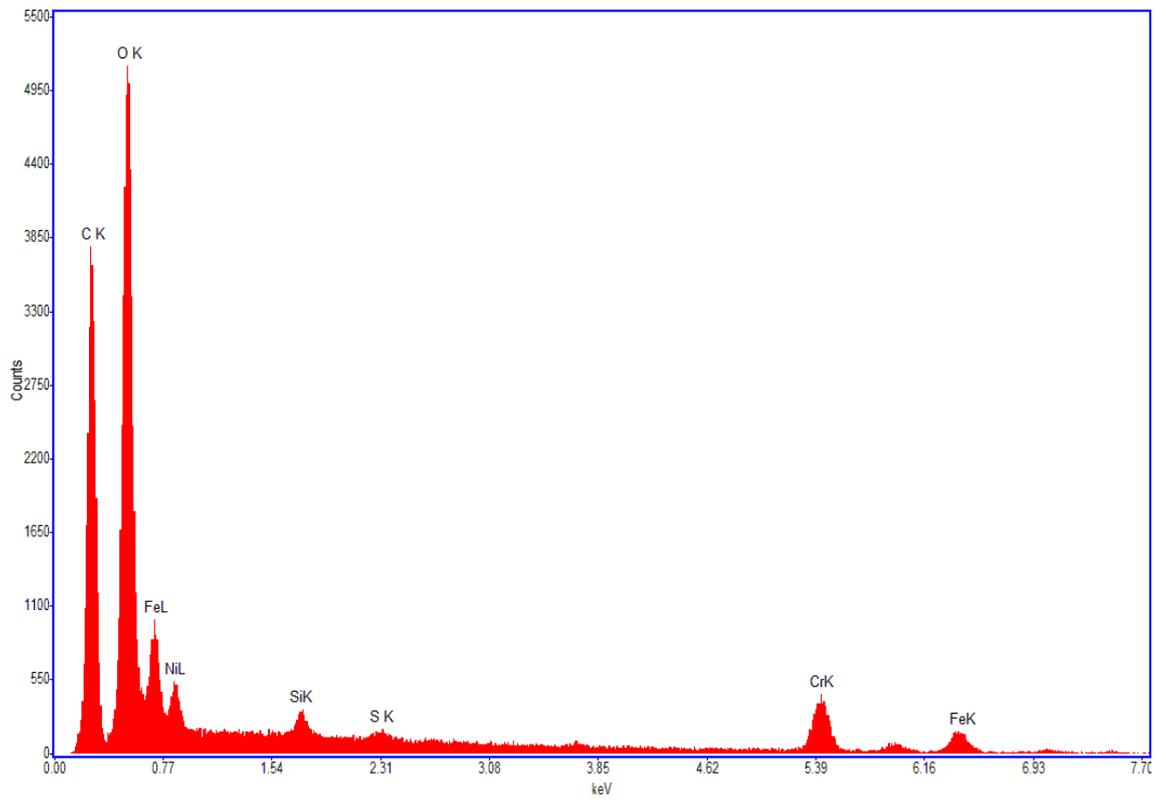


Figure 4.10: EDAX spectrum of the bar AU 1882 / P 51 (doped with sulphur).

VAL 1C martensitic. On figures 4.11 and 4.12 are SEM and EDX analysis of steel VAL 1C martensitic.

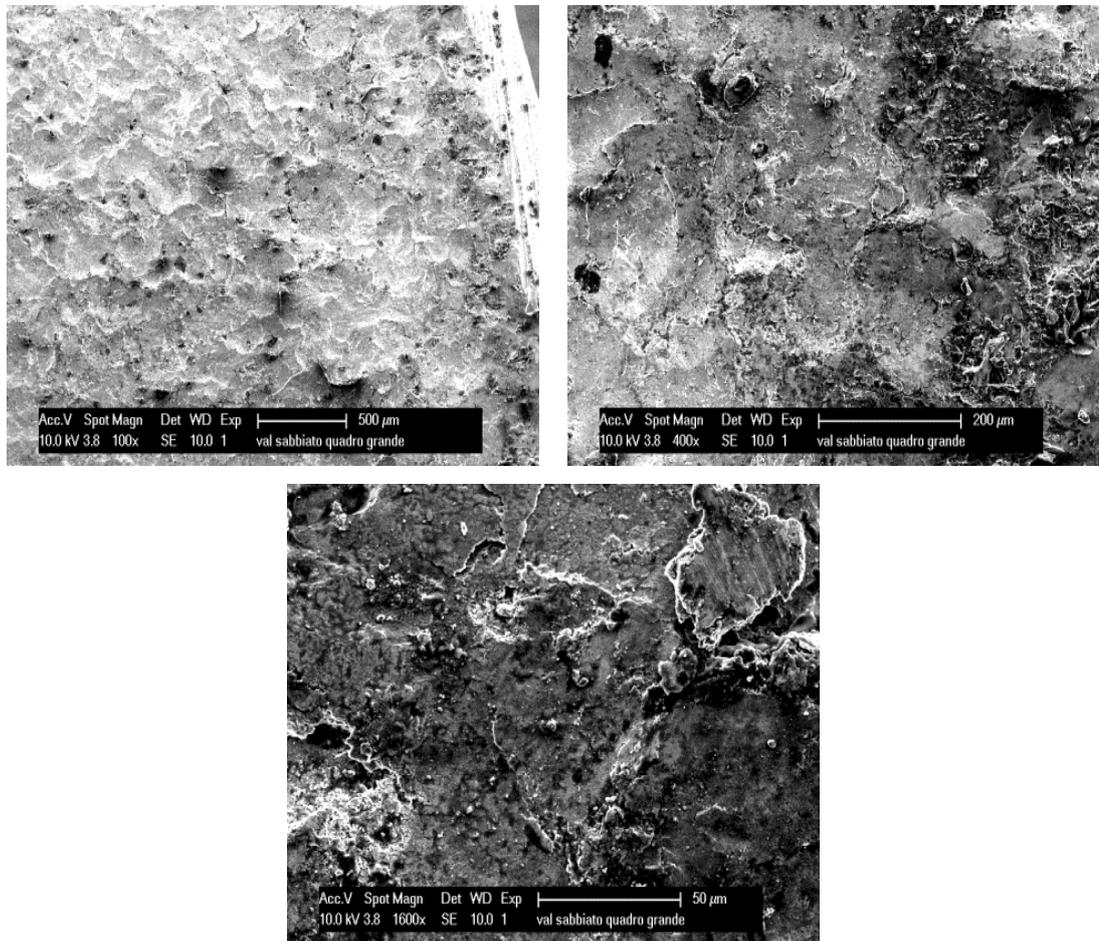


Figure 4.11: SEM micrographs of the bar VAL 1C martensitic, arranged with increasing magnification.

In the sample of VAL 1C martensitic the scale is compact, surface with flakes. The structure develops at different heights, showing roughness and inclusions. The elements identified are the silicon and chromium, both in low percentages.

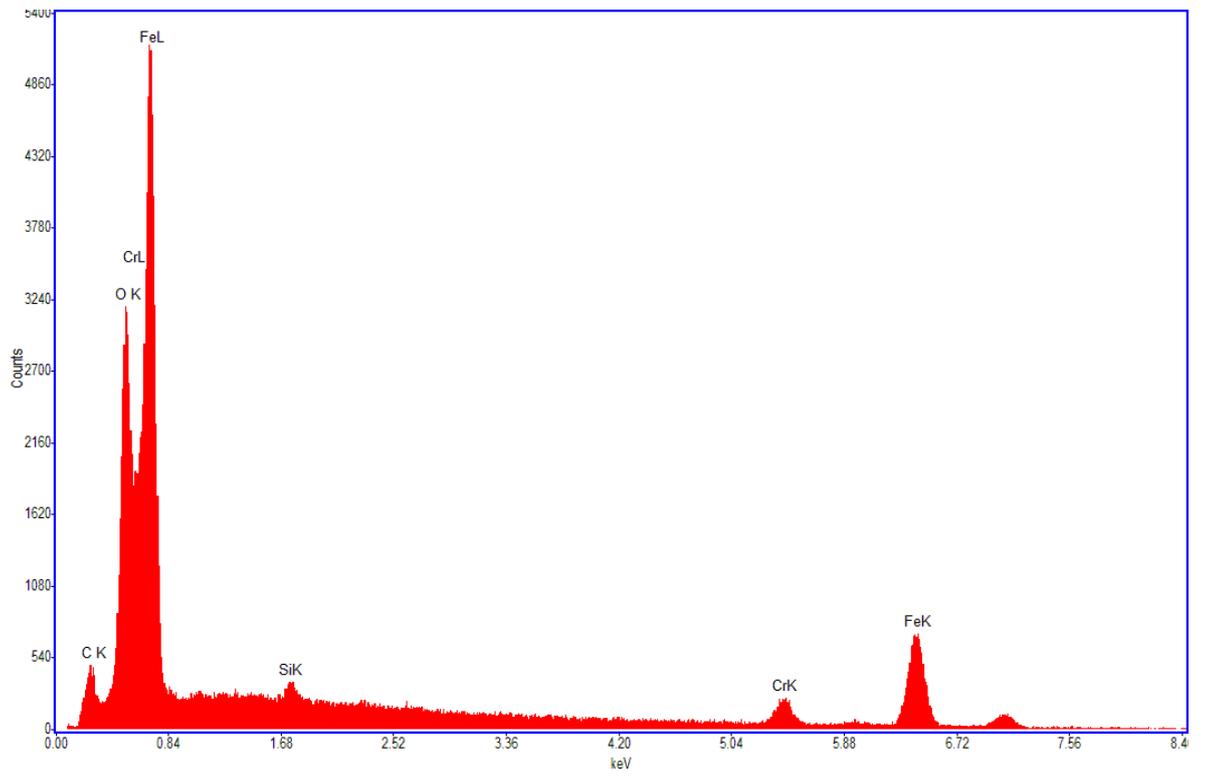


Figure 4.12: EDAX spectrum of the bar VAL 1C martensitic.

Raw rod. On figures 4.13 and 4.14 are presented the SEM and EDX analysis of steel raw rod.

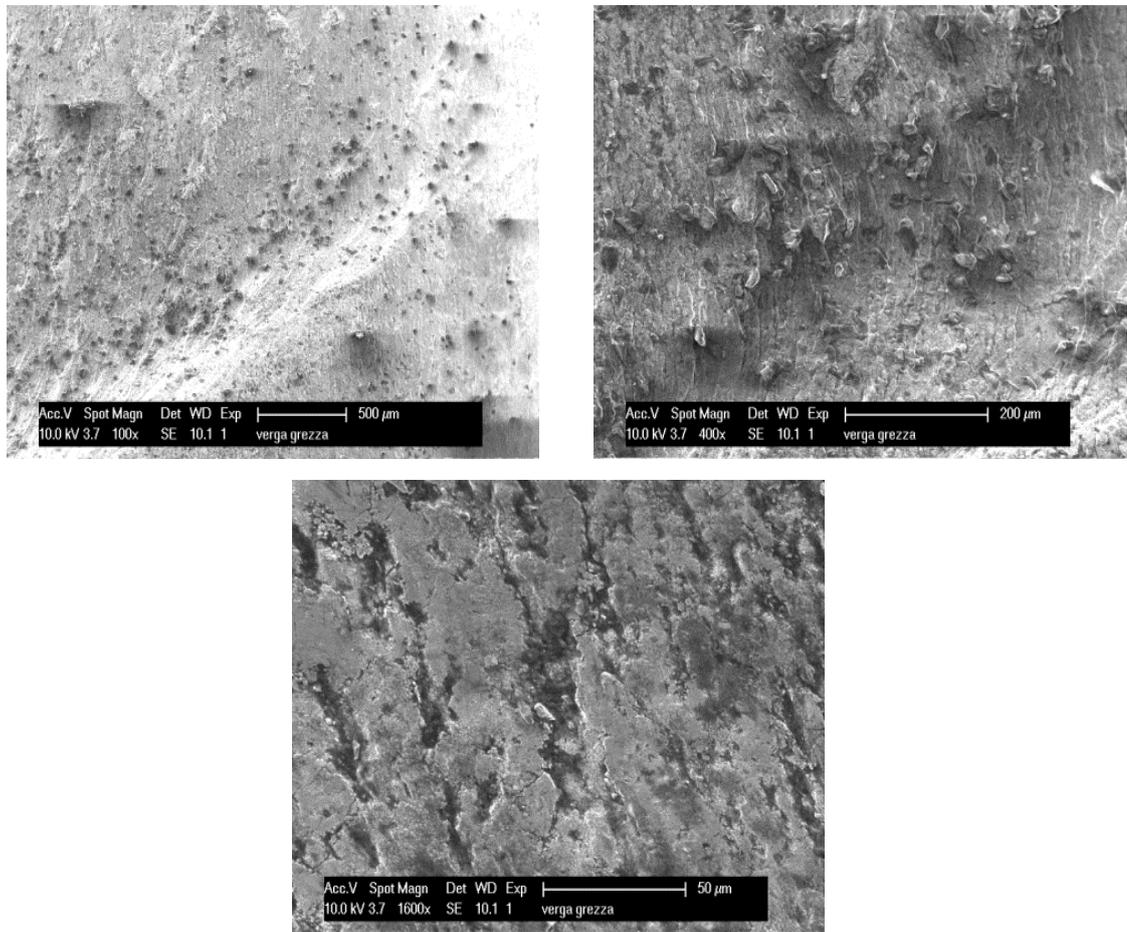


Figure 4.13: SEM micrographs of the raw rod, arranged with increasing magnification.

In the raw rod, morphology of the scale shows a compact structure, with the presence of larger particles. From the elemental analysis it is detected the presence of many elements in addition to oxygen and chromium. We observe the presence of aluminium, silicon and manganese, in addition the small traces of sodium and potassium.

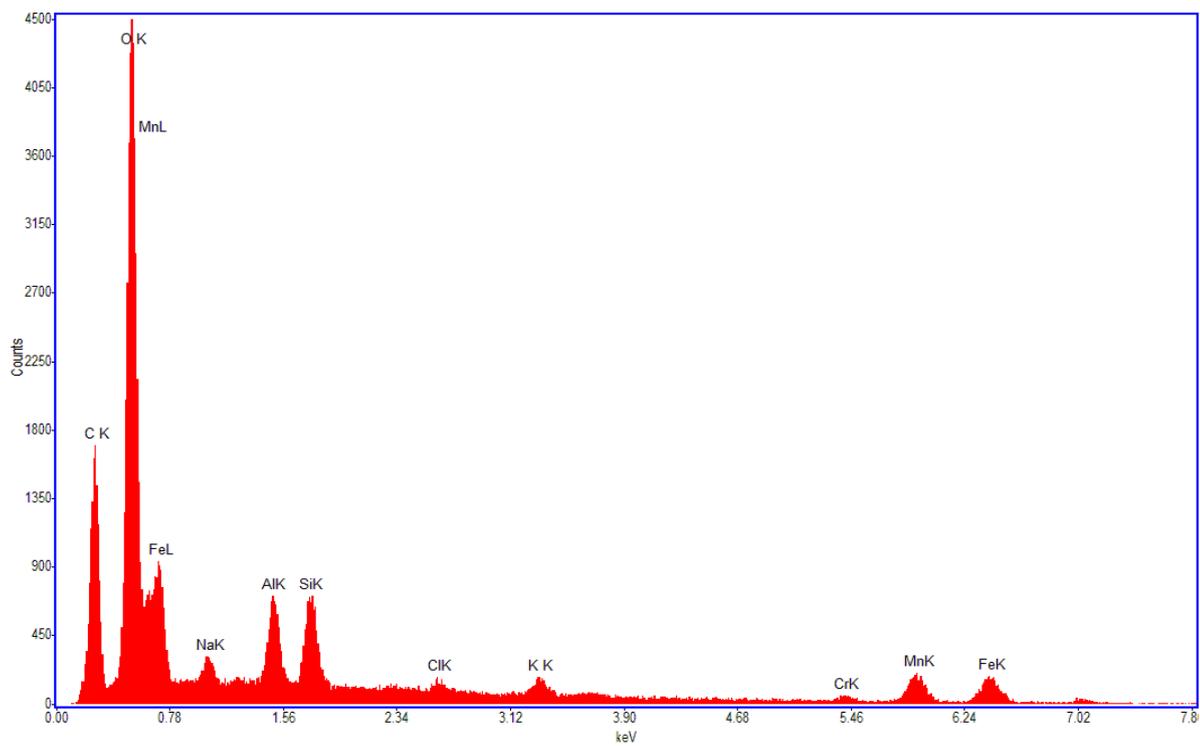


Figure 4.14: EDAX spectrum of the raw rod.

Raw hexagonal rod. On figures 4.15 and 4.15 are presented the SEM and EDX analysis of steel raw hexagonal rod.

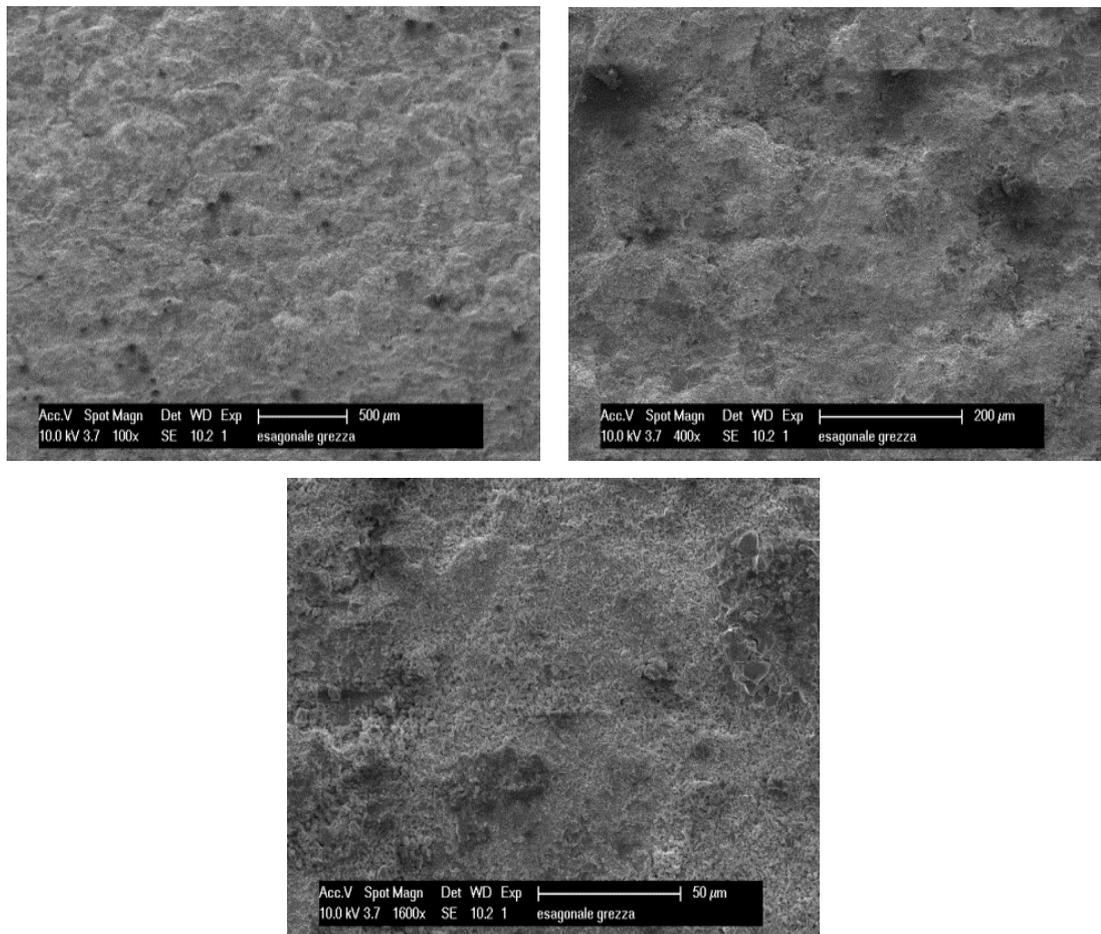


Figure 4.15: SEM micrographs of the raw hexagonal rod, arranged with increasing magnification.

The layer of the scale is compact and adherent, with a structure consisting of small surface pores. The structure is less rugged than the raw bar (shown previously). From the elemental analysis, it is detected the presence of silicon, nickel and chromium.

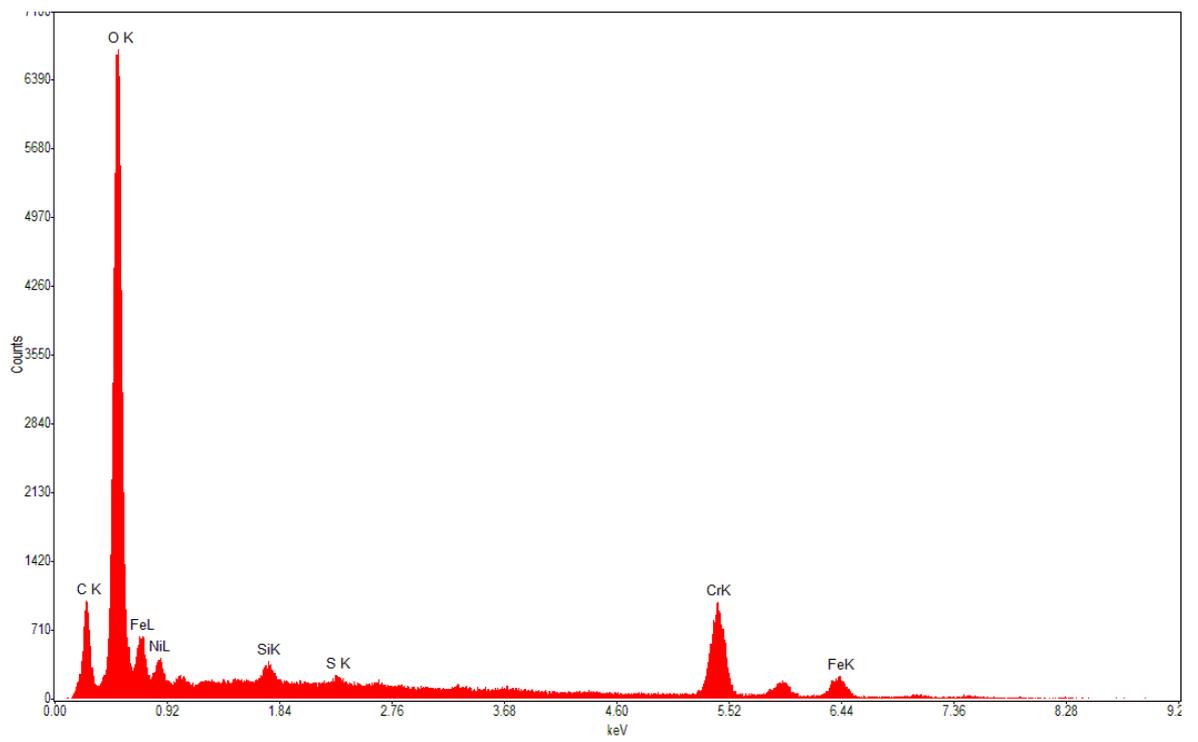


Figure 4.16: EDAX spectrum of the raw hexagonal bar.

Raw square bar. On figures 4.17 and 4.18 are presented the SEM and EDX analysis of steel raw square bar.

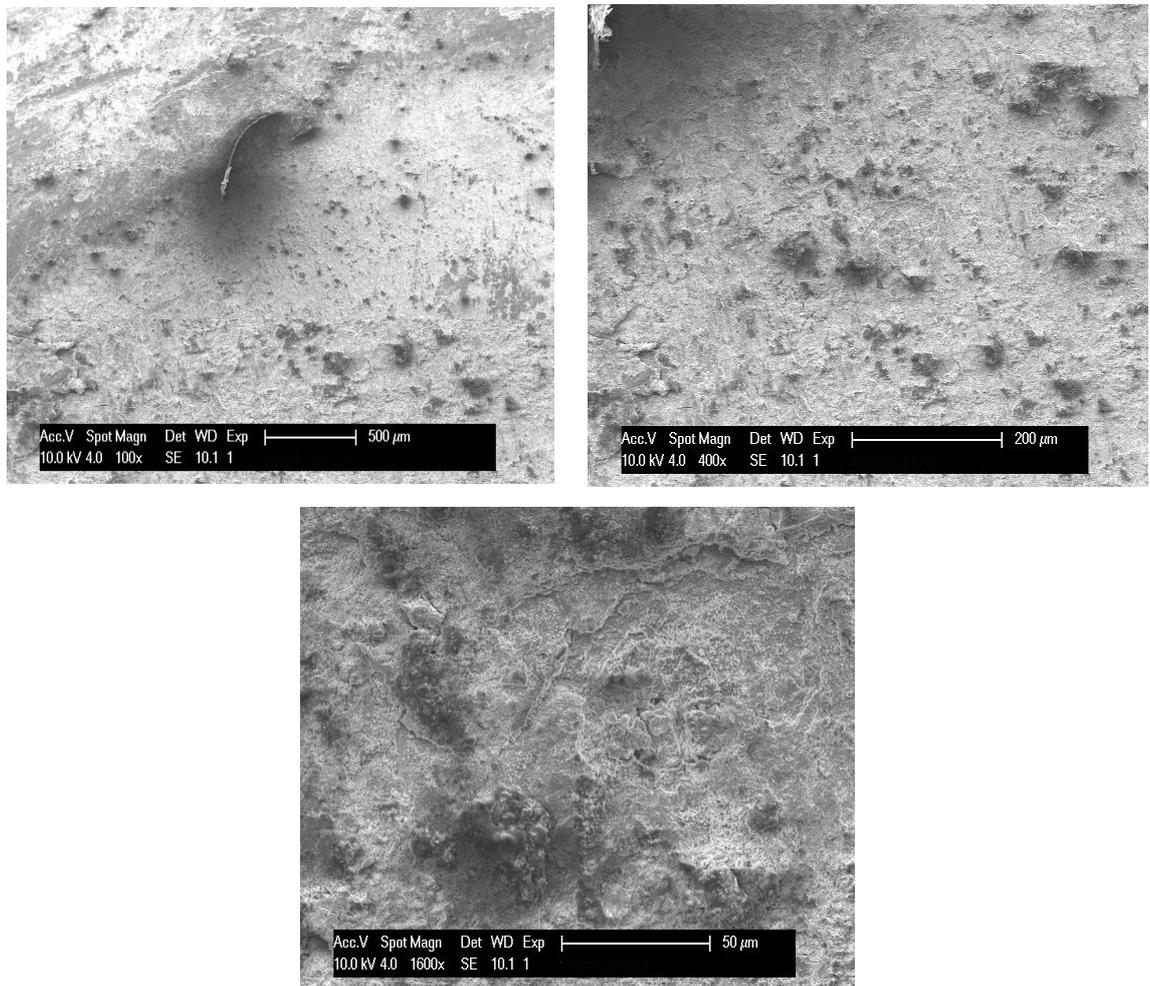


Figure 4.17: SEM micrographs of the raw square bar, arranged with increasing magnification.

The bar shows a compact surface, formed from crystals of variable size. The elemental analysis detects nickel and sulphur, while aluminium and potassium are barely detectable.

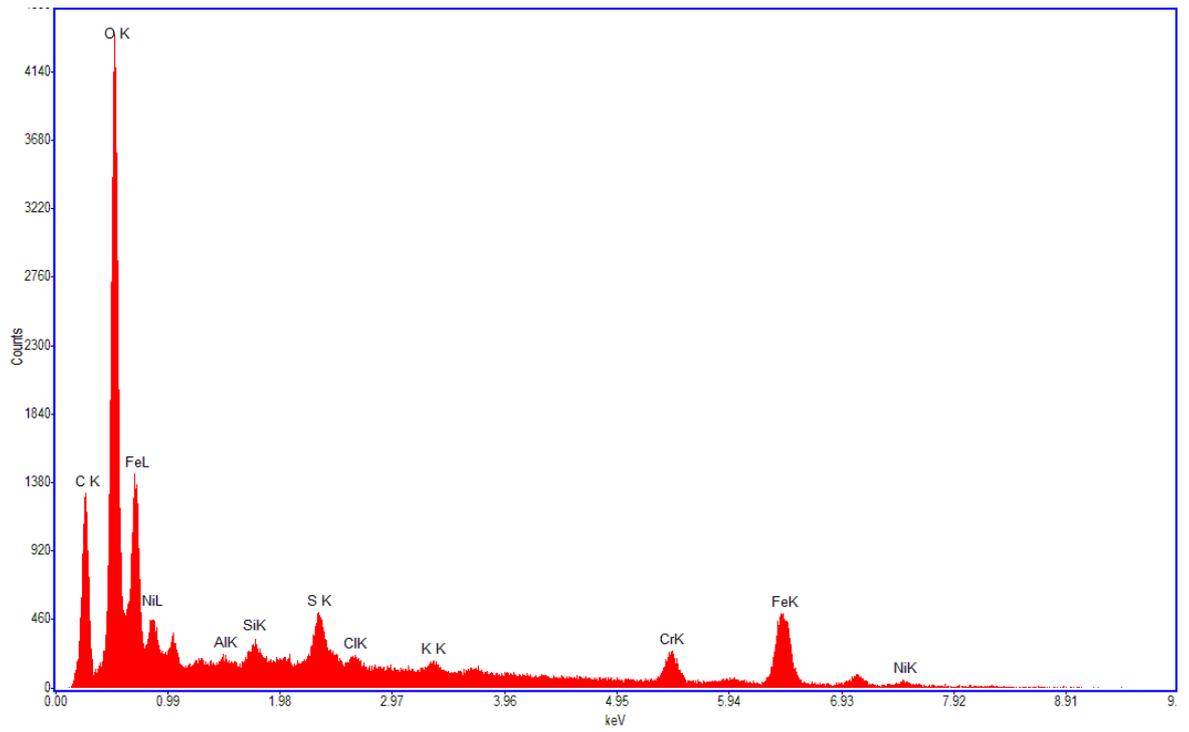


Figure 4.18: EDAX spectrum of the raw square bar.

Raw wire rod. On figures 4.19 and 4.20 are presented the SEM and EDX analysis of steel raw wire rod.

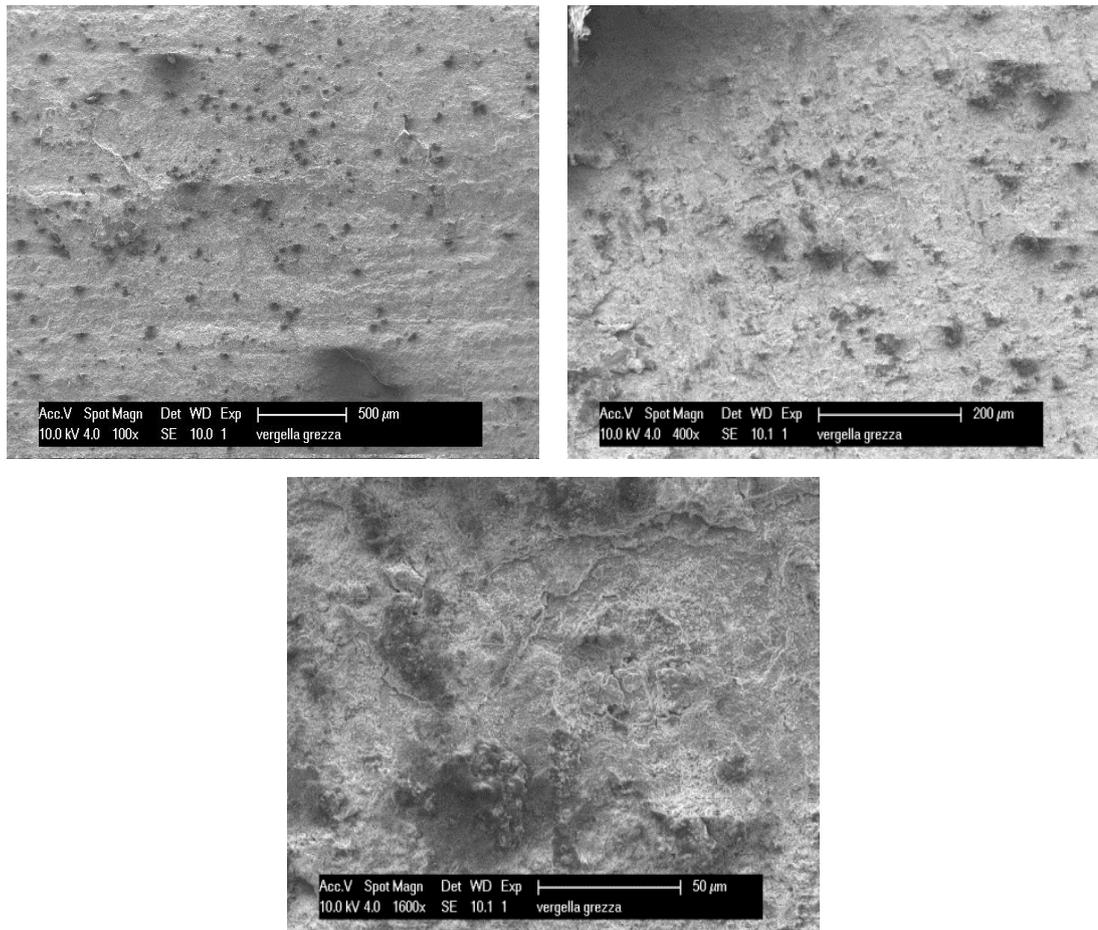


Figure 4.19: SEM micrographs of the raw wire rod, arranged with increasing magnification.

The raw wire rod shows a layer of scale compact and not peeled, with small formations. From the EDAX spectrum, we observe the presence of silicon and chromium, with very little presence of elements coming from the underlying steel.

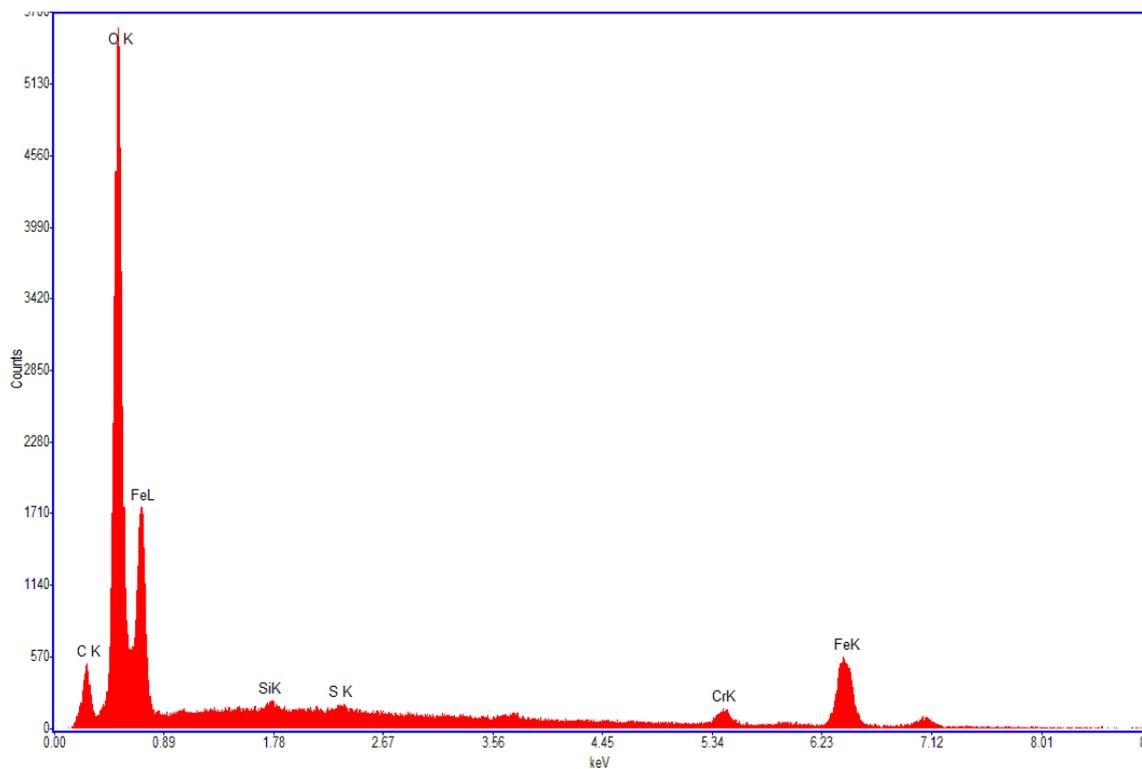


Figure 4.20: EDAX spectrum of the raw wire rod.

4.3. Study of the effectiveness of pre-finish treatment.

4.3.1. Study of the technique of high pressure rinsing.

The treatment of high pressure cleaning uses a water jet pushed at pressures range from 100 to 1000 bar. It is possible to add the water with specific abrasive to increase the effect of the surface.

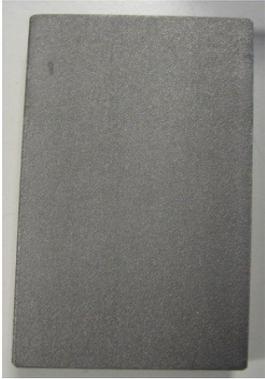
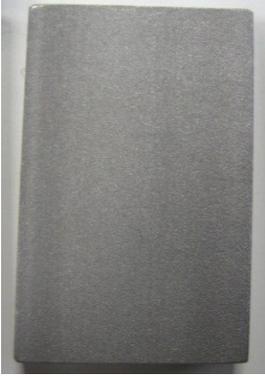
4.3.1.1. The effect of different pressure (100-800 bar).

The samples were subjected with HPWR with increasing pressure, to view the effect on the surface. The treatments were performed on pieces sandblasted and raw. The total treatment time is 2 minutes, 1 minute per side. The results are shown in table 4.2. We see that the treatment with water on the raw samples fails to remove various scale from the surface and is not able to obtain a uniform result. The treatment with HPWR on the sandblasted sample makes the surface more uniform and indicating a uniform removal of the scale, but without being able to achieve the appearance of the surface like after the chemical treatment. The HPWR on the sandblasted samples is not able to remove the scale, but only to reduce the thickness. In table 4.2 and 4.3 are shown results of influence different pressure on treatment raw and sandblasted steel bars.

Table 4.2: The raw samples after treatment with HWPR at different pressures.

№ sample	Pressure	Face 1	Face 2
1	200 bar		
2	400 bar		
3	600 bar		
4	800 bar		

Table 4.3: Sandblasted samples after treatment with HPWR at different pressures.

№ samples	Pressure	Face 1	Face 2
9	200 bar		
10	400 bar		
11	600 bar		
12	800 bar		

4.3.1.2. Study of the influence of the jet angle and different nozzle geometry.

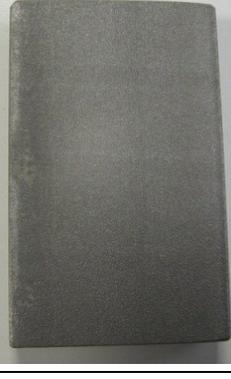
By varying, the angle of the jet it is not possible to improve the finish of the treated pieces.

Besides standard nozzle, it has been tested a nozzle blade. The shape of the blade extends the jet's treatment area but it is less effective than the standard tip. In the following tables 4.4 and 4.5 we can see the results of treatment of raw and sandblasted steel bars.

Table 4.4: The raw samples after HPWR with the nozzle blade at different pressures.

№ samples	Pressure	Face 1	Face 2
5	200 bar		
6	400 bar		
7	600 bar		
8	800 bar		

Table 4.5: The sandblasted samples after HPWR with nozzle blade at different pressures.

№ samples	Pressure	Face 1	Face 2
13	200 bar		
14	400 bar		
15	600 bar		
16	800 bar		

In conclusions: the treatment of high pressure water rinsing did not remove the scale from the steel surface. In case of raw samples or sandblasted, the different

pressures showed the equal appearance of the steel surfaces. The changing of jet angle or nozzle shape did not improve the cleaning.

4.3.1.3. Study of the influence of adding the abrasive.

In HPWR, we added an abrasive to increase the action of the jet. After few minutes of the treatment, we obtained a better finishing on the raw sample than that obtained with industrial sandblasting. There is a visible improvement of the surface of the samples already sandblasted, but not yet comparable to the chemically clean surface. On figures 4.21, 4.22 and 4.23 they are shown comparison of untreated raw and sandblasted steel bars and HPWR with abrasive at 200 and 300 bar.

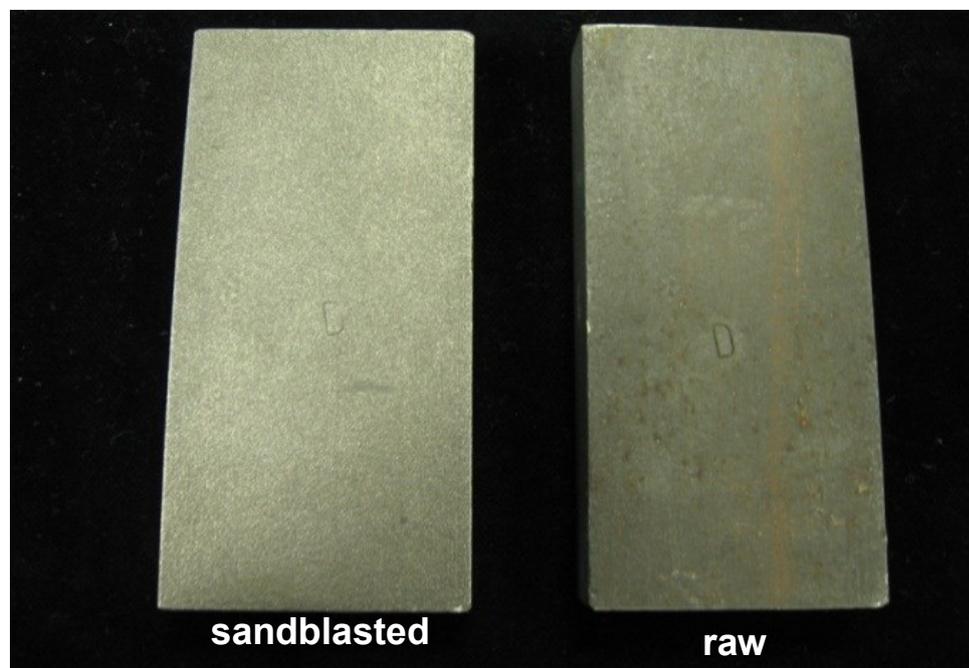


Figure 4.21: Untreated samples raw and sandblasted.

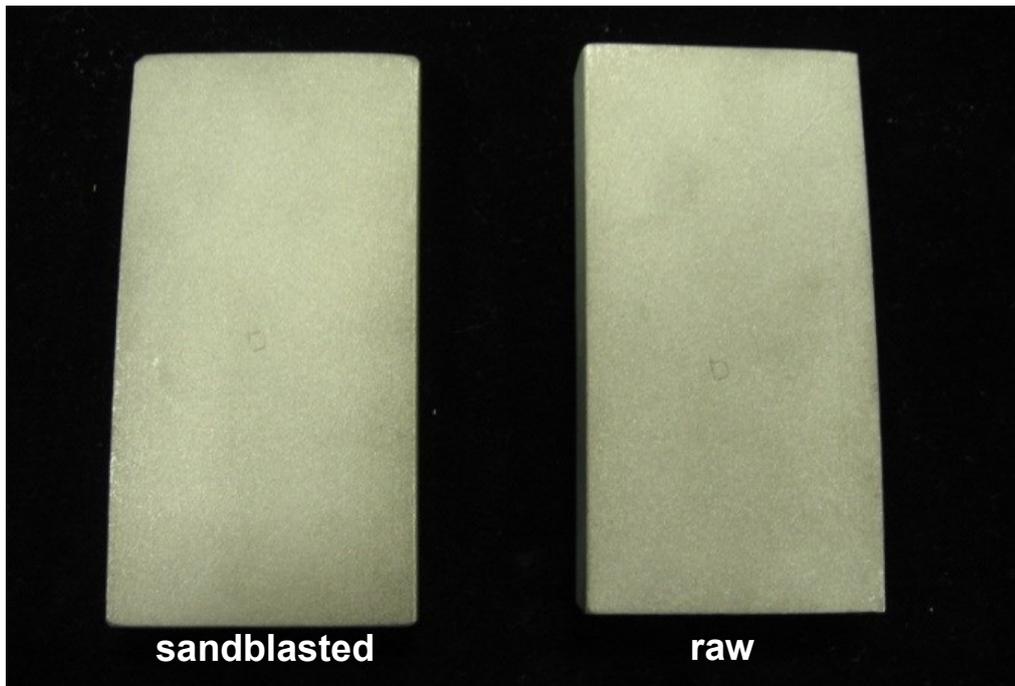


Figure 4.22: Samples after treatment at 200 bar with hot water and sand.

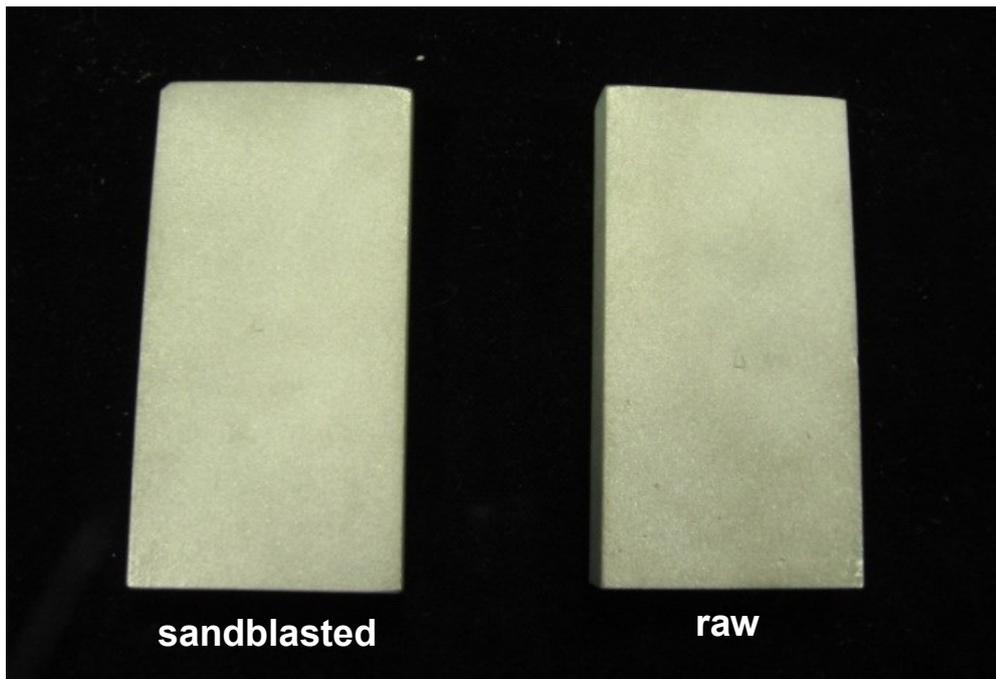


Figure 4.23: Samples after treatment at 300 bar with hot water and river sand.

In conclusion: the HPWR with addition of sand as abrasive depends on the water pressure. As we can see, the result after treatment at 300 bar is better, but we did not reach the desirable quality of surface.

4.3.2. Study of the effectiveness of “dry ice” -blasting (CO₂-blasting).

The “dry ice” blasting is a form of abrasive blasting, where dry ice, the solid form of carbon dioxide is accelerated in a pressurized air stream and directed at a surface in order to clean it. The sandblasted and raw samples were subjected after “dry ice” blasting. Dry ice was ejected from the compressor with variable pressures, while the other working conditions have remained constant:

- flow dry ice: 45 kg / h;
- external temperature: 10 ° C;
- working pressures range from 8 to 14 bar.

The raw steel bars were photographed from both sides after the treatment (Table 4.6). It can be seen that on the back there is a partial removal of the scale layer, where it is less adherent. The effect, however, does not take place on the overall surface.

The sandblasted steel samples were photographed from both sides after the treatment (Table 4.7). The effect is less pronounced compared to the raw samples.

In conclusion: The “dry ice”-blasting did not work better than previous treatments. We cannot remove the scale only by sandblasting.

Table 4.6: The raw steel samples after “dry ice”-blasting at different pressures.

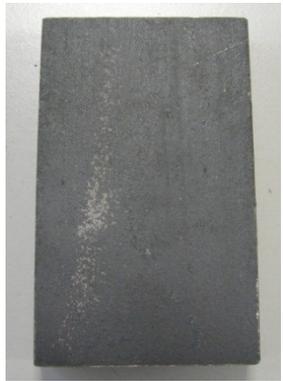
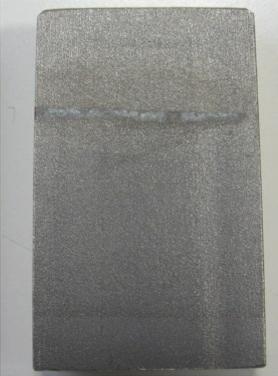
Pressure	Front	Back
8 bar		
10 bar		
12 bar		
14 bar		

Table 4.7: The sandblasted samples after “dry ice”-blasting at different pressures.

Pressure	Front	Back
8 bar		
10 bar		
12 bar		
14 bar		

4.3.3. Summary of the effectiveness pre-finish treatment.

The all kinds of preliminary finishing: HPWR, wet sandblasting and “dry ice” blasting did not show the ability to remove the scale and demonstrate a satisfactory quality of the surface. In table 4.8, it is presented the summary of results after descaling the raw steel samples and sandblasted steel samples.

Table 4.8: Summary of the pre-treatment study.

Study	Sample	Observation
Influence of the different pressure	raw steel	unsuitable for descaling
	sandblaster steel	unsuitable for descaling
Influence of the nozzle geometry	raw steel	unsuitable for descaling
	sandblasted steel	unsuitable for descaling
Influence of the abrasive	raw steel	unsuitable for descaling
	sandblasted steel	unsuitable for descaling
Influence of the CO ₂ -blasting	raw steel	unsuitable for descaling
	sandblasted steel	unsuitable for descaling

5. Green Electropolishing.

5.1. The characterization of samples etched in the standard solution.

The sample chemically etched with the standard industrial recipe has been examined with SEM and analysed with the EDX for observing the surface composition. The micrographs reveal an uneven surface, without typical roughness of the scale.

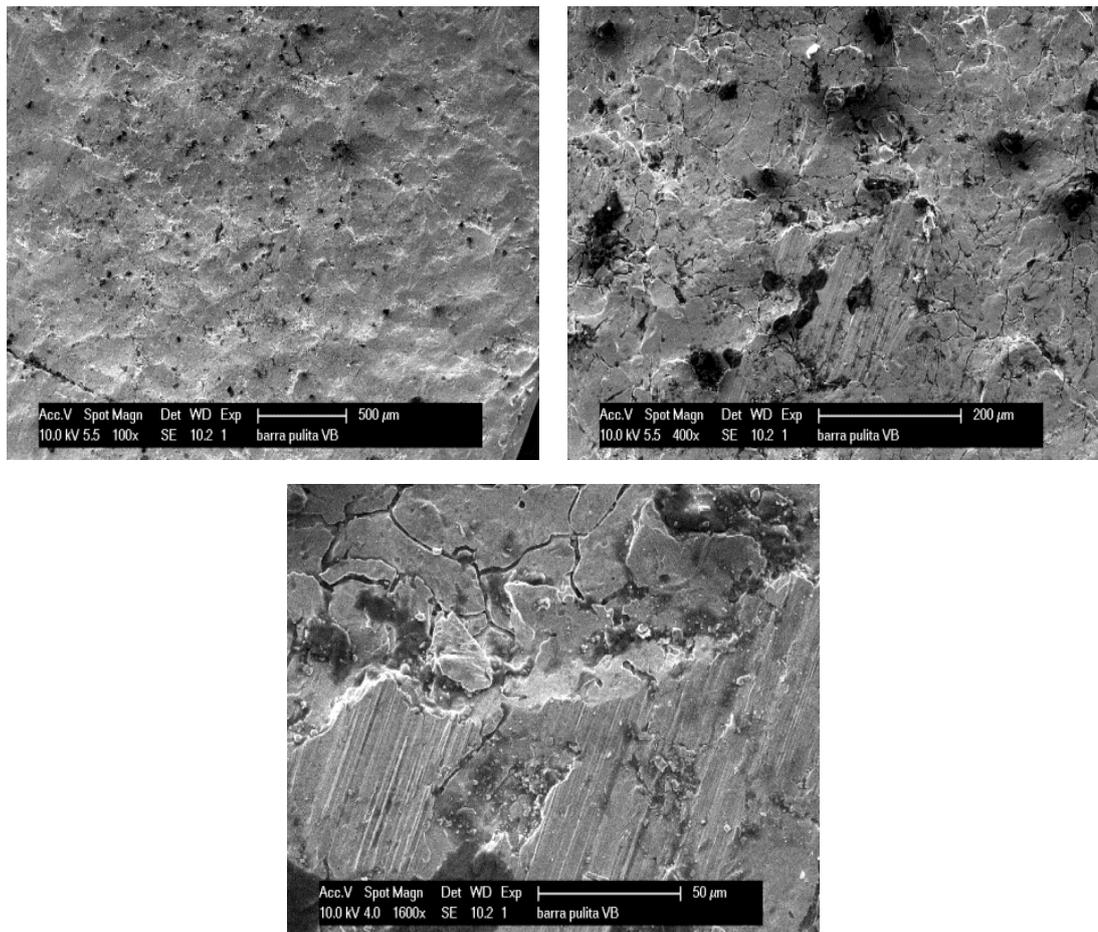


Figure 5.1: SEM micrographs of the bar pickled with standard industrial recipe, arranged with increasing magnification.

The EDAX spectrum shows the same elements present on the surface of the untreated samples, but with different ratio as those in the scale analysed in paragraph 4.1.2.

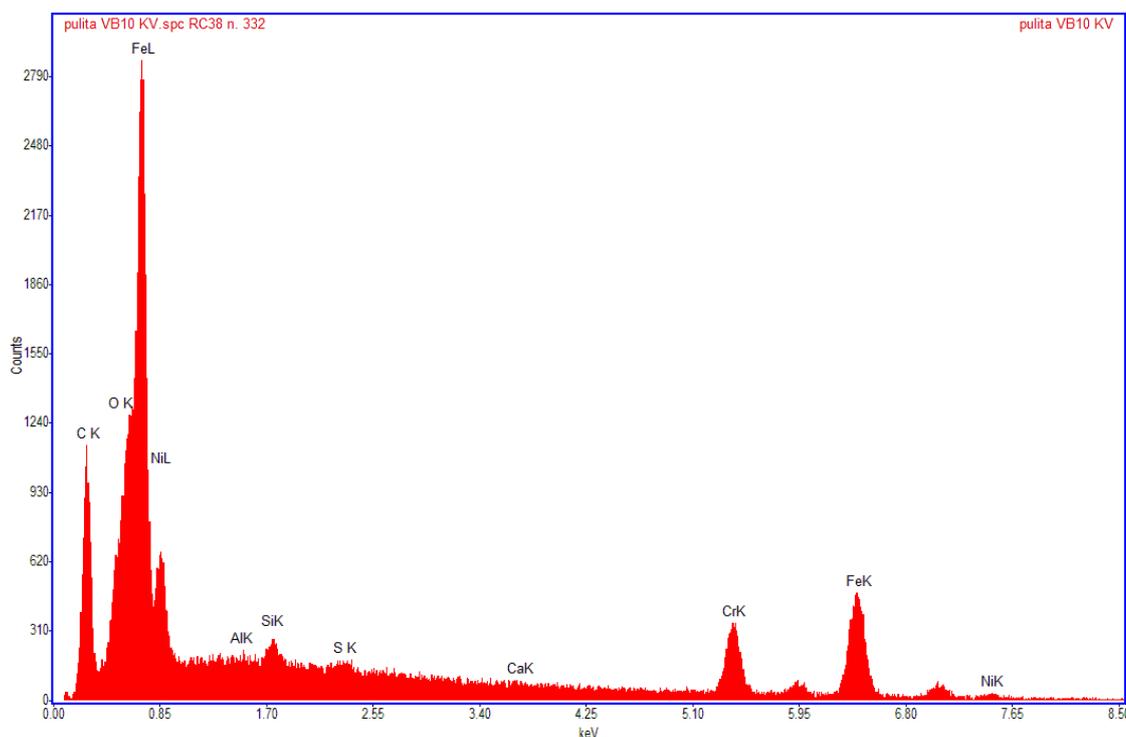


Figure 5.2: EDX spectrum of the bar after etching in standard industrial solution.

This analysis was done in order to compare the alternative descaling with the standard industrial process. The aim of this work is to find the solution that can substitute the industrial finishing, with the same quality of the surface.

5.2. Study of the possibility of ionic liquids to electrochemically polishing of stainless steel.

One of the main objectives of each chemical process is reducing the risk connected with the use of organic and inorganic acids. They often require a system for the storage and use, which are costly and onerous. Existing and potential dangers are pushing on searches equally effective alternatives. Among the various processes it is possible to use solutions without solvent (e.g. water), the processes taking place in supercritical solutions or in ionic liquids.

Since the early nineties, ionic liquids have attracted increasing interest, both in academic and industrial domains. Confirmation of this comes not only by the exponential increase in scientific publications, but also by a number of industrial processes under way or in planning, involving the partial or complete replacement of conventional organic solvents, in favour of ionic liquids.

5.2.1. Ionic liquids as alternative electrolytes.

The usual solvents are used in the processes of production and processing of almost all the products we use. Many of these are relatively small molecules that have weak intermolecular interactions to make them highly volatile and even toxic. Every year thousands of tons of volatile organic compounds are released into the atmosphere causing the destruction of the ozone layer and multiple environmental damage.

In contrast, ionic compounds are not volatile or flammable, nor particularly toxic, and thus potentially safe as solvents. The common ionic compounds are strong interactions between the ions, which promote easy organization of the crystal lattice. For this, the ionic salts usually have a high melting point so that their use as solvents in the liquid phase seems unreasonable. The major obstacle for the development and widespread use of salts as solvents seems to be just their melting point. From thermodynamics, we know that the melting point of an ionic compound is related to the lattice energy, which depends on the size and charge of the ions; as larger the ions as smaller the ion charge, and the less energy is required to break the ionic, bonds (Table 5.1). [24]

Table 5.1: Melting Points ($^{\circ}$ C) of some alkyl halides

Cations	Anions		
	F ⁻	Cl ⁻	Br ⁻
Na ⁺	993 $^{\circ}$ C	801 $^{\circ}$ C	747 $^{\circ}$ C
K ⁺	858 $^{\circ}$ C	770 $^{\circ}$ C	734 $^{\circ}$ C
Rb ⁺	795 $^{\circ}$ C	718 $^{\circ}$ C	693 $^{\circ}$ C
Ca ²⁺	1423 $^{\circ}$ C	782 $^{\circ}$ C	730 $^{\circ}$ C

5.2.2. Testing the new solutions consist of ionic liquids.

From the experience obtained by electropolishing of niobium accelerating cavities in it was decided to start the study electropolishing steel in ionic liquids with the solution of choline chloride - urea, which was found to be optimal for the cleaning of niobium. [25] In particular, we have studied various parameters such as the composition of the bath, the temperature, the anode-cathode distance, the addition of surfactants. All tests were carried out on two kinds of samples: the steel samples with raw surface, the steel samples with sandblasted surface.

Temperature. Among the investigated temperatures from 120 ° C to 170 ° C, the temperature 120 ° C seems to be the optimal value for the electropolishing in choline chloride – urea solution.

In fact, the temperature of 170 ° C is too high, which combined with the current applied during the process, leads to a rapid decomposition of the ionic liquid. At 120° C, the eutectic is electrolytically active and tolerates small current peaks.

Agitation. The agitation removes the bubbles that are formed on the surface but seems that it does not affect the final finish of the sample.

Anode-cathode distance. In addition to the parameters already mentioned, we have also investigated the variation of potential with the distance anode-cathode. Moreover, understandable that a variation of this distance can produce a lack of homogeneity of the electric field, and then electrochemical finishing. Delayen et al. [25] obtain that the variation in voltage is only about 8% to the change of the distance from 100 to 200 mm. In our case, we observe the performance shown in figure 5.3 with a maximum variation of the potential of 30% by varying the distance from 20 mm to 100 mm.

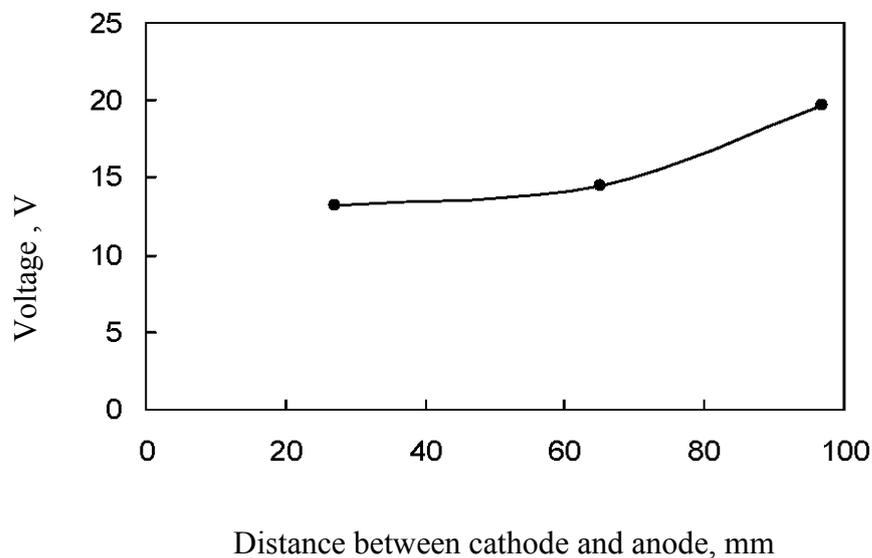


Figure 5.3: Performance of the potential function of the distance cathode-anode with constant current (250 mA / cm²).

It is therefore evident that in the ionic liquids the higher potential drop is not close to the surface of the anode. The result has consequently the need to achieve a

cathode that is complementary to the anode to be polished, to avoid variations of the distance that would affect locally the current density.

The working potential. The sought-for potential is stabilized at 14-15V, which allows a good scale erosion without leading to excessive overheating of the ionic liquid.

Bath composition. The ionic liquid mixture is preparing in following steps. The solution Urea-Choline Chloride in ratio 2:1 – to 2 moles of urea (2x60.1 g) we added 1 mole of choline chloride (139.62g) and slowly heated to 70 ° C for 1 hour. As soon as the transparent and colourless ionic liquid is formed, we increased temperature to 120 ° C, maintaining the temperature for 1 hour.

The solution Urea-Choline Chloride in ratio 3:1- we added to 3 moles of urea (3x60.1 g) 1 mole of choline chloride (139.62 g) and heat to 70 ° C for 1 hour. As soon as the transparent and colourless ionic liquid is formed is heated to 120 ° C and the temperature is maintained for 1 hour.

The eutectic 1:2 allows to use the higher current intensity, reducing the process time, but in some samples it is detected a general "preference" of the dissolution underlying steel instead of scale, which in some cases is eroded more slowly leaving uneven surface. To avoid this problem we carried out tests with addition of specific surfactants.

The eutectic 1:3 does not show significant improvements in the finishing of the sample at low currents. During the electropolishing at high currents, we noticed the increasing of the bath resistivity.

Influence of the additives. For studying the influence of the additives on quality of surface after polishing in ionic liquid, we tested the same additives as we added in electropolishing of niobium cavities. The addition of surfactants gave us three benefits:

- allows to reduce the anodic current;
- increase the average life of electropolishing bath;
- make more homogeneous the distribution of power in the electropolishing.

We have added 5 g / L of component "S" or 2 g / L of component "P". Since the eutectic (1:2) act faster on steel than on the scale, was tested addition of component "S", this leads to a better uniformity of the finishing, lowering the roughness and allowing to obtain a shiny finish.

The action of the component “P” is more negative for the eutectic, has a much shorter duration and degrades rapidly. This aspect has led us not to use the component “P” as an additive.

In conclusion, among the experiments carried out with the ionic liquid - urea with choline chloride, the best results were obtained with eutectic 1 to 2, temperature 120 °C and addition of 5 g / L of the component “S”. This recipe gives a shiny finish, reducing the roughness of the workpiece.

Table 5.2: Electropolishing with ionic liquid choline chloride – urea.

N°	Eutectic	T(°C)	Time,(m)	Cathode	Agitation	Note
1	1:2	120	5	single	+	14 V; 1,9 A
2	1:3 + 5g/L comp. “S”	120	7	single	+	14 V; 2,6 A
3	1:2	133	25	single	+	15,6 V; 8 A
4	1:2 + 2.5 comp. “P”	150	6,5	double	-	19 V; 13,6 A
5	1:2	120	10	double	+	(preheated) 14V, 3.3° with OV and 28V, 12A every 2,5 minutes
6	1:2	130 ↑176	9	double	+	14V; 11A (23A at the end)
7	1:2	170	10	double	+	15 V;12/18A
8	1:2	150 ↑165	5	double	+	HPWR - 150 bar; 3 min (pre-treatment) 14 V; 18/23 A
9	1:2	170	6	double	+	14 V; 23 A HPWR – (after treatment) spots remain

10	1:1	170	6 at 170°C 5 at 200°C	-	+	decomposition 14 V; 20 A
11	1:2	80 ↑110	4	double	+	15 V; 8 A
12	1:2	80 ↑110	5	double	+	distance between cathodes closer to the rolled side 15 V; 7 A
13	1:2	80↑90	6	double	+	15 V; 5,6 A
14	1:2	105 ↑160	6	double	+	problem with a cathode 13,5V ; 11 A
15	1:2	120	5	double	+	15 V; 12 A
16	1:2	140	6+1	double	+	15 V; 15 A
17	1:2	120	6+2	double	+	15 V; 13 A
18	1:2	120	4+2	double	+	14 V; 12-23 A
“dry ice” blasted	1:2	120		double	-	17 V; 7 A
34	1:2	120	11	double	+	14,8 V; 38,9 A
35	1:2	120	12	double	+	OV 18V + 5 V; 2,5 (plateau)
36	1:2	120	10	double	-	7,4 V; 5 A, + 7,4 V; 2 A
41	1:2 + 5g/L comp. “S”	110	8,5	double	+	plateau in V a 5,3V e 3,8A

42	1:2 + 5g/L comp. "S"	110	7	double	+	current constant 8 A
43	1:2 + 3 g/L comp. "S"	120	9	double	+	OV 30V - 1 min; 20V
44	1:2 + 5 g/L comp. "S"	120	10	double	+	OV 36V - 1 min; 20V
45	1:2 + 5 g/L comp. "S"	120	-	-	-	-
46	1:2 + 5 g/L comp. "S"	120	20	double	+	without rinsing in water

The photos below show the results obtained from the various tests of electropolishing in choline chloride and urea.



Figure 5.4: Samples after electropolishing, front from 1 to 10.

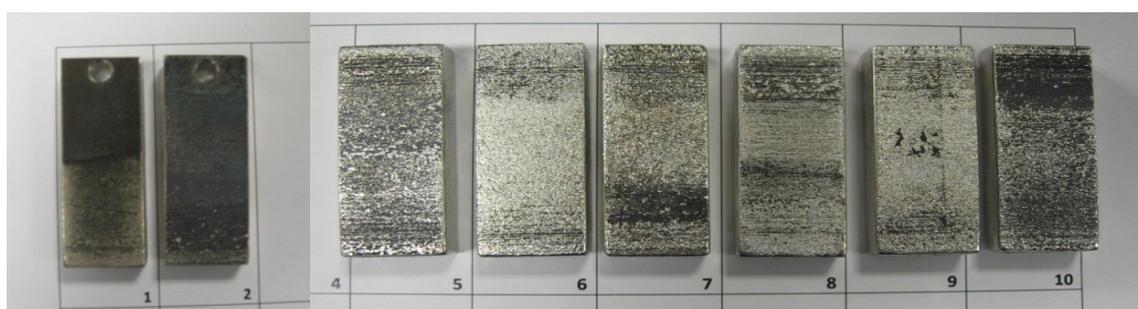


Figure 5.5: Samples after electropolishing, back from 1 to 10.

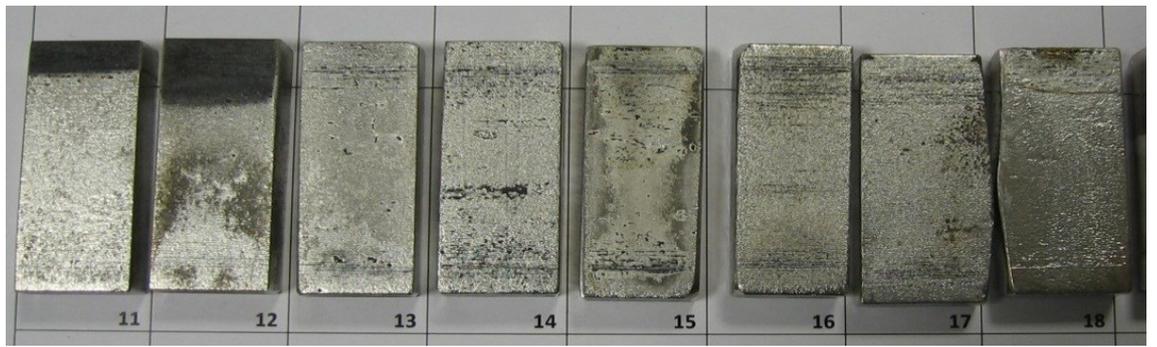


Figure 5.6: Samples after electropolishing, front from 11 to 18.

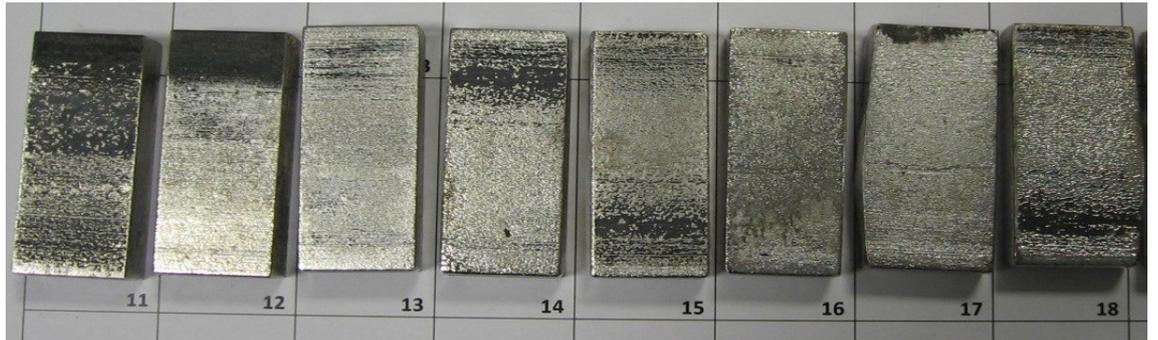


Figure 5.7: Samples after electropolishing, back from 11 to 18.

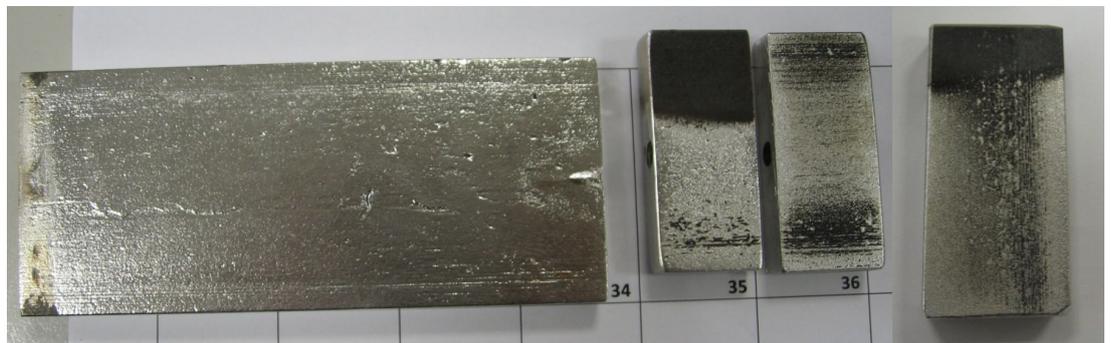


Figure 5.8: Samples after electropolishing, front from 34 to 36 and “dry ice” blasted.

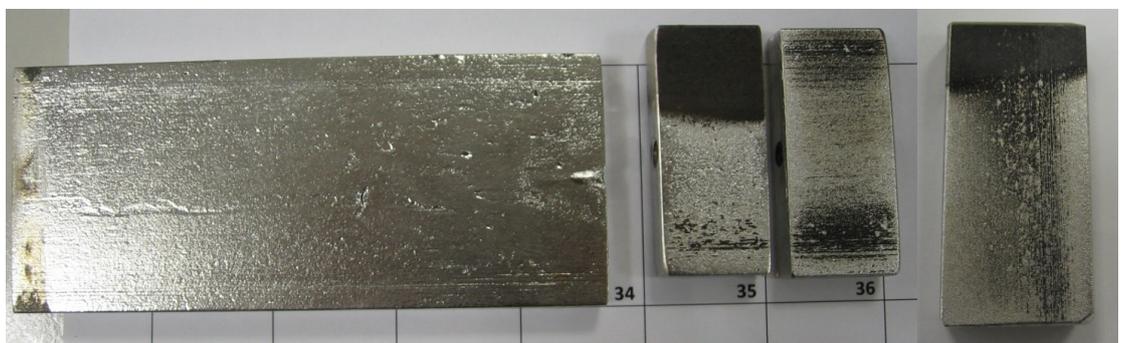


Figure 5.9: Samples after electropolishing, back from 34 to 36 and “dry ice” blasted.



Figure 5.10: Samples after electropolishing, front from 41 to 46 (without 42).



Figure 5.11: Samples after electropolishing, back from 41 to 46 (without 42).

The tests carried out on samples of larger sizes (up to 14 cm in length) show how the solution acts uniformly on large surfaces.

5.3. Study the other eutectics based on Choline Chloride.

Choline Chloride with Ethylene Glycol in ratio 1:2. [21] Mixing 1 mole of choline chloride (139.62 g) and 2 moles of ethylene glycol (2×62) and heating to 75 °C for 1 hour, while the homogenous liquid was prepared.

Choline chloride and two different carboxylic acids in ratio 1:1 or 1:2, we will call them Eutectic “O” and Eutectic “C”. In first case to 1 mole of Choline Chloride (139.62 g) was added 1 moles carboxylic acid and heated to 60 °C for 1 hour, then increased to 80-90 °C till the mixture became totally liquid and transparent. Other case, to 1 mole of Choline Chloride was added the 2 moles of another carboxylic acid and heat to 120 °C for 1 hour until the mixture became liquid and evaporate the residual water.

5.3.1. Deviations of the eutectics and study the process parameters.

In table 5.3, it is presented the parameters of treatment in eutectic ChCl-EG. The finish obtained with the solution of choline chloride and urea is very glossy, while the industrial finishing is preferred a satin surface of the steel. To achieve the purpose we have tested eutectics of different composition, described before.

Table 5.3: The parameters of electropolishing in choline chloride and ethylene glycol.

N°	Solution	T(°C)	Time (min)	Cathode	Agitation	Note
19	1:2	100↑144	6	Double	+	12 V; 16 A
20	1:2	120↑180	3+3	Double	+	3' at 8 V ; 10 A 3' at 20 V ; 20/25 A
21	1:2	80↑90	3	Double	+	1' at 18 V, 1' at 10 V, 1' at 18 V
22	1:2	80	3	Double	+	27 V; 23 A
23	1:2	130↑155	2	Double	+	20 V ; 27 A
24	1:3	120	4+1+1	Double	+	12 V ; 13 A
25	1:2	120↑180	3+3	Double	+	27 V ; 23 A
26	1:2	80	6	Double	+	scotch-bright brush, 3A



Figure 5.12: Samples after electropolishing, front from 19 to 26.



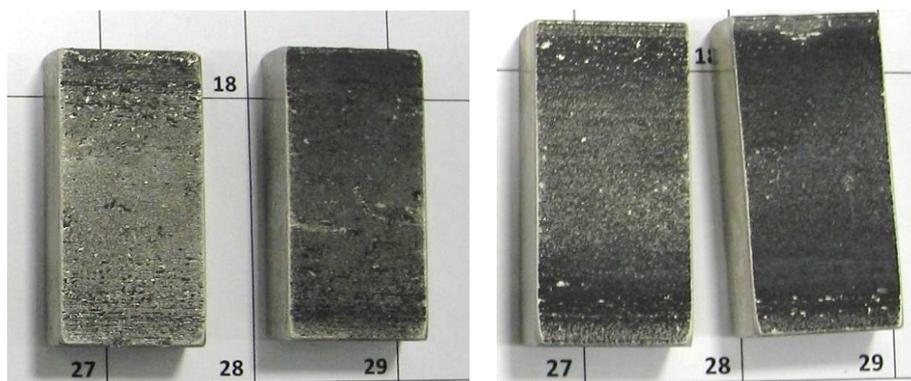
Figure 5.13: Samples after electropolishing, back from 19 to 26.

The finish obtained with mixture ChCl-EG is as glossy as in the solution with urea. In comparison of the eutectic ethylene glycol - choline chloride is less effective and remove the scale slower.

Table 5.4: The parameters of electropolishing in Eutectic “C”.

N°	Solution	T(°C)	Time (min)	Cathode	Agitation	Note
27	1:2	120	6	double	+	16 V ; 0,9 – 1,1 A
	1:2	150	6	double	+	12 V ; 0,9 - 1,2 A
29	1:2	150	6	double	+	25 V ; 1 A

The ionic liquid formed from Eutectic “C” is not effective in the removal of scale as other studied eutectics. After 6 minutes of the process, the surface is still covered with oxide (see figure5.14).



Front

Back

Figure 5.14: Samples after electropolishing in Eutectic “C”, front and back (27 and 29).

In the table 5.5 parameters of electropolishing in Eutectic “O” are presented.

Table 5.5: The parameters of electropolishing in Eutectic “O”.

N°	Solution	T(°C)	Time (min)	Cathode	Agitation	Note
30	1:1	50	9	double	-	18 V; 17A
31	1:1	70	4	double	-	18 V; 6 A
32	1:1	90	4	double	+	18 V; 7.6 A
33	1:1	100↑120	4	double	+	18 V; 7.9 A
37	1:1	95	8	double, 1 closer	+	5' at 3.4V 1,8° ; 6A 3' at 6.4V; 3,8A
38	1:1	95	16	double, 1 closer	+	6.4 V; 4 A follow plateau
39	1:1	95↑120	14	double equal dist.	+	15 V ; 8A another 4' at 20 V;16 A
40	1:1	95	10,5	double equal dist.	+	4'30'' at 22 V; 24 A 2' at 23 V; 16 A 4' at 18 V; 4 A

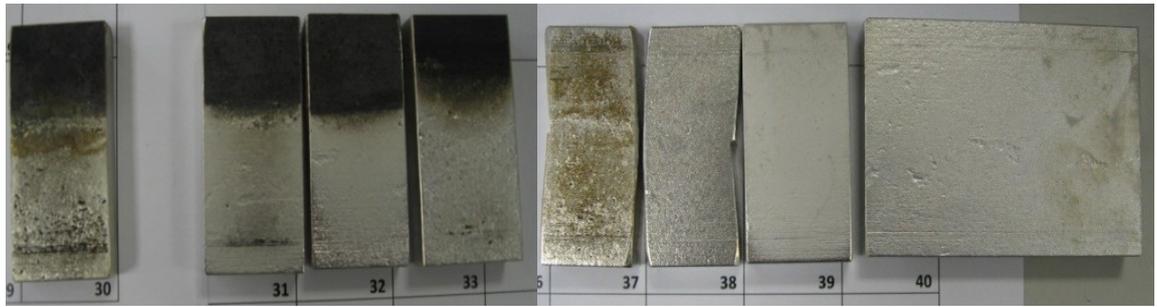


Figure 5.15: Samples after electropolishing, front 30-40.



Figure 5.16: Samples after electropolishing, back 30-40.

The solution of Eutectic “O” allows obtaining a satin finish according to the requirements of the steelworks industry. The finishing appears homogeneous and practically identical to standard industrial cleaning. The best results are obtained for temperatures below 100 ° C and tensions around 18-22V.

For Eutectic “O” the temperature must be in a range from 85 ° C to 95 ° C, to allow the solution to work stable. Temperatures higher than 130 ° C irreversibly degrade the solution. The agitation is not necessary to obtain a uniform finish over the whole sample. The optimal distance between cathode and anode cannot be less than 4 cm per side. The working potential varies during the process, remaining at around 23V initial values and then decreased to 19-20V. These values are optimal for obtaining a satin finish. A big advantage of the solution of Eutectic “O” is to provide the different surface finishing from satin to glossy by varying the working potential.

5.3.2. The influence of ultrasound during the electropolishing.

The aim is to test the effect of ultrasound during electropolishing with ionic liquids for the removal of the scale form sandblasted samples of stainless steel. In particular, we will examine whether the presence of ultrasound allows an increase

of the speed of erosion and / or an improvement of the finishing. It is tested the efficacy of a treatment of electropolishing in ultrasound, performing three processes of different durations (2', 1'30", 1') under the same conditions, with or without ultrasound activated. The six samples were made from the same bar of steel.

Sample 1

$I = 2.5 \text{ A}$ $V = 6 \text{ V}$ $t = 2 \text{ min}$ $T = 85 \text{ }^\circ\text{C}$ without ultrasound

Sample 2

$I = 2.5 \text{ A}$ $V = 6 \text{ V}$ $t = 2 \text{ min}$ $T = 85 \text{ }^\circ\text{C}$ with ultrasound

Sample 3

$I = 2.5 \text{ A}$ $V = 7 \text{ V}$ $t = 1'30''$ $T = 85 \text{ }^\circ\text{C}$ with ultrasound

Sample 4

$I = 2.5 \text{ A}$ $V = 7 \text{ V}$ $t = 1'30''$ $T = 85 \text{ }^\circ\text{C}$ without ultrasound

Sample 5

$I = 2.5 \text{ A}$ $V = 6 \text{ V}$ $t = 1 \text{ min}$ $T = 85 \text{ }^\circ\text{C}$ without ultrasound

Sample 6

$I = 2.5 \text{ A}$ $V = 6 \text{ V}$ $t = 1 \text{ min}$ $T = 85 \text{ }^\circ\text{C}$ with ultrasound

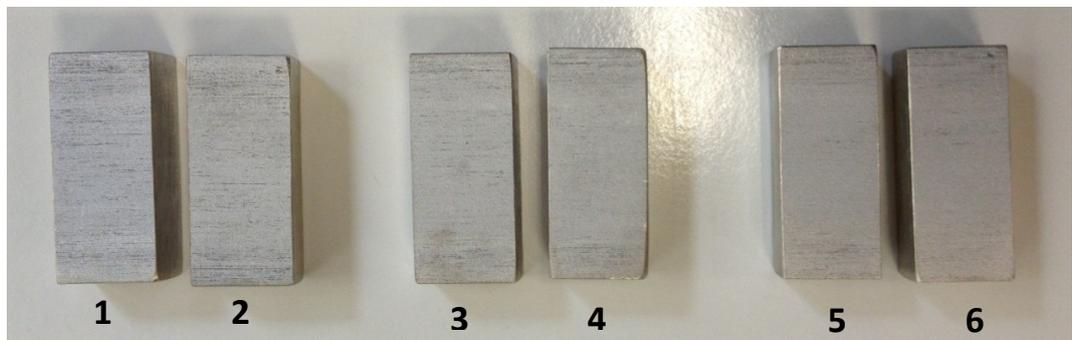


Figure 5.17: Comparison between samples electropolished with or without ultrasonic bath, with different process times.

The samples made with ultrasound are indistinguishable from those made without ultrasound. It thus seems that ultrasound during the process cannot improve the finishing.

5.4. Study of the contents of wastewater.

The wastewater after rinsing was analysed to determine the presence and amount of chlorides, nitrates and nitrous nitrogen.

The result of analysis wastewater solutions after polishing in Eutectic “O” are represented in the table 5.6. Table 5.7 displaces the result of analysis wastewater solutions after the polishing in choline chloride and urea solution.

The amount of chlorides in wastewater after rinsing the Eutectic “O” is lower than in choline chloride and urea.

Table 5.6: Analyses wastewater solution of Eutectic “O”.

Parameter	Method	Value (mg/L)
Nitrous oxide (N ₂ O)	APAT CNR IRSA 4050 Man 29 2003	< 0,02
Chlorides (Cl ⁻)	APAT CNR IRSA 4020 Man 29 2003	360
Nitrates (NO ₃ ⁻)	APAT CNR IRSA 4020 Man 29 2003	<1

Table 5.7: Analyses wastewater solution of choline chloride – urea.

Parameter	Method	Value (mg/L)
Nitrous oxide (N ₂ O)	APAT CNR IRSA 4050 Man 29 2003	< 0,02
Chlorides (Cl ⁻)	APAT CNR IRSA 4020 Man 29 2003	1430
Nitrates (NO ₃ ⁻)	APAT CNR IRSA 4020 Man 29 2003	<1

5.5. Selecting the best solution.

From the four solutions that were tested, only two were suitable for effectively removing the scale from the surface of the steel bars. The solution urea - choline chloride and the solution Eutectic “O”. The first, however, produces a very

shiny finish, while the solution of Eutectic “O” allows obtaining a satin finishing very similar to the standard industrial chemical process used by the steelworks. Another advantage of the Eutectic ”O” is effective at temperatures of 80-85 ° C, compared to urea eutectic that requires temperatures higher than 120 ° C.

The amount of chloride released in the wastewater are lower in Eutectic “O” than in choline chloride - urea. The analysis with the electron microscope is a useful for comparing the state of the surface obtained after polishing in ionic liquids and with the standard industrial recipe.

From SEM micrographs, the surface of steel polished in standard chemical solution shows obvious indentations that are responsible for the macroscopic satin effect characterizes this treatment. The bars electropolished with a solution of choline chloride - urea instead have a flat surface that produces the shiny finishing. The satin finish obtained with the Eutectic “O” is the result of the formation of a very fine “orange peel” at the microscopic level.

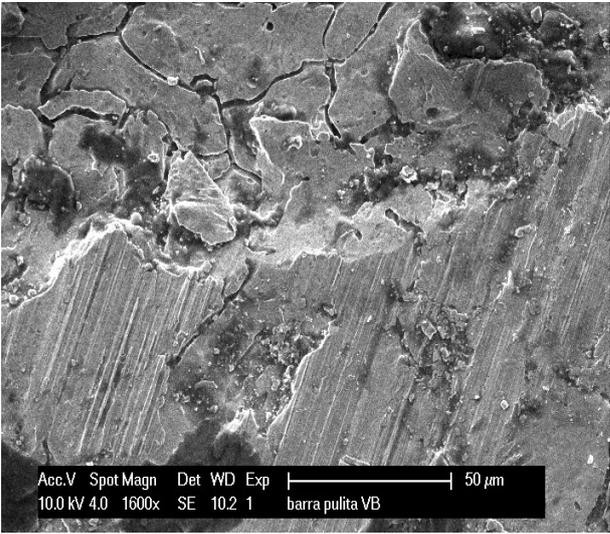
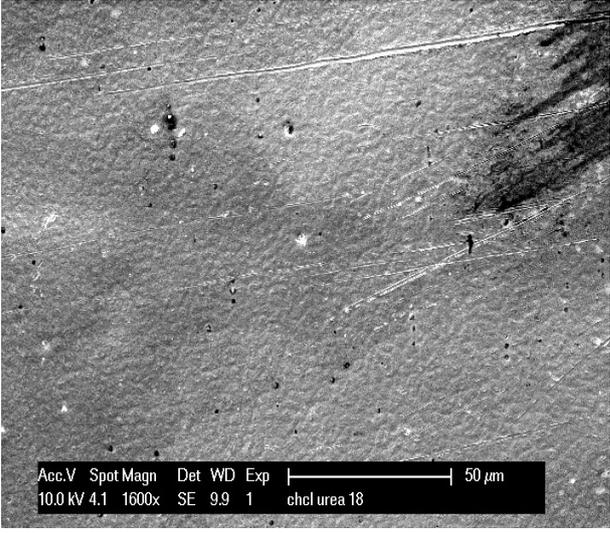
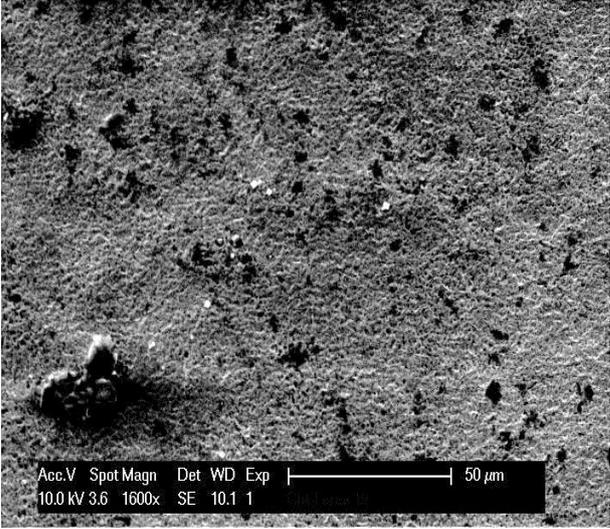
Regarding the surface composition, EDX spectra do not show significant changes (see figures 5.18 and 5.19):

- The spectra of surface after the standard chemical etching and after the electropolishing in eutectic mixture with ChChl - urea are similar, except that the amount of carbon, lower in the case of urea. The analysis does not reveal the presence of chlorine compounds or other residues of the solution.

- The spectra of surface after the standard chemical etching and after the electropolishing in Eutectic “O” are practically equal. The analysis does not reveal the presence of chlorine or other residual compounds of the solution.

In table 5.8 comparison between three different treatments are presented.

Table 5.8: Comparison of SEM micrographs after polishing in ionic liquids and the standard recipe.

Solutions	SEM analysis of samples
<p>Standard industrial etching</p>	
<p>Eutectic 1:2 Choline Chloride : Urea</p>	
<p>Eutectic "O"</p>	

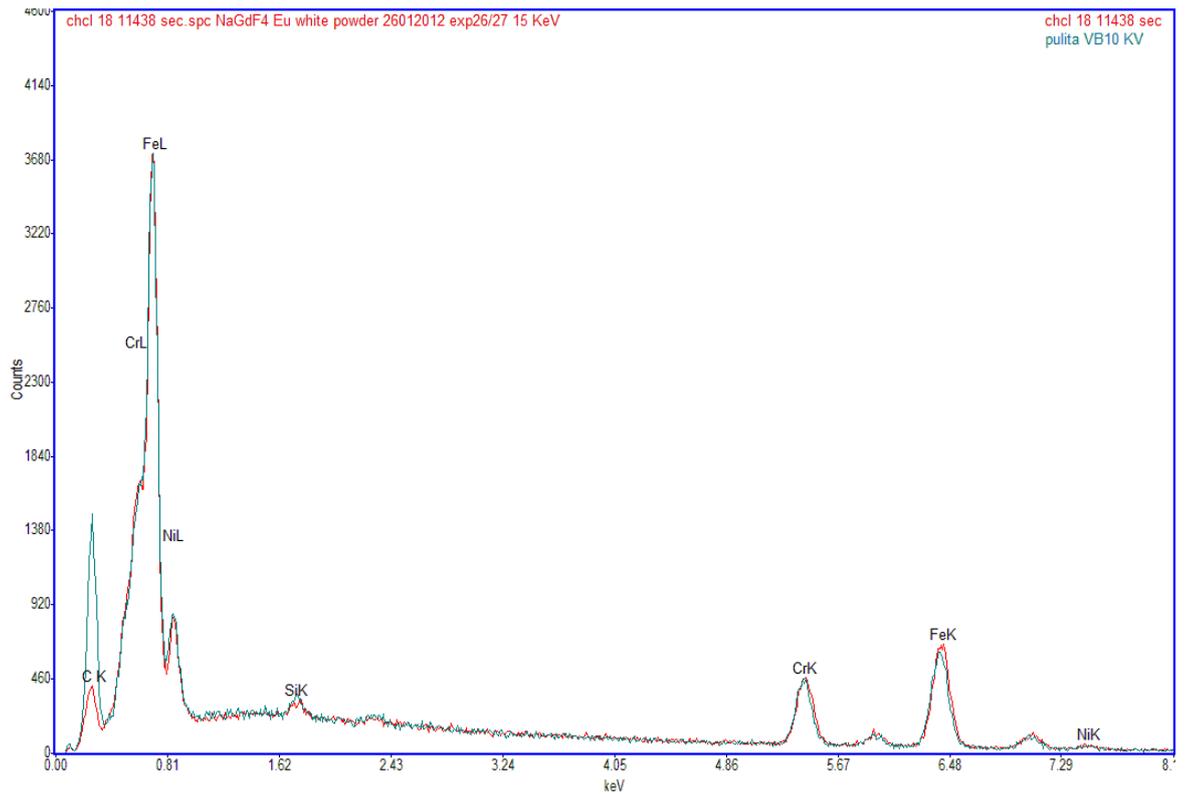


Figure 5.18: EDX spectrum, comparison after treatment in eutectic 1:2 ChChl: urea and the standard recipe.

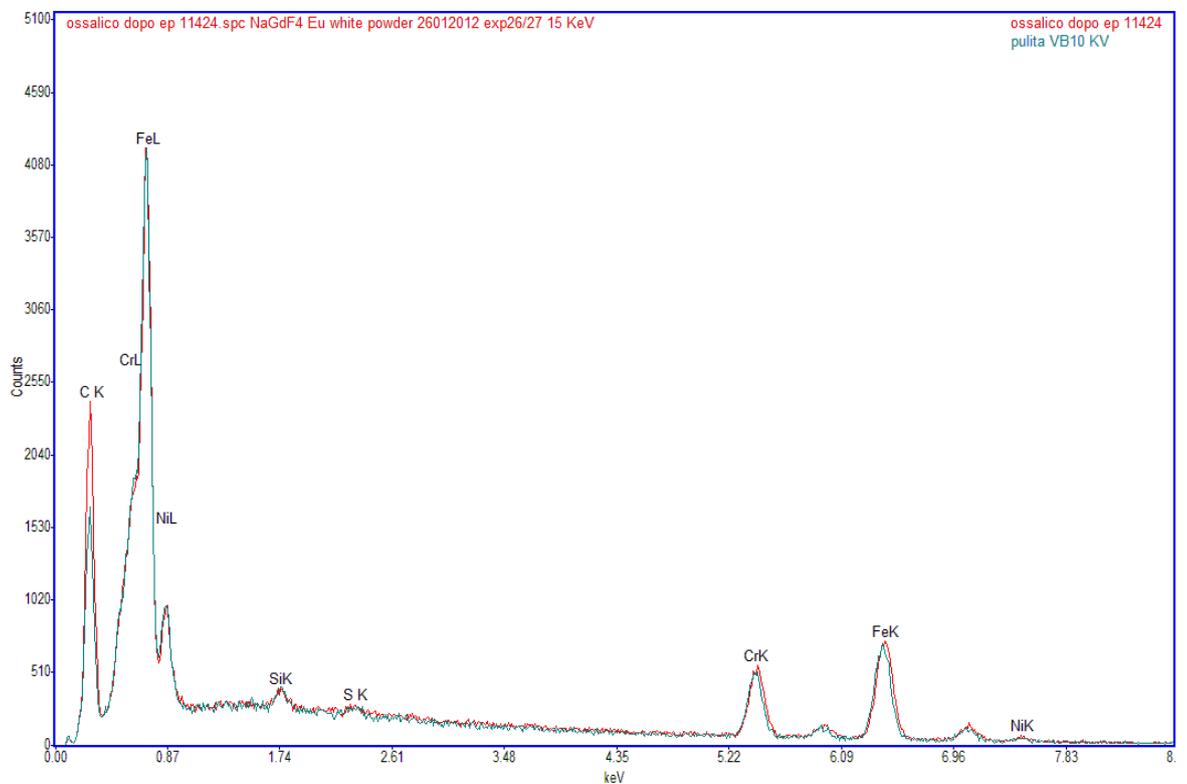


Figure 5.19: EDX spectrum, comparison after treatment in Eutectic "O" and the standard recipe.

5.6. Analysis of the applicability of the alternative solution.

For our future study, we choose the Eutectic “O”, choline chloride: carboxylic acid in ratio 1:1. The satin finish that can be obtained with the solution of carboxylic acid is similar to standard industrial chemical process. Therefore, we decided to study this electropolishing solution more thoroughly.

5.6.1. The measurements of solution lifetime.

The experiment was carried out with the fixed current during the electropolishing of the sample and monitoring the erosion speed until its half-life. The volume of solution was kept constant by topping up with fresh solution, but less than 10%. The heating of the solution by the current during the electropolishing is not negligible and therefore the process runs in thermostatic conditions. The solution during its usage is varied the colour, from transparent to very dark green, almost black. The solution gradually increases the concentration of the dissolved scale, thus increases its viscosity and making the process impractical in an industrial context. With the colour changing, it is possible to monitor the solution degradation. However, the solution is fully functional and has only a lowering of the speed of erosion.

Parameters used and results:

- $I = 3 \text{ A}$ (fixed);
- $V = 8 - 20 \text{ V}$ (variable and dependent on temperature and the life time of the solution);
- $T = 85 \text{ }^\circ \text{C}$;
- Initial size of the sample = 50x20x10 mm;
- Total time of electropolishing = 39 hours;
- Total mass eroded = 85.5 g;
- Solution volume = 1,5 l;
- Final concentration (g steel / l solution) = 57 g / l.

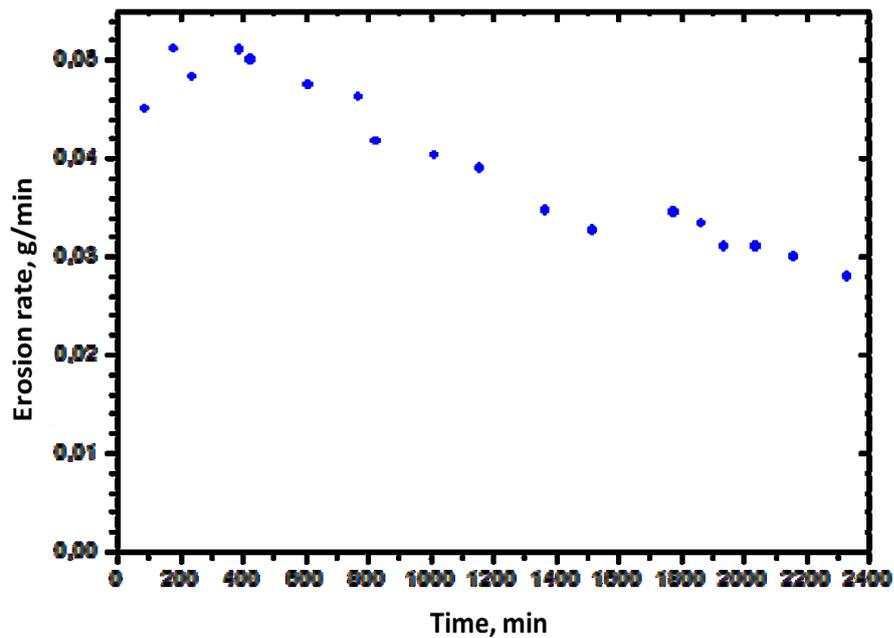
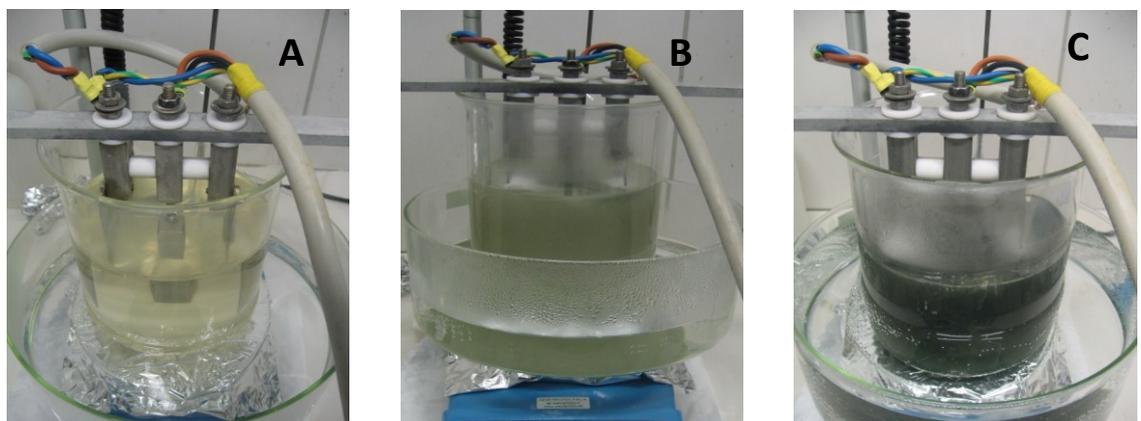


Figure 5.20: Graphic dependence erosion rate on time.

Looking at the graph, we see that in the first 500 minutes the solution increases its effectiveness until the process reaches the maximum speed of erosion that remains constant up to 700-800 minutes, where it begins to decrease linearly. Masking the first 5 points, you get a linear fit, which tells us that, the rate of erosion varies with time and as follows:

$$V \text{ (g / min)} = 0,53 - 1,14 \cdot 10^{-5} t \text{ (min)}$$

On Figure 5.21 and 5.22, you can see the changing of the solution colour during the electropolishing.



A) 0 min

B) 30 min

C) 60 min

Figure 5.21: Degradation of the ionic liquid solution after A – 0 min; B – 30 min; C – 60 min.

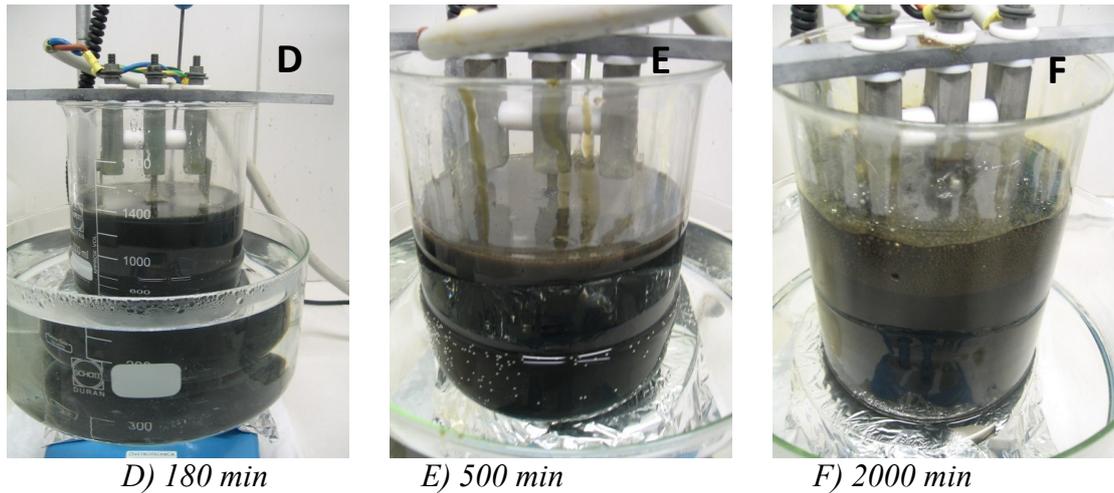


Figure 5.22: Degradation of the ionic liquid solution after D – 180 min; E – 500 min; F – 2000 min.

5.6.2. Vapours analysis.

To compare the vapours produced by the standard chemical etching compounds of nitrogen oxides (NO_x), tests were performed with our instrumentation. The results demonstrated the absence of toxic fumes (NO_x).

5.6.3. Estimation of the process time.

The process of electropolishing in ionic liquid has a variable duration that depends mainly on the pre-finishing of the sample. The comparison of the raw samples and samples blasted with the standard method of the steelwork, in the first case the complete removal of scale takes longer than 15 minutes. The sandblasted samples can have a duration of treatment between 3 - 5 minutes. The processing time is dependent on the applied current, which in turn influences the final finish. The high current leads to the higher rate of erosion, but at the same time provides shinier finishing. The satin finish, required by the steelwork, we could get at lower currents. One possibility, for organizing the cleaning process, it is providing the primary time at high currents to obtain the maximum erosion rate, and then a finishing process at low current. The process was carried out on the samples small size and the rod longer than 1,5 m, with excellent results. In these tests, however, the processing time was dilated.

5.7. Additional tests with Eutectic “O”.

5.7.1. Electropolishing martensitic steel and steel doped with sulphur.

We have tested the ability of Eutectic “O” to electropolished also the various types of steels in addition to austenitic. In particular, we are electropolished samples of martensitic steel and doped with sulphur. On figures 5.23 and 5.24 are presented result after electropolishing in ionic liquid the steel doped with sulphur and martensitic steel.

Parameters used for steel doped with sulphur:

- Current - 5 A (fixed);
- Voltage - 6-15 V (variable);
- Temperature - 85 ° C;
- Total time - 5 min electropolishing;
- Initial size of the electropolished specimen - 50x20x10 mm.



Figure 5.23: Sample of the sulphur doped steel after electropolishing.

Parameters used for martensitic steel:

- Current - 5 A (fixed);
- Voltage - 6-13 V (variable);
- Temperature - 85 ° C;
- Total time = 3 min;
- Initial size of electropolished specimen = 50x20x10 mm.



Figure 5.24: Sample of the martensitic steel after electropolishing.

As we can see, the solution is also effective for martensitic steels and sulphur doped steels and processing times rather low, 3 and 5 minutes, respectively.

5.7.2. Comparison of the electrolytes with carboxylic acid pure and technical grade.

We have studied the possibility of lowering the price of the electrolyte by decreasing the purity of reagents.

The test consisted on electropolishing two pieces taken from the same bar in the two solutions of Eutectic “O”, prepared with pure carboxylic acid and acid technical grade. We have compared the pieces before the complete elimination of scale and then performed a 90-minute process to compare to the erosion rate.

Parameters used were:

- Current - 2 A (fixed);
- Voltage - 3-4 V (variable);
- Temperature - 85 ° C;
- Process time - 4 min;
- Initial size = 50x20x10 mm;
- Solution composition 1: Eutectic “O” (pure);
- Solution composition 2: Eutectic “O” (technical grade).

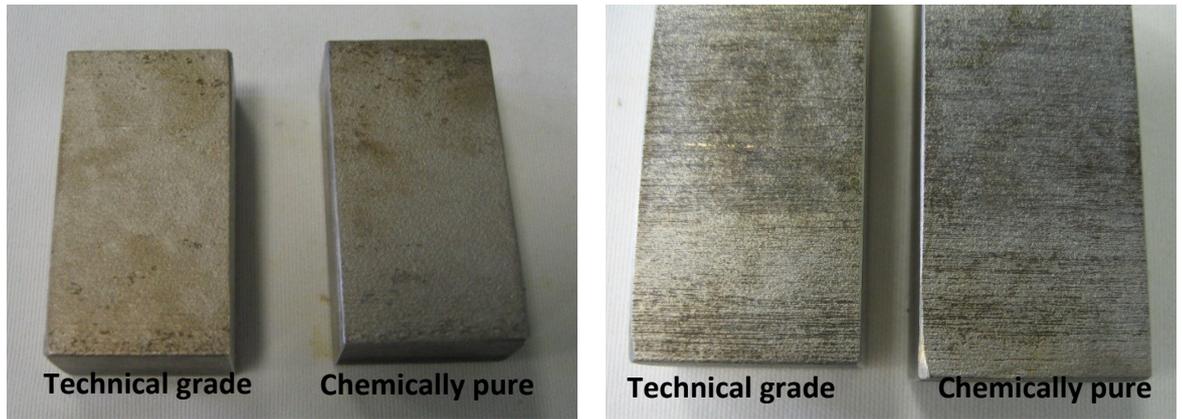


Figure 5.25: Comparison between the samples obtained in solutions technical grade and pure grade, after 4 min.

Then the samples were electropolished completely and we have continued the process in order to decrease the error in measurements of the mass of eroded material.

Parameters used were:

- Current - 2 A (fixed);
- Voltage - 4-6 V (variable);
- Temperature - 85 ° C;
- Total time - 90 min;
- Samples initial size = 50x20x10 mm
- Solution composition 1: Eutectic “O” (pure);
- Solution composition 2: Eutectic “O” (technical grade).

Results:

The eroded mass in solution pure grade = 3,0 g.

The eroded mass in solution technical grade = 3,1 g.

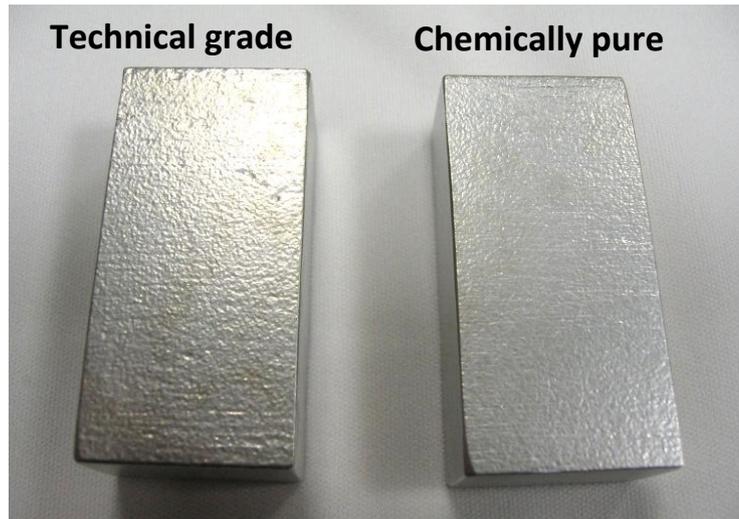


Figure 5.26: The samples after 90 minutes of treatment with the two different solutions.

Conclusion: the results confirm that the technical grade solution works in the same way of chemically pure solution. It gives us the possibility to reduce the total price of the electrolyte for polishing without losing the quality of the final finishing.

5.7.3. Study of the influence of preliminary treatment.

The purpose is to compare two different cleaning treatments before the actual electropolishing, in order to understand the usefulness of these procedures.

The sandblasted samples, before being electropolished, were cleaned in order to remove grease and dirt that could slow or limit the electropolishing process.

Two treatments have been studied: mechanical cleaning with a paper dipped in acetone and cleaning in an ultrasonic bath with alkaline soap.

The process conditions are following:

Sample 11: without pre-treatment;

Sample 12: mechanical cleaning with paper dipped in acetone;

Sample 13: cleaning in ultrasonic bath with alkaline soap.

We have electropolished the three samples in the same conditions, which allowed a partial removing of the scale, in order to assess if the pre-cleaning produces the increasing of the electropolishing speed.

Parameters of the electropolishing:

- Current - 2.5 A;
- Voltage - 5 V;
- Time - 2 min;
- Temperature - 80 ° C.

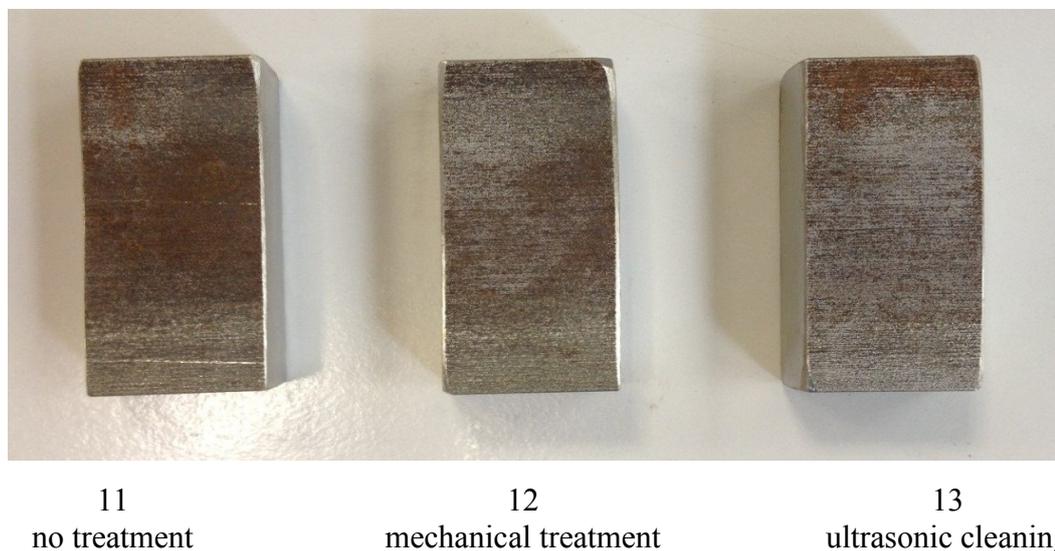


Figure 5.27: Samples after different pre-treatment and half electropolishing process.

The photo shows the face of the samples, where the thickness of scale is higher. The other side is already perfectly clean. After another 2 minutes of electropolishing, all three samples are free from scale on the surface.

In the middle of the process, it can be noticed on the photo a slight improvement in the pre-treated samples. Moreover, it is important to note that the electropolishing in ionic liquid is effective even without a pre-treatment cleaning or degreasing.

Therefore, the conclusion is following the efficiency of the mechanical treatment and ultrasound cleaning is very low, and additional process can increase the total cost of the process. For this reason, the possibility to provide only electrochemical polishing is a significant advantage in industrial process.

5.8. Optimization of the parameters of electropolishing in ionic liquids.

We have found the working temperature of Eutectic “O” is 85 ° C. We also wanted to study working temperatures 60 ° C and below. We also searched and studied new bath composition that would allow working at lower temperatures.

Working at lower temperatures would allow lowering the costs of the process, both for eliminating the use of heaters, and having the possibility to build the plant with cheaper materials that do not need to withstand high temperatures.

5.8.1. Study of lower working temperatures.

The experiment was carried out on the sandblasted samples (AISI 304) by removing the layer of scale at a temperature of 40, 60 and 80 °C, applying the fixed current and recording the process time and performing the process of electropolishing. At temperature below 40 °C, the solution is too viscous and the conductivity is low, the process requires voltages higher than 40 V, the limit of our power supply. Working at such high voltages is however uneconomical, because it requires working at very high powers, with a consequent increase in the cost of the electricity. From the results reported in Table 5.9 we see that the treatment time totally to remove the scale is 10 minutes, at 60 °C and at 80 °C. It has, however, a significant difference in the process voltage. The working temperature - 40 °C, shows not uniform surface and requires longer process times.

The possible lowering of the working temperature to 60 °C will increase the power cost for the electrochemical process, about 30%.

Table 5.9: Test at different temperatures of Eutectic "O".

Temperature	Current	Voltage	Time	Samples	Note
40 °C	3 A	14-26	15		The scale removed completely. Finishing is not perfect. Increased tension of the process.
60 °C	3 A	19-28	10		The scale removed completely. Satin finishing. Increased tension of the process.
60 °C	3 A	19-24	10		The scale removed completely. Satin finishing. Increased tension of the process.
80 °C	3 A	14-16	10		The scale removed completely. Satin finishing. Tension is stable.
80 °C	3 A	16-14	10		The scale removed completely. Satin finishing. Tension is stable.

5.8.2. Study of the different ratios Choline Chloride – Carboxylic acid.

We have studied also the different ratio of mixing ionic liquid, choline chloride with carboxylic acid, Eutectic “O”. The results, however, did not show the improvements over the original solution (see table 5.10).

Table 5.10: Tests at different concentration ratios Choline Chloride- Carboxylic Acid.

Ratio ChCl: CA	Tem-re	Current	Voltage	Time	Samples	Note
1:2	60 °C	3 A	8-22 V	10 min		Voltage is jumping. The surface is slightly stained.
1:2	50 °C	3 A	7-13 V	10 min		Voltage is jumping. The surface is slightly stained. The solution tends to freeze.
2:1	50 °C	3 A	6-22 V	20 min		Voltage is jumping. The surface is slightly stained. The time of process is twice longer.

We have noticed that with increasing the quantity of carboxylic acid in the mixture the liquid becomes more viscous. Also with lowering temperature of the solution, the viscosity is changing. This can be the reason for voltage jumping during the electropolishing. The spots on the surface can be the result of partially passivation during the electrochemical process.

5.8.3. Study of the influence of additives in Eutectic “O”.

To the studied solution of choline chloride: carboxylic acid (1:1) were added some additives to lower working temperatures. The additives are following:

- Citric Acid;
- Butyl Acetate;
- Glycerol;
- Acetic Acid.

It can be seen (Table 5.11), the addition of acetic acid allows working at 40 °C, limiting the increase in power required for the electropolishing process.

This solution, however, is problematic in use. Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Hazardous in case of skin contact (corrosive), of eye contact (corrosive). Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

Table 5.11: Result of electropolishing in Eutectic "O" with additives.

Solution	Temp (°C)	Current (A)	Voltage (V)	Time (min)	Samples	Note
Eutectic "O" + Citric acid (1:1:1)	75	3	23-17	10		Very viscous solution. High gas evolution.
Eutectic "O" + Citric acid (1:1:1)	60	3	30	10		Very viscous solution. High gas evolution.
Eutectic "O" + Citric acid (1:1:1)	40	2	30	10		Solution is very viscous.
Eutectic "O" + + 5% Butyl Acetate	75	3	7-12	10		Very strong and unpleasant odour
Eutectic "O" + Glycerol (1:1:1)	60	3	7-10	10		High gas evolution. Shiny surface.
Eutectic "O" + Glycerol (1:1:1)	40	2	10-12	10		High gas evolution. Shiny surface.

Solution	Temp (°C)	Current (A)	Voltage (V)	Time (min)	Samples	Note
Eutectic "O" + Glycerol (1:1:1)	30	3	20-30	25		Shiny surface. Oscillating voltage.
Eutectic "O" + 5% Acetic acid	60	3	5-15	10		Visible gas evolution. Very strong and unpleasant odour.
Eutectic "O" + 5% Acetic acid	40	3	8-25	15		Very strong and unpleasant odour.
Eutectic "O" + 10% Acetic acid	40	3	10-22	10		Very strong and unpleasant odour.

5.8.4. Study of the influence of water on electropolishing process in ionic liquids.

The experiment has been carried out in the laboratory, where the working environment can be controlled; this is not possible in industrial process. The industrial treatment of the wire rod consists of the washing in the water and thus can bring the water inside electrochemical solution. Even the cleaning of the tank will leave some amount of the water. It was, therefore, tested the effect of water (5%, 10% and 20%) in the cleaning process at different temperatures.

Table 5.12: Influence of water on electropolishing in ionic liquid.

Solution	Temp (°C)	Current (A)	Voltage (V)	Time (min)	Samples	Note
Eutectic "O" + 5% Water	80	5	9-13	10		Sample is clean.
Eutectic "O" + 10% Water	80	5	15-22	10		Sample is clean. Surface shine.
Eutectic "O" + 10% Water	80	3	7-11	10		Sample is clean. Surface shine.
Eutectic "O" + 10% Water	60	5	11-17	10		Sample is clean. Surface shine.
Eutectic "O" + 10% Water	60	3	10-30	10		Sample is clean. Surface shine.
Eutectic "O" + 10% Water	40	3	15-30	10		Sample is clean. Surface shine.
Eutectic "O" + 20% Water	40	3	5-12	10		Sample is clean. Surface is very shine.

We can see that the solution became less viscous and, as a result, the process is more controllable. In conclusion, small percentages of water in the electrolytic bath (below 10%) did not affect the process and surface finishing. While the higher percentages lead to a shine finishing.

5.8.5. Search of a new Choline chloride based ionic liquid for electropolishing.

Observing a good result given by the ionic liquid choline chloride with carboxylic acid in polishing of steel, we were interested in finding alternatives solutions to lower the temperature and reduce the cost of the process. It was tested at low temperature ionic liquid following compositions: binary Choline Chloride with Glycerol, Urea, and others carboxylic acids, ternary Choline Chloride – Alcohols - Carboxylic Acids. The results (see. Table 5.13) were not satisfactory: the binary ionic liquids produces a shiny surface (and not satin as required by steelwork), while the ternary ionic liquid is not able to uniformly remove the scale. In the case of Glycerol, also a bath with the addition of water has been tried. Alternatively, it was tested the possibility of forming an ionic liquid by mixing a metal salt and Choline Chloride. The Tin Chloride in the ratio 1:2 with Choline Chloride has shown excellent results. In particular, the satin finish is obtained at comparable times in the standard recipe and works very well even at 50 ° C, even if it requires time and higher voltages to totally remove the calamine. The limit of the solution is the presence of a heavy metal in solution (tin) to be disposed and the high cost.

Table 5.13: Research alternative Choline Chloride-based ionic liquids.

Solution	Temp (°C)	Current (A)	Voltage (V)	Time (min)	Samples	Note
ChChl : EG : CA (2:1:1)	55	1	8,2	5		Polishing is not efficient.
ChChl : EG : CA (2:1:1)	65-75	9	18	4		Polished surface is spotted.
ChChl : EG : CA (2:1:1)	80	5	12	5		Polished surface is spotted.
ChChl : EG (2:1)	40	1	4,5-6,5	40		Shiny surface. Process is time- consuming
ChChl : EG (2:1)	60	3	12-25	20		Shiny surface. Process is time- consuming.
ChChl : Urea (1:2)	60	3	12-25	20		Polished surface is spotted.

ChChl : Urea (1:2)	45	10-3	50-18	5		Polished surface is spotted.
ChChl : Glycerol (1:1)	60	3	10-15	10		Polished surface is spotted.
ChChl : Glycerol (1:1) + 40% Water	40	3	5-8	10		High quantity of foam form during the process. Extremely shin surface.
ChChl : Glycerol (1:1) + 40% Water	40	1	3-8	30		Surface clean in 30 min, but surface is spotted.
ChChl : Glycerol (1:1) + 40% Water	40	2	4-7,5	30		Increase current, but surface is still spotted.
ChChl : Malic acid (1:1)	100	1-3	14-45	35		It forms a gray film on the surface.
ChChl : Malic acid (1:1)	100	3	50-20	30		It forms a gray film on the surface.

ChChl : Lactic acid (1:1)	60	3	15-20	30		Polished surface is spotted.
ChChl : Tin Chloride (1:2)	65-80	1	6-9	5		Surface is perfectly clean and satin finish.
ChChl : Tin Chloride (1:2)	50	1	20-27	10		Surface is perfectly clean and satin finish. Required twice long time than at 80 ° C.
ChChl : Tin Chloride (1:2)	40	0,5	15-30	30		Surface is not perfectly clean. Very viscous solution. Temperature too low.

5.8.6. Summary of the ionic liquids mixtures, applicable to the electropolishing of the stainless steel.

We have carried out tests with different ionic liquids in order to find a solution for the replacement of the industrial chemical etching. In this case, the new solution has to present the same quality of steel surface. In table 5.14, we present the summary of ionic liquids used for electropolishing stainless steel. The mixtures contained alcohols, ethylene glycol and glycerol, and urea after electropolishing give the clean but shine surface. The mixtures with carboxylic acid and tin chloride gave the most suitable result. The rest solutions are not suitable for descaling stainless steel.

Table 5.14: Summary of the ionic liquids mixtures, applicable to the electropolishing of stainless steel.

Ionic liquid mixture	Observation
ChCl - Urea	Shiny surface, not uniform descaling
ChCl - EG	Shiny surface, pitting
Eutectic "O"	Matte surface, uniform descaling, the best result in EP stainless steel
ChCl - CA - Citric acid	Shiny surface, a lot of foam
ChCl - CA - Butyl Acetate	Shiny surface, strong odour
ChCl - CA - Glycerol	Shiny surface
ChCl - CA - Acetic acid	Shiny surface, strong odour
Eutectic "C"	Non uniform polishing, a lot of foam
ChCl - Glycerol	Shiny surface
ChCl - Malic acid	Gray film on the surface
ChCl - Lactic acid	Spots on the surface
ChCl - Tin chloride	Matte surface, very viscous solution

5.9. Study of the recycling of ionic liquid.

We have studied the possibility to recycle the solution in order to increase the lifetime of ionic liquid. We have added a quantity of water equal to the volume of working solution, waited for the separation of liquid part and the precipitation (Figure 5.28), filtered and then evaporated the water by heating over 100 ° C.

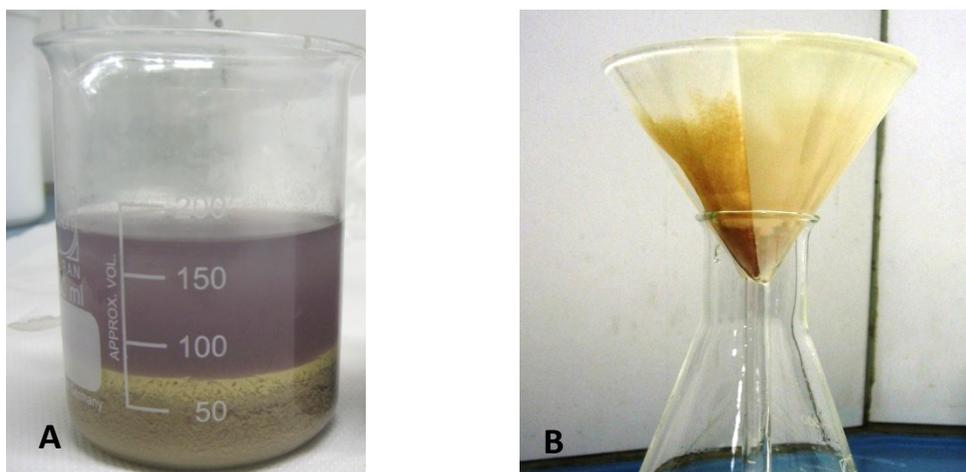


Figure 5.28: Separation (A) and filtration (B) of the solution after the addition of water.

After evaporation, we repeated the electropolishing of steel in recycled solution. In order to monitor the rate of erosion of the solution we recycled solution few times. In table 5.15 we can see results after recycling.

The results are amazing: the solution after recycling has a higher erosion rate. It should be considered, however, that solution after recycling contained some quantity of metallic ions that possibly increased the conductivity of solution and worked better. In conclusion, we can say that ionic liquids can be recycled and give us the possibility to reuse electrolyte for few times.

Table 5.15: Test of the recycled solution.

Solution	Temp (°C)	Current (A)	Voltage (V)	Time (h)	Δm (g)	Erosion Rate (g/h)
Eutectic "O" Fresh solution	60	3	≈ 50	10,1	20,95	2,1
Eutectic "O" After 1st recycling	60	3	≈ 50	10,2	30,63	3,0
Eutectic "O" After 2nd recycling	60	3	≈ 50	9,6	39,27	4,1

5.9.1. Study of the velocity of metal dissolving in fresh solution and recycled.

We have prepared the new solution and started to dissolve the samples. Every hour we have controlled the weight. This study also allows us to have an indication of the lifetime of the solution, and absorption ability of ionic liquid.

The graph (see figure 5.29) shows that the absorption is rather constant up to 20 hours of the process. The first point shows that the erosion rate is low, probably because the metal ions are absent in the solution and the sample is covered with scale. Another important point is that the solution, even after 35 hours of work, has an efficiency higher than 50%.

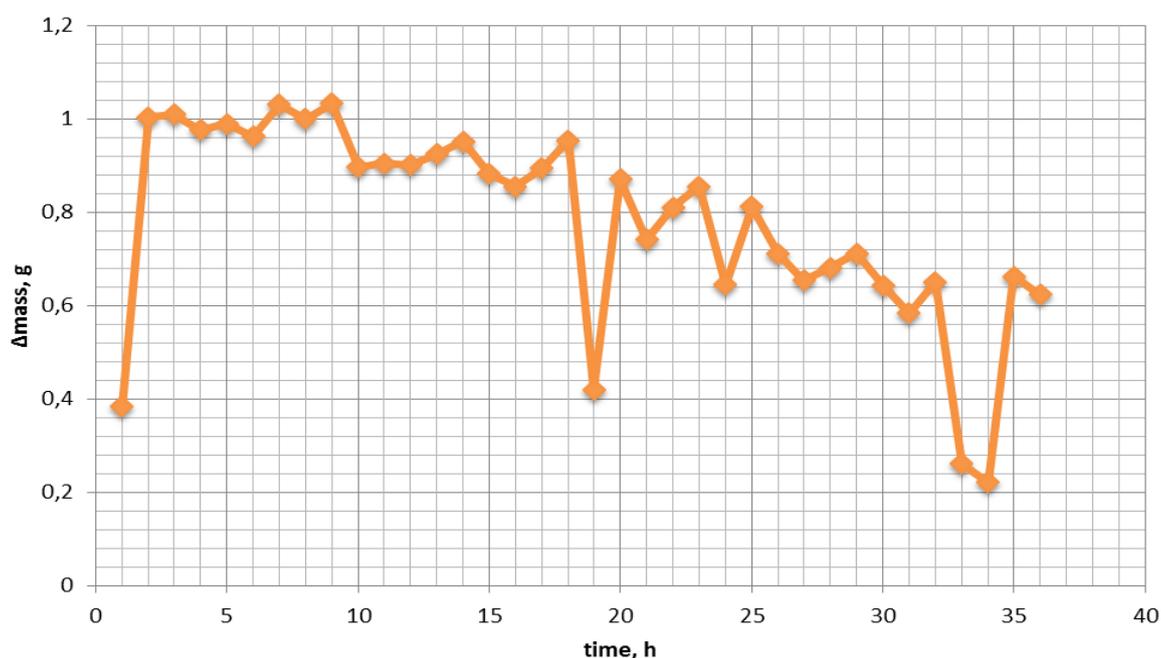


Figure 5.29: The change of sample mass with time in fresh solution.

In the recycled solution, we carried out the test at the same conditions. In confirmation of what we have told before (see paragraph 5.11), we see the increasing of erosion rate that shows around 80% of the initial value.

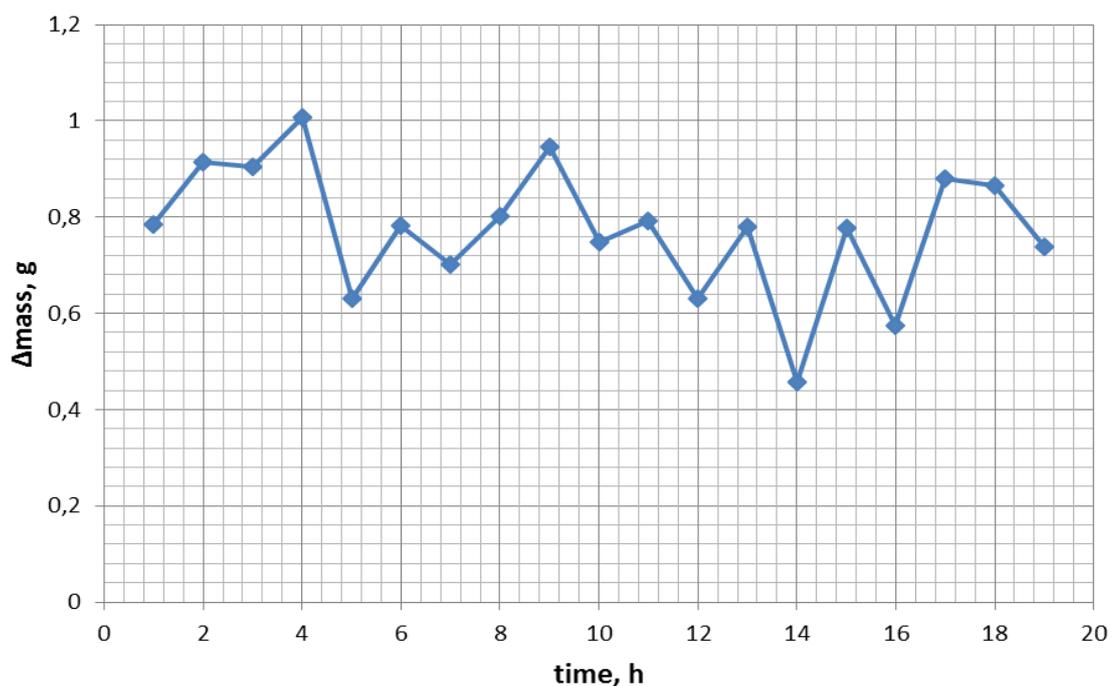


Figure 5.30: The change of sample mass with time in recycled solution.

In conclusions: The ionic liquid solution can be applicable to industrial process due to the possibility to recycle and reuse with higher erosion rate. For future electrochemical plant, we need to take into account the step with recycling electrolyte by separating and evaporating the water and precipitation.

5.10. Study of the possibility to use AC power supply.

The industrial process of electropolishing requires large power plants, and the cost of the power supply is an important task in the evaluation of total process cost. For this, we carried out the tests using a simple three-phase current rectifier as a power supply. The use of a rectifier, in fact, would allow us to fabricate the power supply that significantly reduces the costs.

The purpose of a rectifier is to convert an AC waveform into a DC waveform. There are two different rectification circuits, known as 'half-wave' and 'full-wave' rectifiers. Both used components called diodes to convert AC into DC.

A diode is a device that only allows current to flow through it in one direction. In this direction, the diode is said to be 'forward-biased' and the only effect on the signal is that there will be a voltage loss of around 0.7V. In the

opposite direction, the diode is said to be 'reverse-biased' and no current will flow through it. [27]

It is preferable and customary to rectify three-phase AC with full-wave rectification. This yields a curve that is full-wave, three-phase rectification. There is a ripple (variation) of less than 5 percent in voltage, occurring at a frequency of 360 cycles per second. This electrical current is entirely satisfactory for electrocleaning. [28]

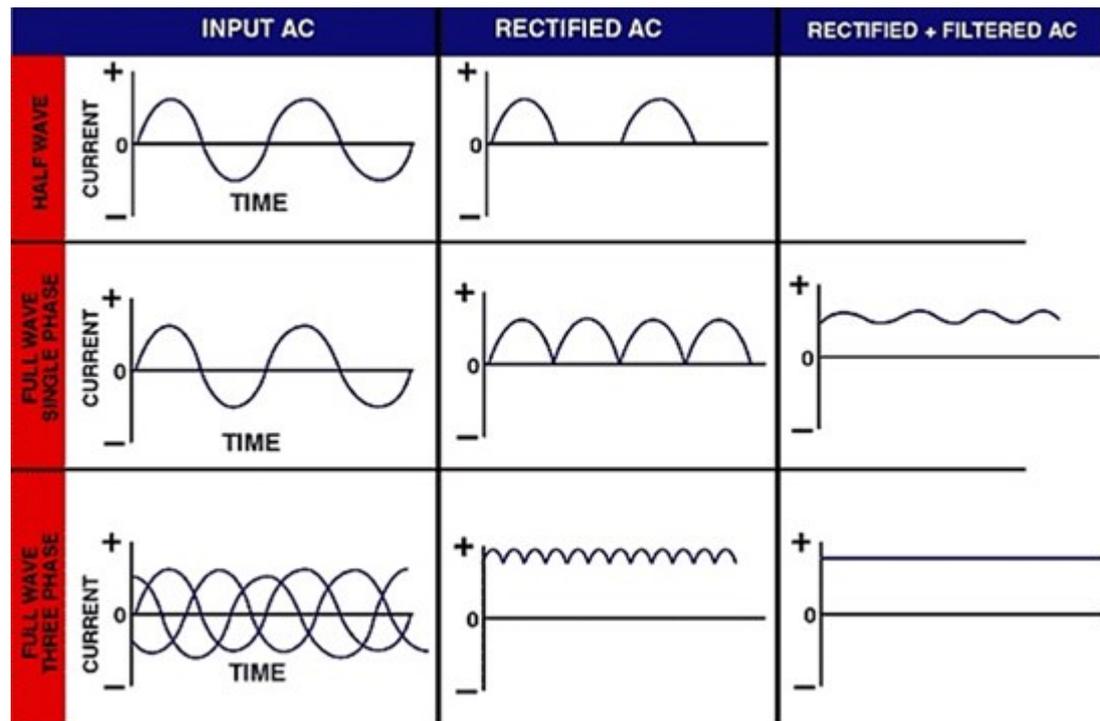


Figure 5.31: Typical rectification curves: half-wave rectification; full-wave, single-phase rectification; full-wave, three-phase rectification. [29]

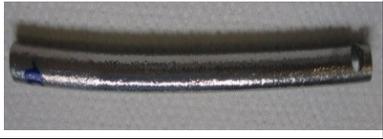
The electropolishing was done on the samples cut from steel rod and the result was compared with electropolishing DC-mode.

As we can see the results after electropolishing with rectifier are almost comparable with those obtained at the DC-mode, although slightly less uniform (see table 5.16). Therefore, we can conclude that the rectifier is a possible alternative to the more expensive AC and DC power supplies.



Figure 5.32: The electropolishing with rectifier.

Table 5.16: Comparison result of electropolishing with different power supplies.

Solution	Temp (°C)	Current (A)	Voltage (V)	Time (min)	Samples	Power supply
Eutectic "O"	80	2	13-14	14		DC
Eutectic "O"	80	2	7-9	16		rectifier
Eutectic "O"	80	3	7-12	12		DC
Eutectic "O"	80	3	5-6	12		rectifier
Eutectic "O"	80	5	5-10	9		DC
Eutectic "O"	80	5	5-6	7		rectifier

6. The first test in the construction of the new cleaning machine.

6.1. Experiments with samples in form of coils.

After studying the polishing process for rectangular samples cut from bar, and samples cut from rod, we decided to check ionic liquid ability to polish coil made from steel rod. For this, we have constructed a first prototype of cleaning machine for polishing stainless steel in ionic liquid electrolyte. We constructed a system for polishing the coil only partially immersed in solution. The current densities necessary to treat the steel samples, taken from experimental data, allow us to estimate the power needed to treat an entire wire rod, the weight of which normally is 1.2 tons and the diameter of 1 meter. The size of the working area requires the high amounts of solution to fully immerse them (several thousand liters), and very high values of current (near 20,000 A).

For the industrialization of electrochemical process in ionic liquids, we have to apply high currents and a big amount of the solution. These aspects make process uneconomical and difficulty in implementation. We decided to use the samples in form of coil made of steel rod, to simulate the real conditions of electrochemical process. The innovative idea is to immerse only part of the coil in the solution and rotate it continuously. In this way, we can reduce the volume of solution and decrease the currents for electrochemical process.

On figure 6.1, we can see the new system for polishing steel in ionic liquid solution. The structure provides that two wheels support the coil. One of it is aluminium, electrically insulated, and connected to the motor, which serves to transmit motion (rotation wheel). The second wheel (wheel-anode) also is aluminium, which has the double task of pressing the coil on the first wheel to facilitate the transfer of motion and to provide the current for the process of electropolishing. The upper wheel is connected to the positive pole of the power supply. The wheels do not participate in the electrochemical process because they are not immersed in the solution. The electrochemical cell is formed only where the coil is immersed in the solution because the ionic liquid closes the circuit between the anode and the cathode. The cathode is a C-shape steel immersed in the solution and placed in such way that the coil is equidistant from all three inner sides of the

cathode. For the first test, we have used the following process parameters (see table 6.1)

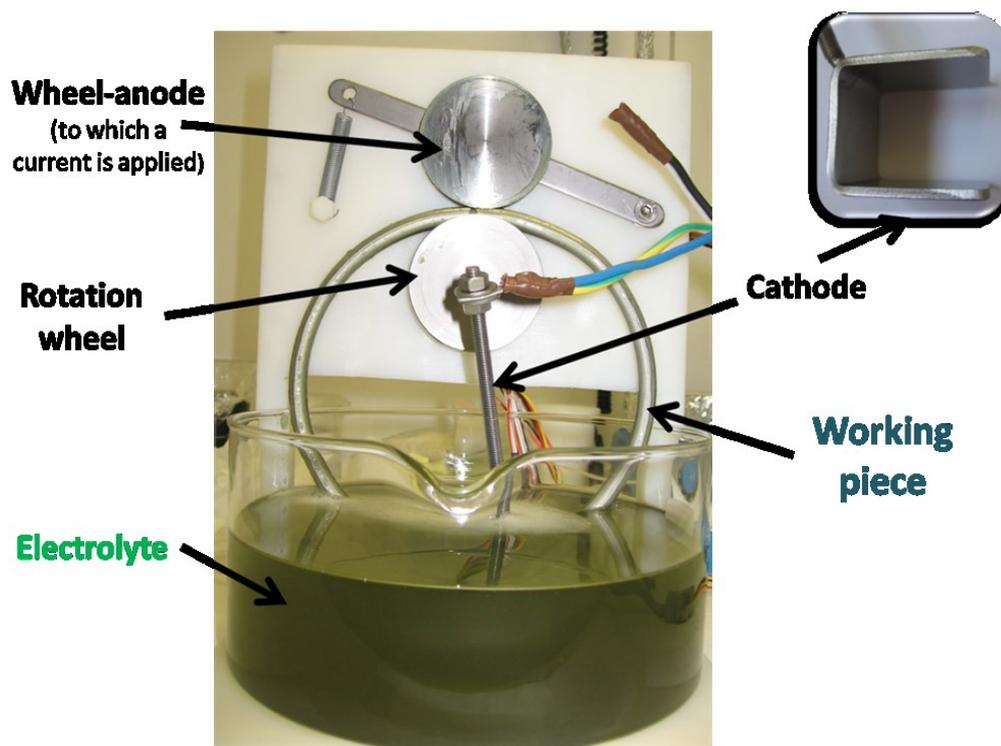


Figure 6.1: System for the electropolishing of a coil in ionic liquid solution.

Table 6.1: The working parameters for electropolishing the coil in ionic liquid.

Solution	Temperature (°C)	Current (A)	Voltage (V)	Current density (A/cm ²)	Time (min)	Velocity turns/min
Eutectic "O"	60	1	25	0,008	10	1

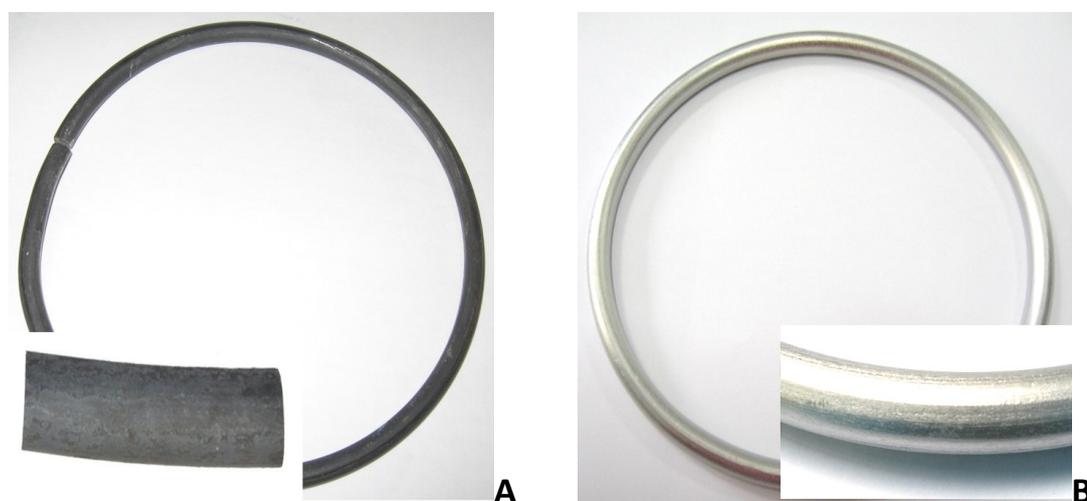


Figure 6.2: Coil before (A) and after (B) the electropolishing.

The result is satisfactory (see figure6.2), due to this new configuration with quite low current, we achieved the clean surface in short time.

6.2. Testing the material for tank.

The next step in construction of future machine for electrochemical polishing the steel in ionic liquid was searching the proper material for the tank. Requirements for the reservoir are the resistance to high temperature and chemical influence. For the test, we have chosen the steel and polyethylene tanks. The advantage of steel tank is the high resistance to mentioned parameters. We can use the steel tank as a cathode. In this case, we will have more uniform current distribution and, as a result, faster and smooth electropolishing. On the other hand, we have the risk of short circuit between the coil (anode) and the steel tank (cathode). The corrosion of steel tank can lead to damages of the surface and leakage of the ionic liquid. On figure 6.3 is the system for polishing coils in ionic liquid with steel tank.

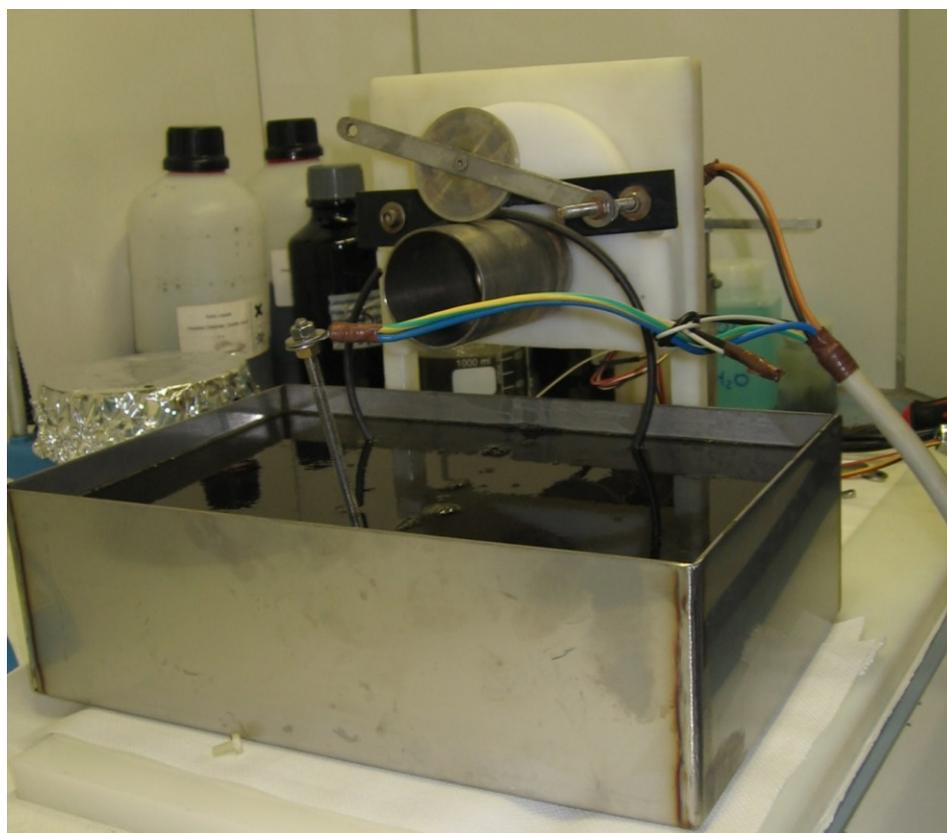


Figure 6.3: System for electropolishing in ionic liquid with steel tank.

We have carried out the electropolishing of coil also in polyethylene tank. In this case, the cost of the tank is lower than the steel tank, but any damage of surface integrity can lead to electrolyte leakage.

Both tanks resist at working temperature of ionic liquid (60-80°C). We decided to complicate the task and work with not a single coil. From the original rod, we have made coil with 12 turns (see figure 6.4). In all cases, we have used C-shape cathode. The aim of this test was to check the current distribution in conditions closed to real.

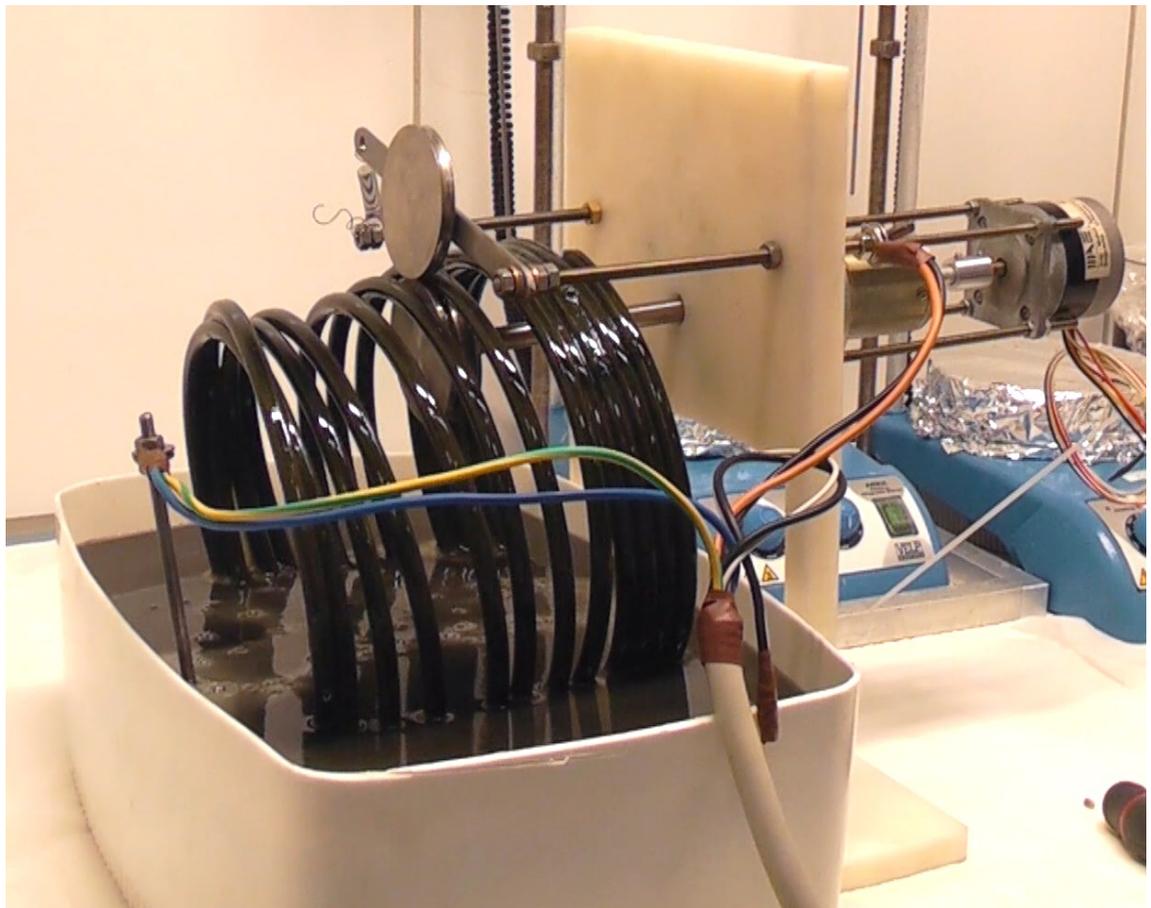


Figure 6.4: System in scale with polyethylene tank.

The parameters are reported in table 6.2, while the figure shows the perfect finishing, even at the point where the coils are pressed close to each other.

Table 6.2. The working conditions for electropolishing coil with 12 turns.

Solution	Temperature (°C)	Current (A)	Voltage (V)	Time (min)
Eutectic "O"	80	10-15	18-26	60

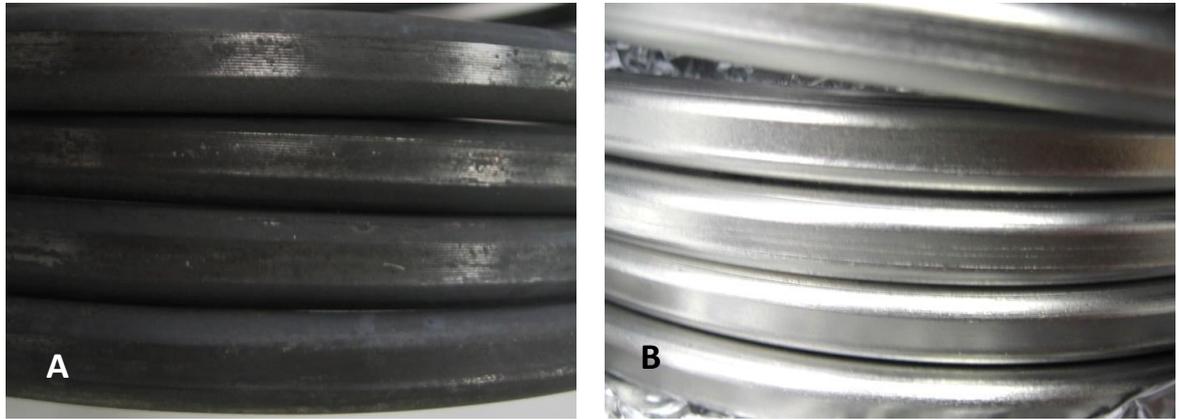


Figure 6.5: The rod 12 turns side by side A - before electropolishing; B - after electropolishing.

The next step was to descale a wire rod with the coils overlapping. The figure 6.6 shows the good finishing. The table 6.3 shows the parameters of electropolishing.



Figure 6.6: The rod with overlapped coils A- before and B- after electropolishing.

Table 6.3: The process conditions for polishing the rod with overlapped coils.

Solution	Temp (°C)	Current (A)	Voltage (V)	Time (min)
Eutectic "O"	60	5-10	20-35	90

For descaling, the rod with the overlapped coils took longer but it is perfectly clean. The purpose of this test was only to demonstrate the possibility to clean between the coils.

In conclusion, we can say that metallic tank is more suitable because it can be used as a cathode, and we have more uniform dissolution of the scale. Also, metallic tank is more resistant to high temperature. In general, ionic liquids have showed the proper current distribution and removed the scale from inaccessible areas.

6.3. The construction of electrochemical plant for descaling stainless steel coils close to real conditions.

The previous laboratory system for electropolishing in ionic liquid with the possibility to immerse partially the coils, has demonstrated good results. We have enlarged this system and built the new electrochemical plant. The figure 6.7 shows the new plant: it is conceptually identical to the first prototype. We have chosen the steel tank that also serves as a cathode. It was not necessary to use the second cylinder, since the coils rotated without it. The presented cylinder was connected to the motor, which allows rotation of the coils and provides the electric potential. The structure is made of aluminium profile. We have placed the system under the hood. The installation is completed with heaters that heat the solution and maintain the working temperature.

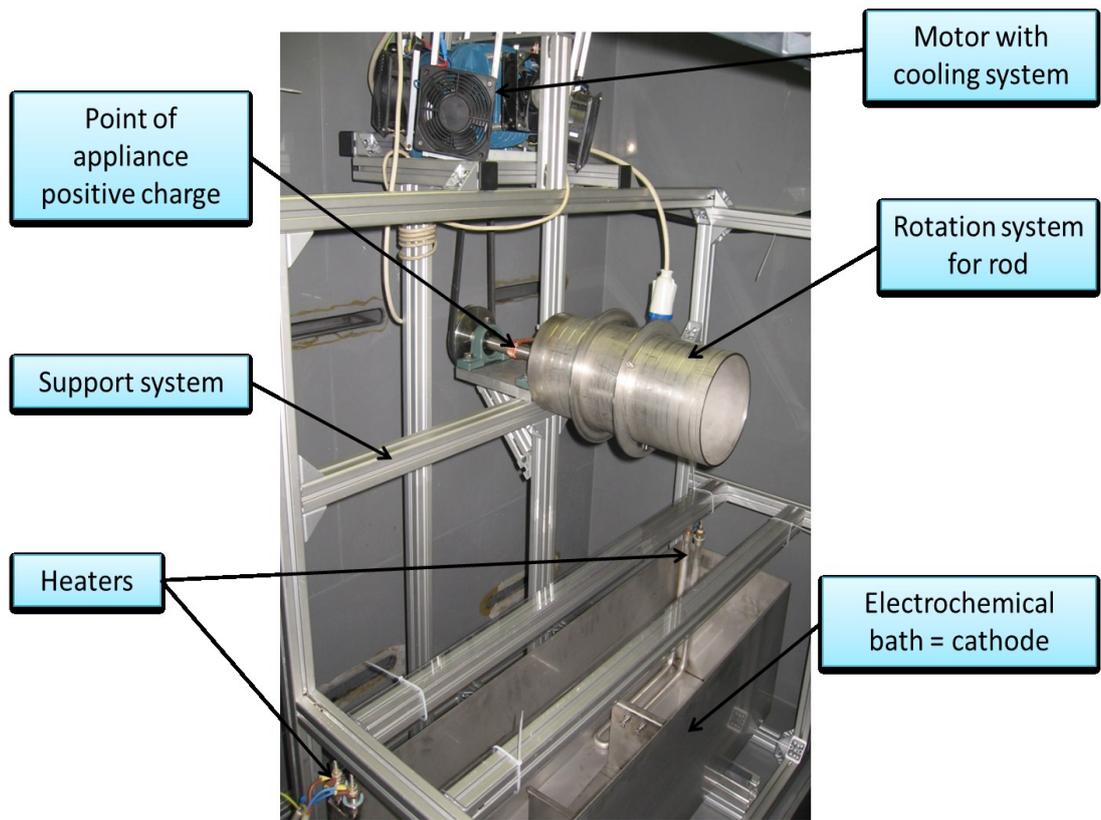


Figure 6.7: The electrochemical plant for descaling stainless steel wire rod.



Figure 6.8: The electrochemical plant during the cleaning process.

To provide power to the system we have used “Ametek” Sorensen SGI power supply with three feeders connected in parallel, with maximum parameters of current - 564 A and voltage - 80 V.

The Sorensen SG Series power supplies are general–purpose power supplies designed specifically for laboratory tests and systems applications, requiring variable DC sources with good ripple and regulation characteristics. These power supplies are constant current/constant voltage supplies with an automatic crossover feature.



Figure 6.9: The front panel “Ametek” Sorensen SGI power supply.

6.3.1. Preparation of the solution and study of the process parameters.

The solutions were prepared by mixing the components of ionic liquid, heating at 80 ° C in our customized ultrasonic bath. The obtained solution was poured into the process tank and maintained at a constant temperature of 80 ° C with the heaters. In general, we have prepared 75 liters of ionic liquid solution. For electropolishing, we have taken two types of stainless steel wire rods of diameter 5 mm and squared rods 23*23 mm. Both types of rods were perfectly clean, with complete removal of scale. The process parameters were varied continuously during the tests; it is difficult to provide reference value. It may indicate that the voltage varies from 30 to 60 V. The system proves that partially immersed technique gives the possibility to descale stainless steel. We have cleaned wire rods 15 and 25 kilo of weight. The following pictures show the wire rod and squared rod before and after the treatment.



Figure 6.10: The wire rod 5mm diameter before treatment.



Figure 6.11: The wire rods 5mm diameter after treatment.

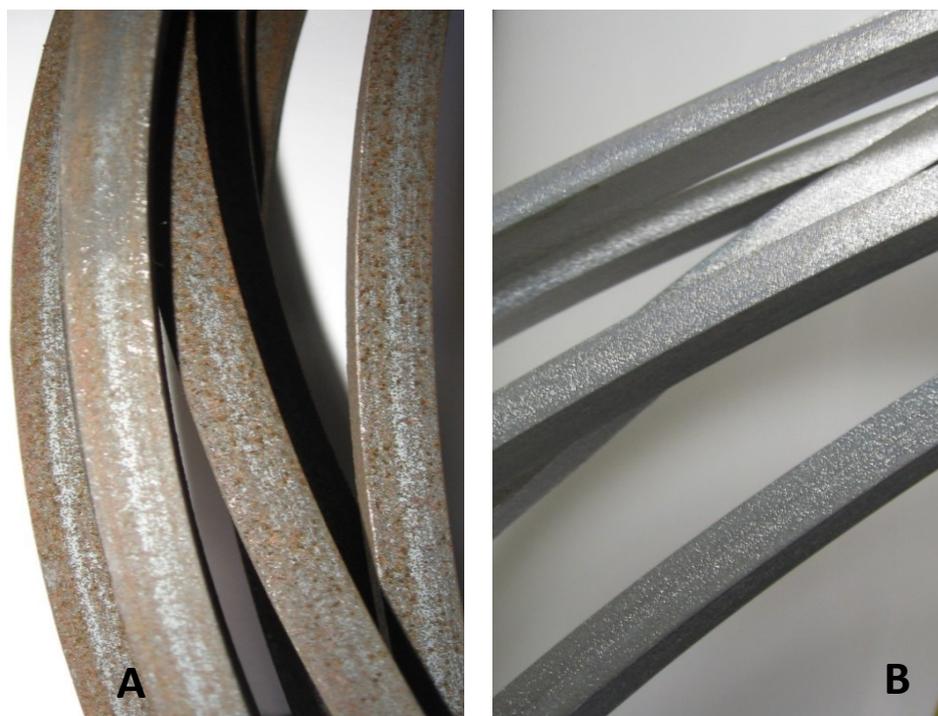


Figure 6.12: The squared rod 23 x 23 mm A – before and B- after treatment.

Conclusions: The idea of partially immersed surface inside solutions shows good results on the samples and with wire rod of 25 kilos. In planning future electrochemical plant, this can give us an advantage in the economical point: less quantity of the solution and less power. In a construction of the electrochemical bath, we will realize this concept.

6.4. The design of prototype for electropolishing of the wire rods in ionic liquid.

In the design of the system developed for the treatment of the wire rod, the idea is to imitate a washing machine: that is to say using a single pool both for the process and for rinsing. The tank will be filled and emptied from the electrolyte by pumps. The rinsing is needed to remove the residual solution on the wire rod, will be carried out with high pressure. The rotating cylinder based on a mobile structure, for which the loading of the wire rod can be done out of the plant and then the insertion of system will be done by the crane. There will be a mobile cover connected to the suction tube during the electropolishing process, rinsing, passivation. The main bath connected to the external tanks for recirculation of the electrolyte and water for rinsing.

The process can be summarized:

1. Place the wire rod on mobile support located externally of the plant;
2. Move the support with wire rod inside the process tank by special crane;
3. Shutdown and startup the aspiration;
4. Fill the tank with the solution for electropolishing;
5. Start rotating of the rod;
6. Set working parameters on the power supplies and start the process of electropolishing;
7. At the end of the electropolishing process the chemical solution is drained from the working bath to external tank;
8. Rinse the wire rod with high pressure water jets;
9. Rinse the working tank and pump out wastewater;
10. Fill the tank with the passivating solution;
11. Rotate the rod to ensure uniform passivation;
12. Remove the passivating solution and rinse the wire rod with water;
13. Clean the tank and remove wastewater;
15. Shut down of the suction and displace the movable support with wire rod outside the process tank;
16. Remove the clean wire rod.

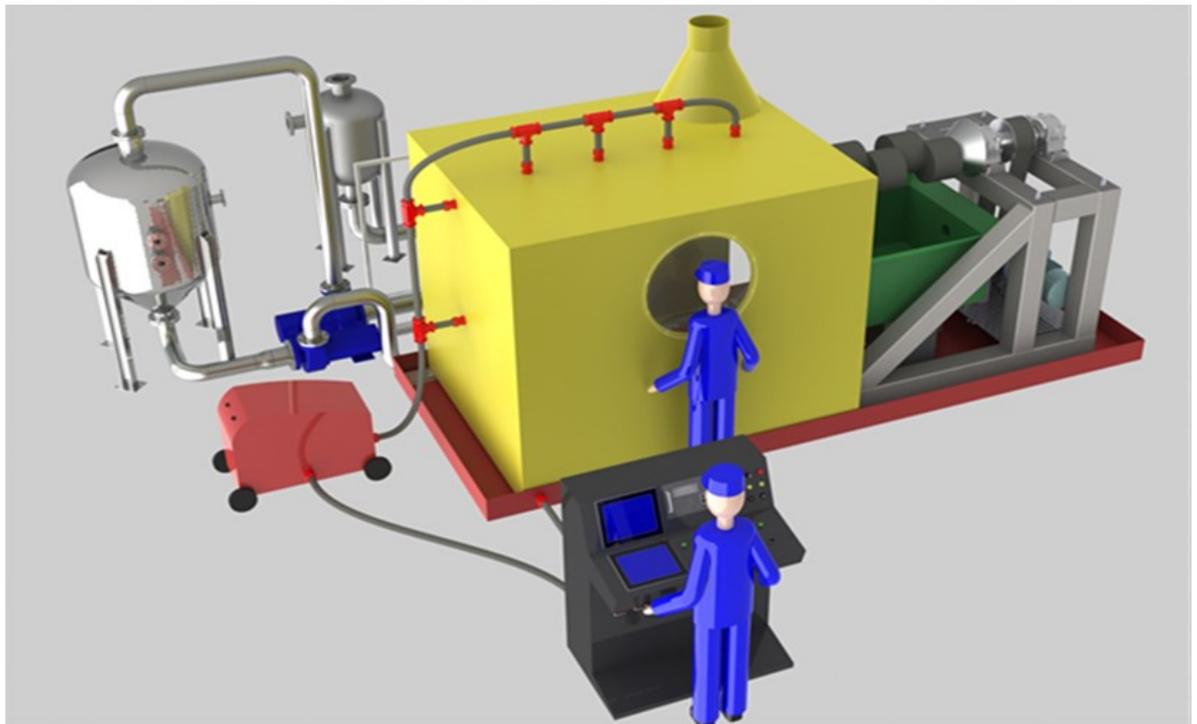


Figure 6.13: The design of electropolishing plant

7. Study of the steel passivation after electropolishing.

We have studied the new passivation solutions, with the aim of obtaining a process to remove the scale in the safest conditions. In fact, besides the replacement of standard etching solution with the electropolishing in ionic liquids, it would be interesting to replace also the standard nitric acid passivation with a more environmental-friendly solution. For alternative passivation, we have chosen two different acids (passivating solution - 2 and passivating solution - 3). We have used the passivation in industrial solution (passivating solution - 1) as the reference example.

Visually, the passivated samples were identical (see figure 7.1), and we left the samples in the open air for one month, to check the anticorrosive protection of a passive layer (see. figure 7.5).

The EDX analysis and comparison of SEM images did not show any differences. With EDX analysis (figures 7.2-7.4), we want to quantify the amount of oxygen in the passive layer. This analysis may be can give us information on what solution creates the oxide thicker and is more protective on the steel surface.

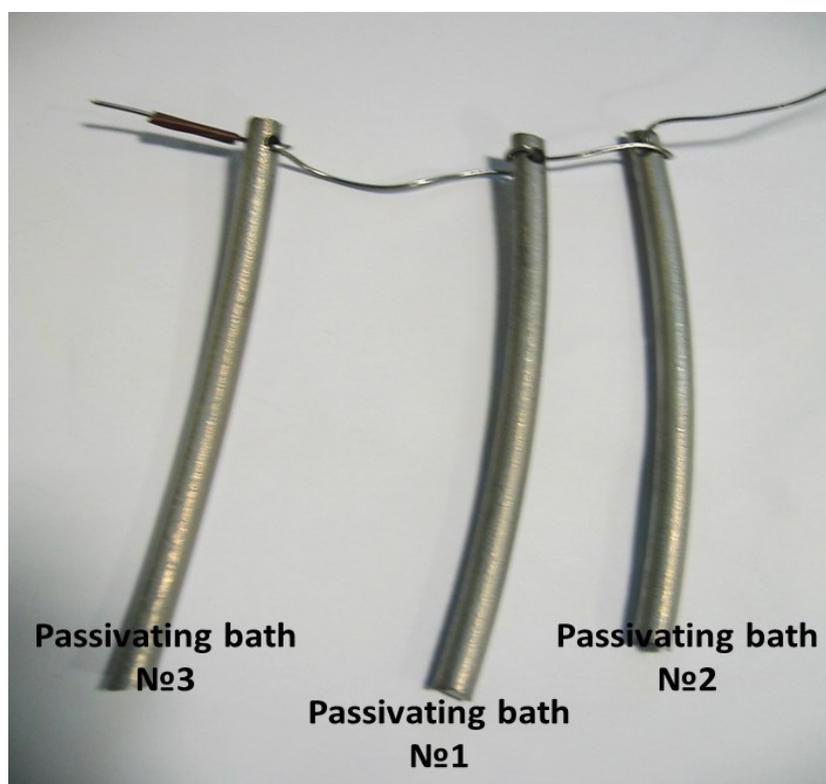


Figure 7.1: Samples passivated in different solutions.

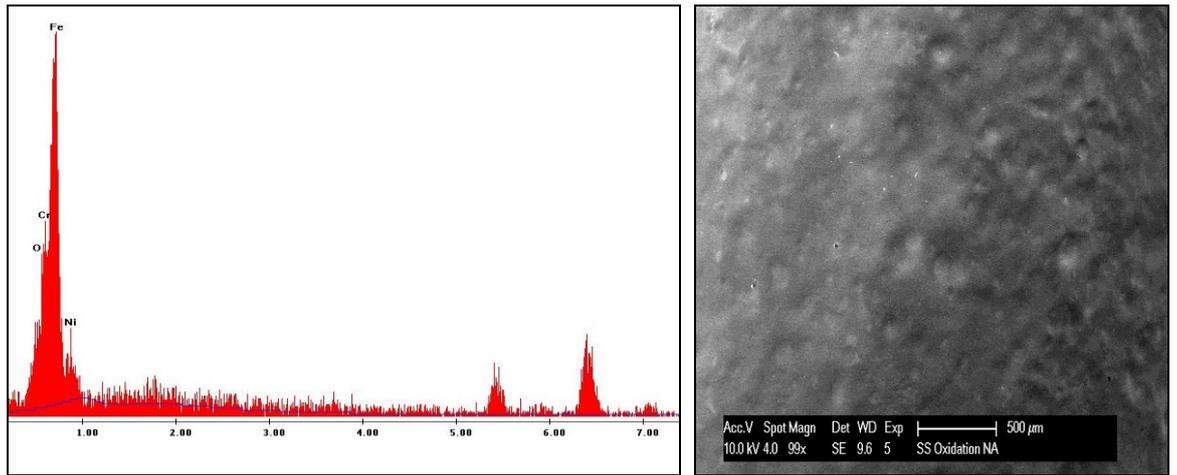


Figure 7.2: EDX spectrum and SEM micrograph of the sample without passivation.

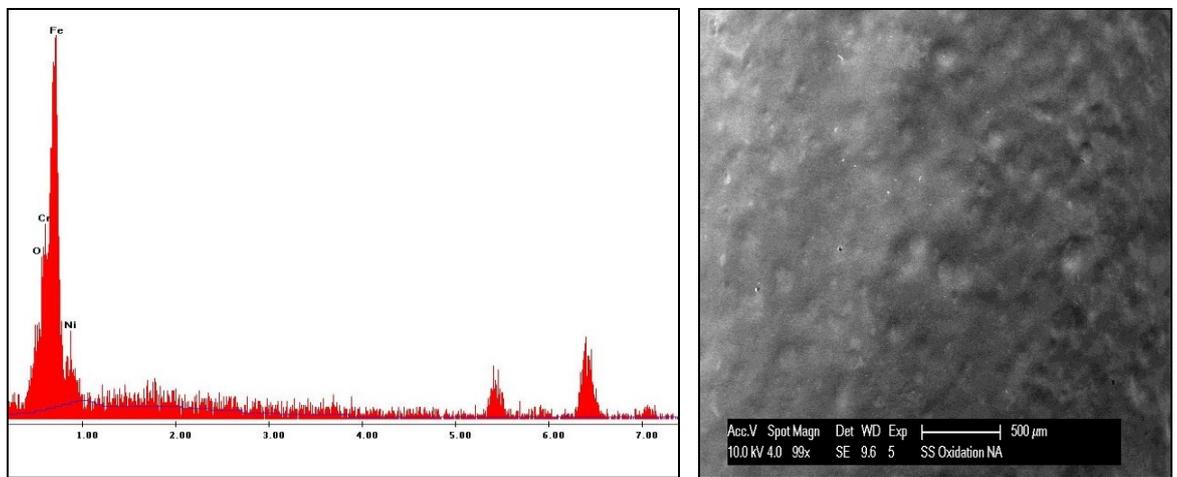


Figure 7.3: EDX spectrum and SEM micrograph of the sample passivated in solution-1.

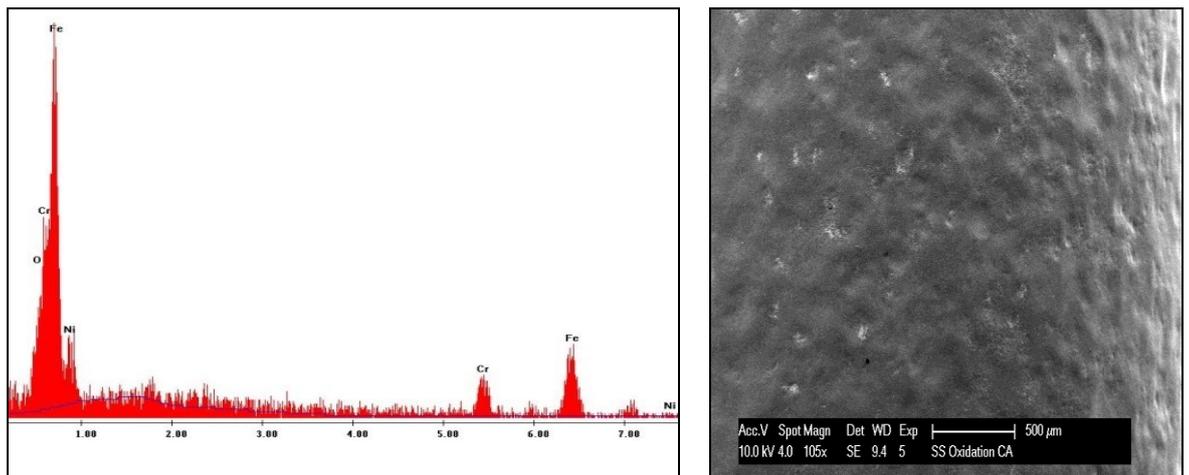


Figure 7.4: EDX spectrum and SEM micrograph of the sample passivated in solution-2.

The EDX analysis did not give the possibility to identify the presence of additional oxygen layer; we decided to carry out the atmospheric corrosion test. We

have polished steel samples and passivated in industrial solution and solution -2, solution -3.



Figure 7.5: Samples passivated and left outside for 30 days.

The interesting observation is that even the non-passivated sample has the same characteristics of the surface and resistance to atmospheric corrosion after more than one month of testing outdoors. The possible explanation is that during the electrochemical process the following chemical reactions take place at the anode:

- 1) $\text{Me} \rightarrow \text{Me}^{n+} + n\text{e}^-$: Dissolution of metal ions in solution ($\text{M} = \text{Fe}, \text{Ni}, \text{Cr}$).
- 2) $\text{Me} + 2\text{OH}^- \rightarrow \text{Me}_x\text{O}_y + \text{H}_2\text{O} + n\text{e}^-$: Formation of the passivating layer.
- 3) $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$: Evolution of oxygen.

We decided to carry out faster corrosion tests with anodic polarization in 0,5M H_2SO_4 solution by applying an increasing voltage and monitoring the current. The minimum voltage at which the current starts to rise up is the potential at which the passivating layer is broken. For this test, we prepared samples passivated at different conditions, temperature of solution and time of passivation (see table 7.1).

Table 7.1: Result after different passivation and obtained potential.

Solution for passivation	ΔE (V)
Solution-1 (20 %; 30 min; 20 °C)	4,3
Solution-3 (20 %;30 min; 20 °C)	4,0
Not passivated	3,8
Solution-2 (5 %;30 min; 20 °C)	3,6
Solution-2 (5 %; 30 min; 65 °C)	3,4
Solution-2 (5 %; 5 min; 65 °C)	3,3
Solution-2 (15 %; 30 min; 20 °C)	3,3
Solution-3 (20 %; 20 min; 65 °C)	3,1
Solution-2 (15 %; 30 min; 65 °C)	3,1
Solution-2 (5 %; 5 min; 65 °C)	3,1
Solution-2 (5 %; 5 min; 20 °C)	3,1

The table shows that the solution-1 is actually the best pickling agent for stainless steel treated with ionic liquids, but the solution-3 at ambient temperature can give good results, too. The sample not passivated seem has thick protective layer. In general, this test shows similar values of potential probably, as we mentioned before, the oxide layer was growing during the electropolishing and additional passivation does not influence the thickness of oxide. To compare the passivation we have carried out tests without electropolishing in ionic liquid. For cleaning samples, we have used standard etching solution, and passivated samples after descaling with our alternative solutions. We measured the potential of anodic polarization. In total, to obtain an adequate statistic data, we pickled 40 samples: 10 samples were treated without passivation, 10 samples had passivation in solution-1, 10 were passivated in solution-3 (20%; 30 min), while the last 10 were passivated in solution-2 (5%; 30 min). From the following table 7.2 we can see that breaking down potential of the passivating layer formed after pickling with standard solution is lower than obtained after electrochemical polishing in ionic liquid. All solutions

show similar breaking point values, but solution-1 is however the solution with the higher breaking point. Figures 7.6 - 7.9, show the graphs of steel anodic polarization and values of breaking points.

Table 7.2: The average values of breakdown potential for different passivation.

Solution for passivation	ΔE (V)
Solution-1	$3,4 \pm 0,5$
Not passivated	$3,3 \pm 0,3$
Solution-3 (20 %; 30 min; 20 °C)	$3,1 \pm 0,2$
Solution-2 (5 %; 30 min; 20 °C)	$3,0 \pm 0,1$

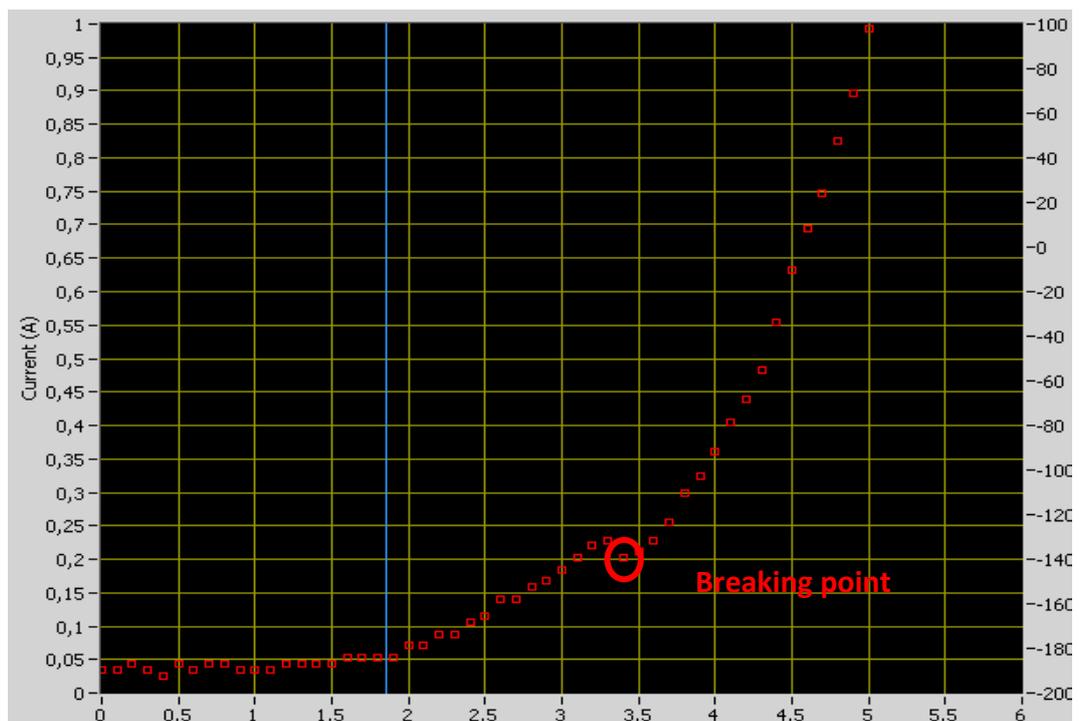


Figure 7.6: Graph of the anodic polarization for non-passivated sample.

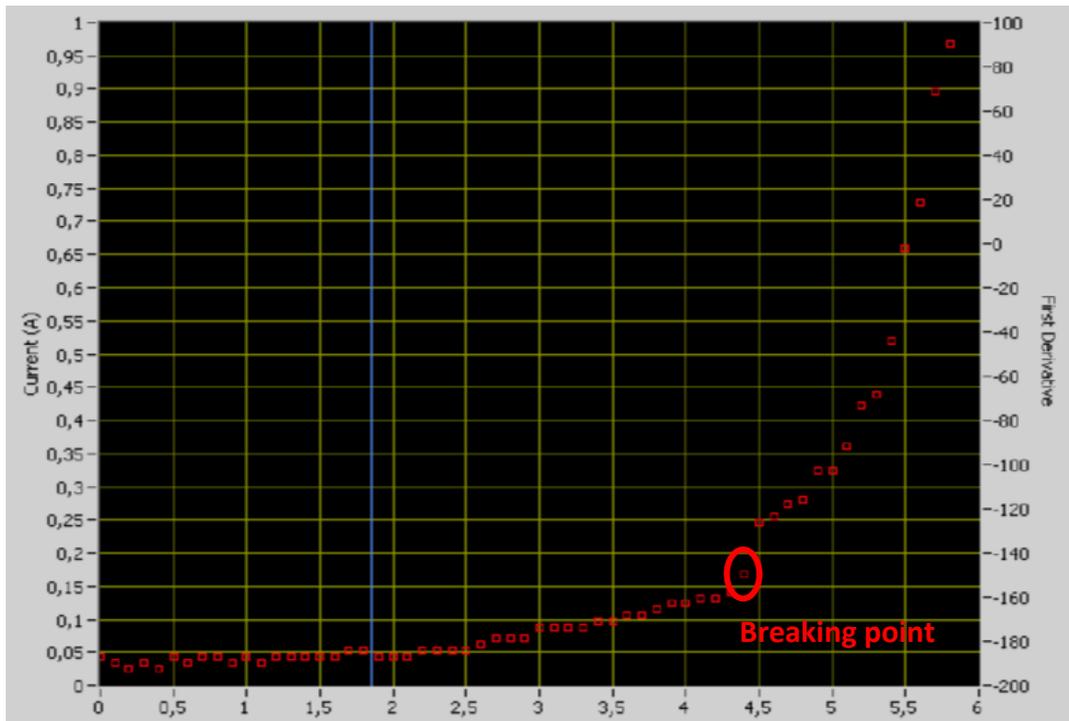


Figure 7.7: Graph of the anodic polarization for the sample passivated in solution-1.

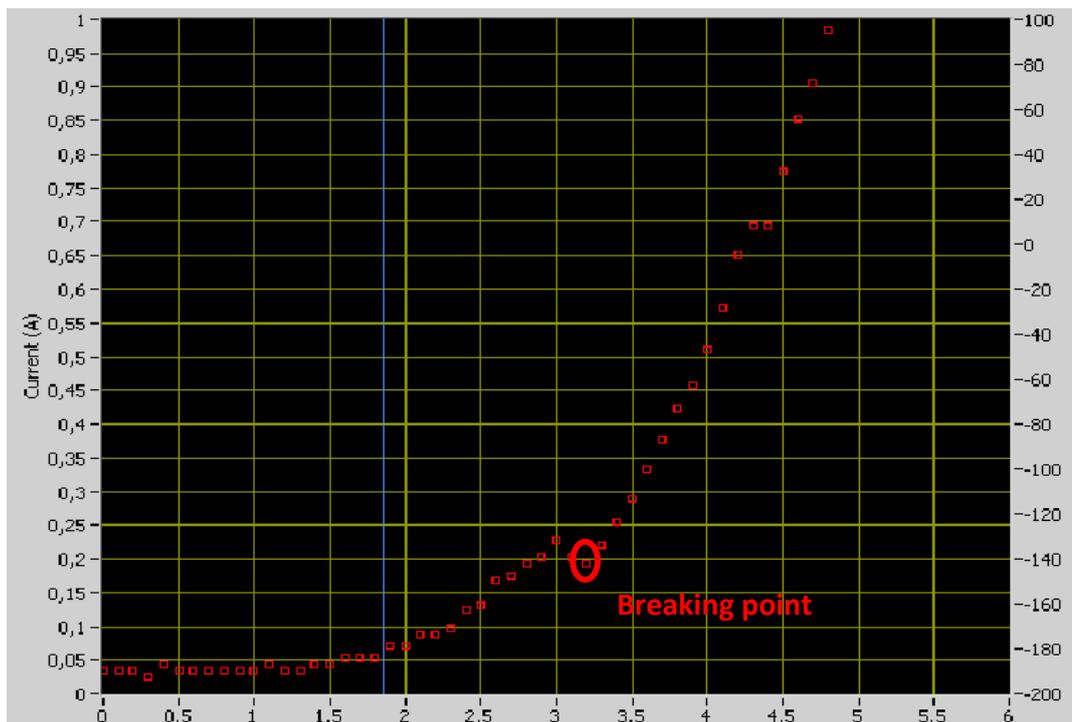


Figure 7.8: Graph of the anodic polarization for the sample passivated in solution-3.

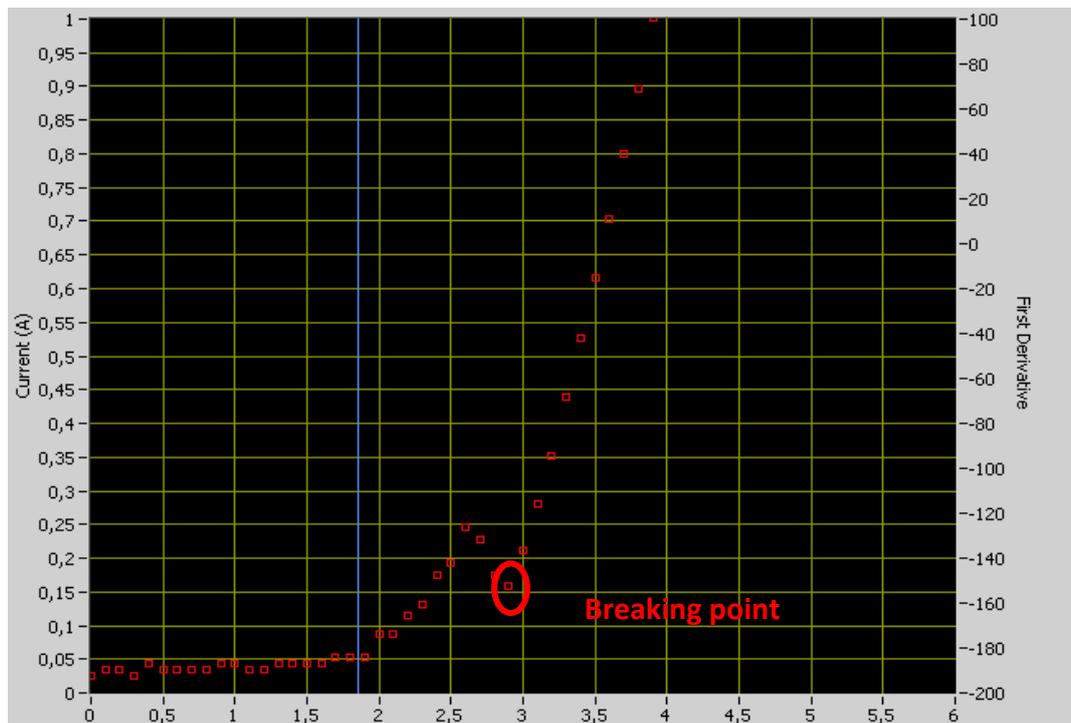


Figure 7.9: Graph of the anodic polarization for the sample passivated in solution-2.

Conclusion: the test results are ambiguous; we can say that the passivation in alternative solutions gives the same result as the standard solution. The samples polished but not passivated show a high breakingdown potential. This is due to the formation of an oxide layer during the electropolishing. To be more confident in the results we carried out other corrosion tests.

7.1. Corrosion test in seawater.

To study the corrosion behaviour of passive layers we decided also to carry out the tests in seawater. A popular and cheap technique corresponds to salt spray test, but it does not required the use of special testing chamber. We prepared solution 30g/l of sea salt, during the test solution was kept on a stable temperature of 50°C. We have supplied the air into the solution by customized tube (see figure 7.11), in order to saturate it with oxygen.

We have provided two different tests. For the first test, we have polished two samples in ionic liquid solution: only one sample was passivated in the standard industrial solution. For the second test, we did standard chemical etching and passivate samples with our solutions.

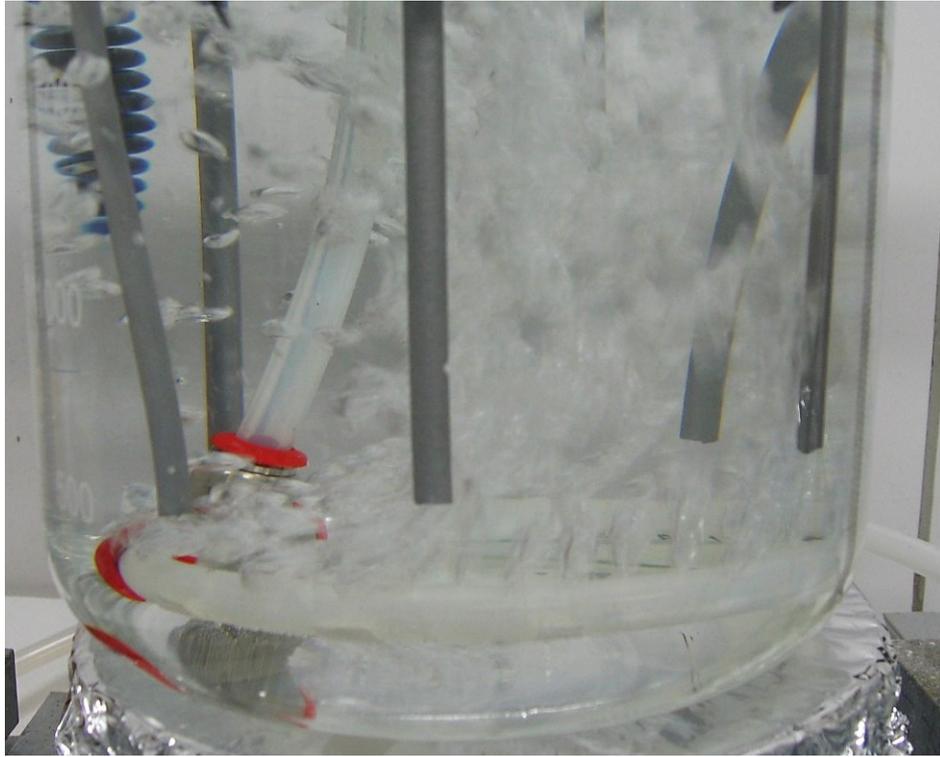
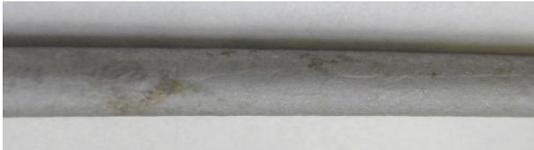


Figure 7.10: The seawater test.

In table 7.3, we can see the results after 40 hours inside the seawater. We have stopped after this time, because the steel started to corrode. We visually determined the degree of corrosion and we can say that all the samples corroded equally.

Table 7.3: Result after 40 hours in seawater.

Description	Samples
1. Polished in IL and without passivation	
2. Polished in IL and passivated in standard industrial solution	
3. Chemical etched in standard industrial solution and passivated in solution-1	
4. Chemical etched in standard industrial solution and passivated in solution-2	
5. Chemical etched in standard industrial solution and passivated in solution-3	

7.2. Test on atmospheric corrosion for the wire rods.

After the tests with small samples, we decided to carry out corrosion tests with wire rods that simulate the real conditions. As we know, the steel wire rods after fabrication can be stored outdoor so that it is important to provide the optimal corrosion resistance. We have prepared samples pickled in industrial standard solution with following passivation in our alternative solutions and samples electropolished in ionic liquid with passivation in the standard industrial solution and without passivation. We left one of the samples polished in ionic liquid without passivation in order to understand if we really needed additional passivation. The previous test has showed that it grows the oxide layer during the polishing. After passivation, we left sample outside for 5 weeks (see figure 7.12).

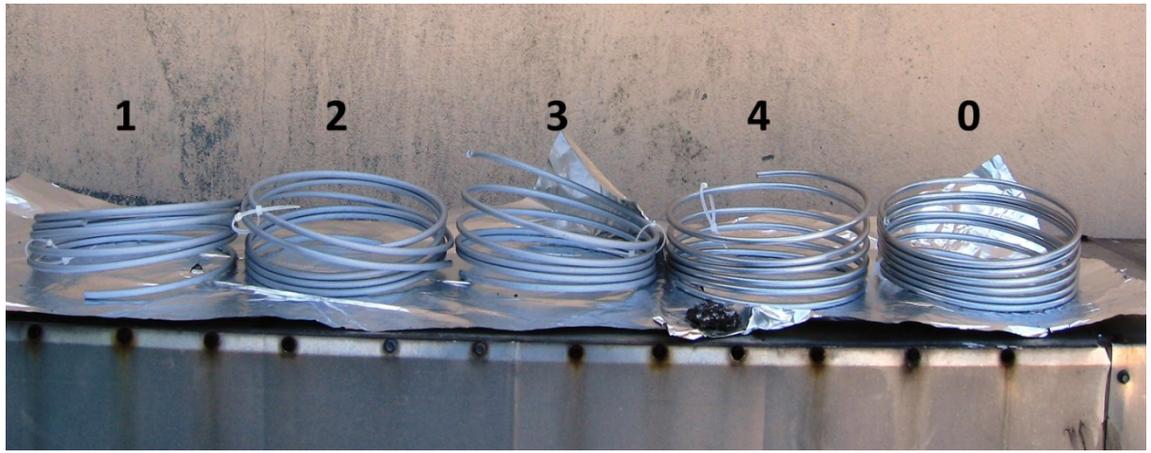


Figure 7.11: Atmospheric corrosion test.

We can see in table 7.4 the result of the atmospheric corrosion test. As it can be noticed, the samples that have been passivated in alternative solutions after tests on atmospheric corrosion behave no worse than the samples passivated in the standard solution. Only the no passivated samples have more pronounced corrosion traces. It means that even after electropolishing, it is better to add operation of passivation.

Table 7.4: Result after 5 weeks in outdoors environment.

Description	Samples
1. Chemical treated in standard solution and passivated in 5% solution-2	
2. Chemical treated in standard solution and passivated in 20% solution-3	
3. Chemical treated and passivated in standard solutions	
4. Electropolished in IL, passivated in 10 % solution-1	
0. Electropolished in IL, without passivation	

Conclusions: we have suggested two alternative solutions for the passivation of stainless steel. For analysing the quality of this passivation, we have carried out the corrosion tests: atmospheric corrosion test, polarization curves, seawater corrosion test. We have compared the results with samples passivated in a traditional solution. As we can see, the alternative solutions gave the same velocity of the corrosion in all tests. The most interesting evidence is that samples polished in ionic liquids and tested without passivation, also have showed good results. For further work, we decided to skip the procedure of passivation after electropolishing.

8. Aqueous solution for descaling stainless steel.

8.1. Study of the possibility of electropolishing in aqueous electrolytes.

As we mentioned in previous paragraphs, the acid cleaning is used more often for descaling steels. Acids have the ability to dissolve oxides, which are usually insoluble in other solutions. Straight mineral acids, such as hydrochloric, sulphuric, and nitric acid, are used for most acid cleaning. However, organic acids occupy a prominent place in acid cleaning because of their chelating capability [22]. Organic acid chelating agent are functionally attractive because of their ability to serve as acids, buffers, and sequestrants. Derusting and descaling formulations can be constructed from them to function at any pH from strong acidic to high levels of free caustic. The acids form stable water-soluble chelates with metal ions and prevent the formation of insoluble oxides and hydroxides during the cleaning and rinsing.

Organic acid cleaning is frequently used to remove rust and mill scale from newly fabricated stainless steel destined for the food, chemicals, and other industries where purity is important. Surfaces are not prone to chlorides stress cracking and hydrogen or caustic embrittlement.

Fabricators also use solutions of dibasic ammonium citrate to remove embedded iron and scale from the surface of stainless steel. The low corrosion rate of ammonium citrate solutions and their retention of iron dissolving power at pH up to 7,0 make them attractive pickling media for general metal finishing application. Operating conditions for the efficient removal of the iron contamination include a temperature of 80 °C, wetting agent concentration of 0,1%, dibasic ammonium citrate concentration of 2-5%. [30]

8.1.1. Chemical etching of stainless steel.

As we mentioned in the previous section, the solution of ammonium citrate is widely used for descaling. We have carried out tests in order to check if it cleans our kind of scale. In the initial solution, for etching, we have added 5% ammonium citrate, but since after 20 minutes nothing has changed, we have doubled the concentration and continued processing for 4 hours (see table 8.1). As wetting

agent, we have used sodium dodecyl sulphate (SDS) and ethylenediaminetetraacetic acid (EDTA).

The result is poor: increasing the concentration of components did not show any improvement in chemical etching. In conclusion, this recipe is good for light scale or residual iron ions, but it cannot remove hard oxide layer.

Table 8.1: The result of etching in ammonium citrate based solutions.

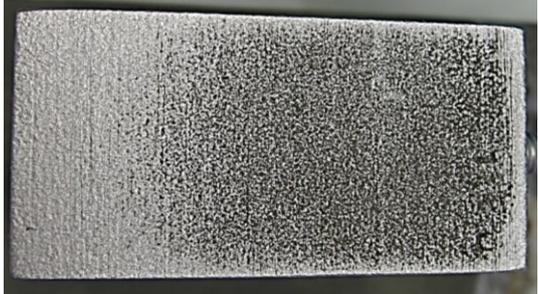
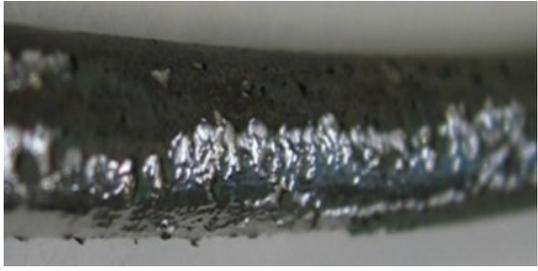
Description	Samples
1. Ammonium Citrate -10%, SDS, 4 hours, 80°C	
2. Ammonium Citrate-20%, SDS, 4 hours; 80°C	
3. Ammonium Citrate-5%, EDTA, 4 hours, 80°C	
4. Ammonium Citrate-10%, EDTA, 2,5 hours, 80°C	

8.1.2. Electrolytic cleaning in organic acids.

The chemical cleaning based on organic acid solutions (solution “C”) did not show significant results and we decided to intensify action of solution by electrochemical process. The electrolytic pickling can remove scale twice as fast. We have prepared solution “C” contained different concentrations and studied the influence of additive “A”. The result is presented in table 8.2. We have studied the electrochemical finishing in solution “C” on two types of stainless steel, sandblasted bar and wire rod. As we can see, the result is not satisfactory, since the electropolishing is not uniform. The additive “A” is working better in

electrolytically cleaning. Increasing the concentration did not show the good quality of electrochemical polishing. The surface is dissolved partially and created the islands of the scale. Meanwhile, the clean metal surface is shiny.

Table 8.2: Result after electropolishing in solution “C”.

Description	Samples
<p>1. Solution “C” 15 %; 30 min , 2A↑5 A, 40°C</p>	
<p>2. Solution “C” 15 %, additive “A” 1%; 60 min, 6 A, 25°C</p>	
<p>3. Solution “C” 60 %; 50 min (20 min - 2A; 30 min - 5 A), 25°C</p>	

8.2. Pulse reverse finishing.

The anodic pulse is set to increase mass transport and control current distribution. The cathodic pulse is set to depassivate the surface. While the pulse/pulse reverse, waveform contains off-time and cathodic pulse, the material removal rate during pulse/pulse reverse electropolishing is generally higher than, or equal to, that obtained under DC conditions. This is because the instantaneous anodic pulse current is much higher than steady state current obtained under DC conditions and compensates for off-times and cathodic periods, such that the

average material removal rate is equivalent to, or greater than, DC electropolishing (electropolishing and through mask electro etching). The final consideration for developing a pulse/pulse reverse electropolishing waveform is for the case of passive materials. For these materials, anodic only pulses lead to a rougher surface due to the non-uniform breakthrough of the passive film. In order to depassivate the surface, we intersperse cathodic impulses within the anodic pulses in place of, or in conjunction with, the off-times. In general, we assume the cathodic pulse remove the oxide film and restore the virgin metal surface as the reverse of reaction. [31]

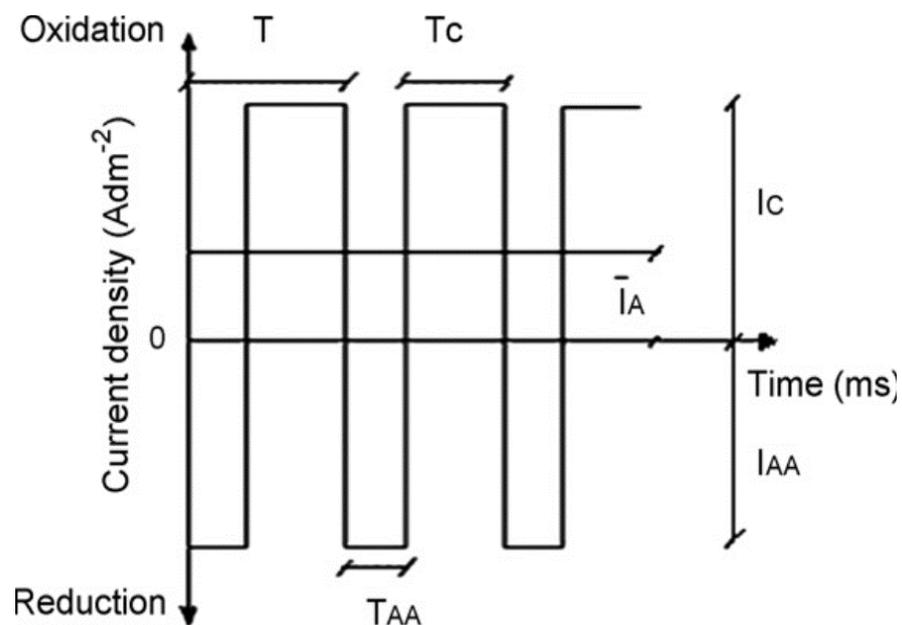


Figure 8.1: A typical pulse reverse waveform.

On figure 8.1 it is shown the typical pulse reverse waveform where T_{AA} is the anodic time, T_C is the cathodic time, I_{AA} is the anodic current density, I_C is the cathodic current density, \bar{I}_A is the average current density, and T is the cycle time. [32]

8.2.1. Pulse reverse electropolishing in aqueous solutions.

For these strongly passivating metals (stainless steel 300 series, titanium and nickel and their alloys among other materials), continued electropolishing leads to a roughened surface similar to pitting corrosion. [33] Consequently, to the treatment solutions, hydrofluoric acid is added to depassivate the metal surface. As we described before with pulse reverse technique, we can substitute the

hydrofluoric acid and create ecological electrolyte. For the test, we have chosen the Solution “C”, inorganic salt solution and our alternative recipe, based on inorganic acid (Solution “S”). As power supply, we use Pulse Reverse rectifier type “Power Pulse pe 861UA-40-166-240-s”. The software gives the possibility to individual pulse pattern design and online monitoring shows the activity, set value curve; oscilloscope function (actual value curve). On the figure, it is shown the software of the settings and the figure 8.3 shows the actual values of current and voltage. We have worked in voltage/current control mode and set the same parameters for all tests:

- Voltage = +7/-3 V (anodic/cathodic);
- Current = +10/-10 A (anodic/cathodic);
- Pulse time = 13/3 ms (anodic/cathodic).

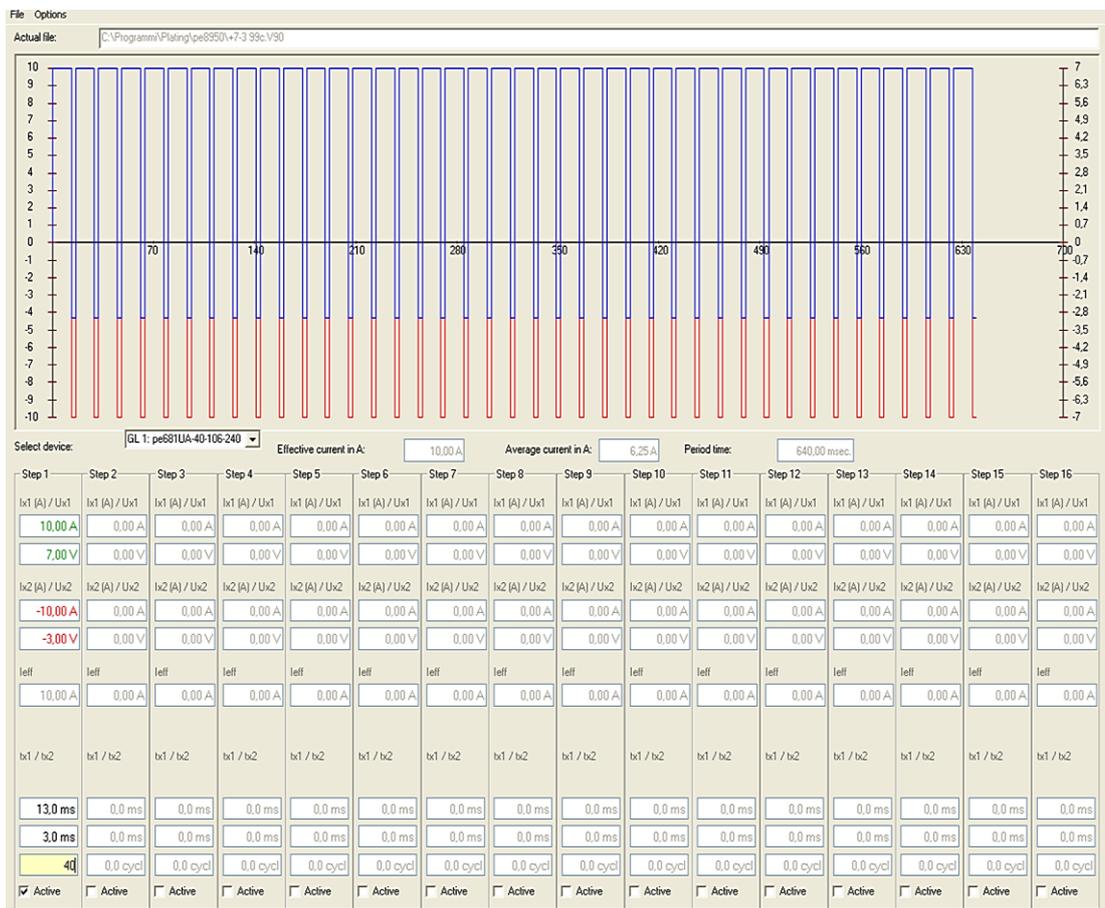


Figure 8.2: Pulse reverse electropolishing settings.

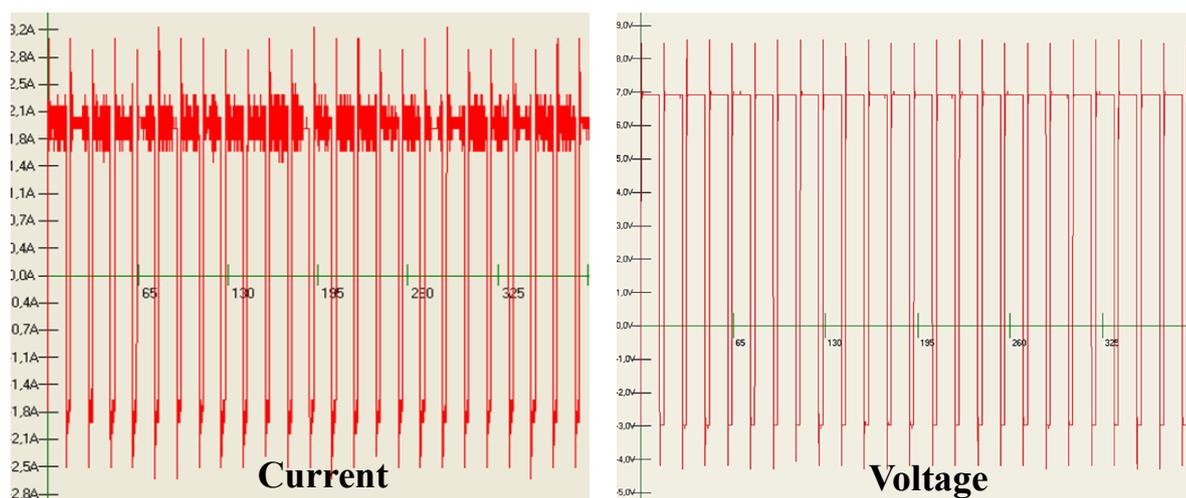
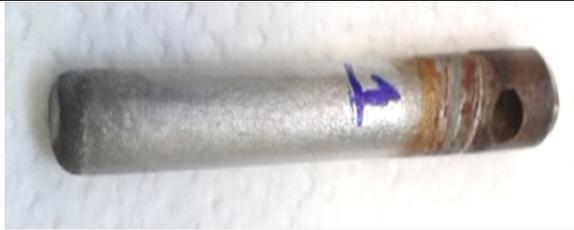


Figure 8.3: Actual current and voltage waveform of pulse reverse electropolishing.

In table 8.3, the results of pulse reverse electropolishing in different aqueous solutions: solution, contained Cl^- ions; organic acid solution, Solution “C”; inorganic acid solution, Solution “S”; are presented. We tested also pulse reverse technique in ionic liquid solution, but did not notice any changes.

Table 8.3: Result of pulse reverse electropolishing in aqueous solutions.

Description	Samples
1. Aqueous solution, contained Cl^- ions; 50 °C; 45 min.	
2. Solution “C”; 75 °C; 90 min.	
3. Solution “S”; 45 °C; 45 min.	

As we can see, the solution containing chlorides does not polish enough the steel surface. In addition, the presence of chlorides leads to steel corrosion, due to

the destruction of chloride ions to the passive layer on the metal. The chloride ions convert the passive layer of iron oxide in a soluble ferric chloride. Thus, the idea to use electrolyte contained chloride ions is not appropriate. The second solution is based on organic acid. The third electrolyte base on inorganic acid and has shown the best result. Therefore, we have stopped out attention on these two solutions.

8.3. Alternative solution for descaling stainless steel.

8.3.1. Organic acid solution for electropolishing.

We have already performed chemical etching in organic acid solution and the result was poor. The advantage of Solution “C” is low corrosion rate and safe handling properties. This makes them good candidates for replacing hazardous acids. In our case the thickness of scale is enough thick and need additional impact. We have combined pulse reverse finishing with Solution “C”. In table 8.4 are presented samples treated in mix of Solution “C” with additives, constant concentration at different temperatures. The value of voltage in all cases is the same (see paragraph 8.2.1.). As we can see, the time of treatment and cleaning ability is depending on temperature of electrolyte.

We have performed electropolishing of rod coil in Solution “C” with the pulse reverse technique. On figure 8.4 the result after electropolishing is presented: we have used the system for partially immersing, and C-shaped steel cathode. As we can see, the finishing is satin and the surface is clean. During the pulse reverse electropolishing, the solution changes the pH, from acidic to neutral. It means that during the process we need to control pH and correct it. In addition, the working temperature is high (70-80 °C), and the solution evaporates: for this reason we need to control the level of electrolyte.

Table 8.4: Samples after pulse reverse electropolishing in Solution "C".

№	Method	Temperature, °C	Time, min	Samples
1	Pulse reverse finishing	23	90	
2	Pulse reverse finishing	70	60	
3	Pulse reverse finishing	80	60	



Figure 8.4: The wire rod A - before and B - after the pulse reverse finishing in solution "C".

In conclusion, pulse reverse finishing in the solution "C" can substitute the traditional electropolishing and it is deserving of further study.

8.3.2. Inorganic acid solution for electropolishing.

The alternative solutions based on inorganic acid, Solution “S”, were also studied during this research. In the literature, a great number of different recipes for the treatment of steel are presented. In general, they are based on inorganic acids, more aggressive for thick and dense scale and less aggressive to remove lime. We decided to take non-hazardous solutions for chemical etching and combine with electrochemical finishing in order intensifying the acid ability to remove the scale. We have realized the tests for the electropolishing of steel in Solution”S”, with pulse reverse technique, and usual DC-mode finishing. In table, 8.5 samples after the treatment are presented: we can observe the tendency of increasing the time with lowering the temperature.

Table 8.5: Samples after electropolishing in Solution “S”.

№	Method	Temperature, °C	Time, min	Sample
1	Pulse reverse finishing	60	30	
2	Pulse reverse finishing	50	46	
3	Pulse reverse finishing	40	52	
4	DC finishing	70	20	
5	DC finishing	22	45	

As we can see, the standard electropolishing at ambient temperature gives the same good result as other tests. The pulse reverse finishing in this case did not show significant difference.

8.4. Study of the parameters for electropolishing stainless steel in inorganic acid solution.

From the previous paragraph, we can see that the Solution “S” works equally with pulse reverse power supply and DC – power supply. However, with DC current, the processing time is shorter. We have decided to carry out tests in order to find proper conditions for electropolishing in a new solution. In table 8.6, it is presented the study of the current density influence on the electropolishing parameters.

Table 8.6: Influence of the current density on the electropolishing of stainless steel.

Current density, A/cm ²	Current, A	Voltage, V	Temp-re, °C	Time , min
0,1	3,9	2,3	40 (initial)	30
0,2	7,0	4,0	40	26
0,3	10,6	7,1	42	20
0,4	13,5	8,0	42	18
0,5	18,8	10,9	43	15
0,6	19,8	11,5	40 ↑ 47	12
0,7	26,4	13,2	40 ↑ 50	12
0,8	30,4	14,2	40 ↑ 53,6	10
0,9	33,1	16,1	40 ↑ 52,8	8
1,0	34,5	16,8	40 ↑ 52	8

As we can see, the increasing of the current density (or current) leads to decreasing of the process time. However, during the electropolishing, the high current is the cause of high gas evolution.

We have also studied the influence of ultrasound and different concentration of the acid on the electropolishing of stainless steel. On figure 8.5, the electropolishing of stainless steel inside ultrasound bath is shown.



Figure 8.5: Electropolishing of stainless steel with ultrasound.

As we can see, in table 8.7 the ultrasound as additional treatment did not accelerate process or improve the quality of surface. The increasing of the concentration and temperature has shown the perfect cleaning and smooth, satin surface. Of course, high temperature and concentration mean higher costs of the process. In further investigations, we have decided to study these parameters on coils and choose the optimal parameters for industrial polishing.

Table 8.7: The influence of the concentration and additional treatment.

Current, A	Voltage, V	Temp, °C	Time, min	Conc., g/l	Notes	Samples
5,1	15,0	18↑31	40	20	Ultrasound bath	
6,1	15,0	18↑35	40	20	Ultrasound bath	
8,0	15,0	50	22	20	Ultrasound bath	
7,6	15,0	45	20	20	Ultrasound bath	
6,2↑10	15,0	17↑72	30	30	Standard EP	
7,0	15,0	18	20	50	Standard EP	
7,6	15,0	50	20	20	Standard EP	
10	15,0	17↑55	17	100	Standard EP	
10,2	15,0	60	12	100	Standard EP	

8.5. Electropolishing of stainless steel coils in Solution “S”.

We have accomplished the electropolishing of wire rod coil, partially immersed inside the Solution “S”, concentration 20g/l at ambient temperature. On figure 8.6, we can see the surface is covered with bubbles of gas that evaluated during the electrochemical process. The steel wire with single coil was successfully cleaned (see figure 8.7) and we have continued to work with the Solution “S” and carried out electropolishing the wire with n-turns of coil. On figure 8.8 is shown the system for partially immersed electropolishing. The alternative aqueous solution has shown the good result after polishing (see figure 8.9).

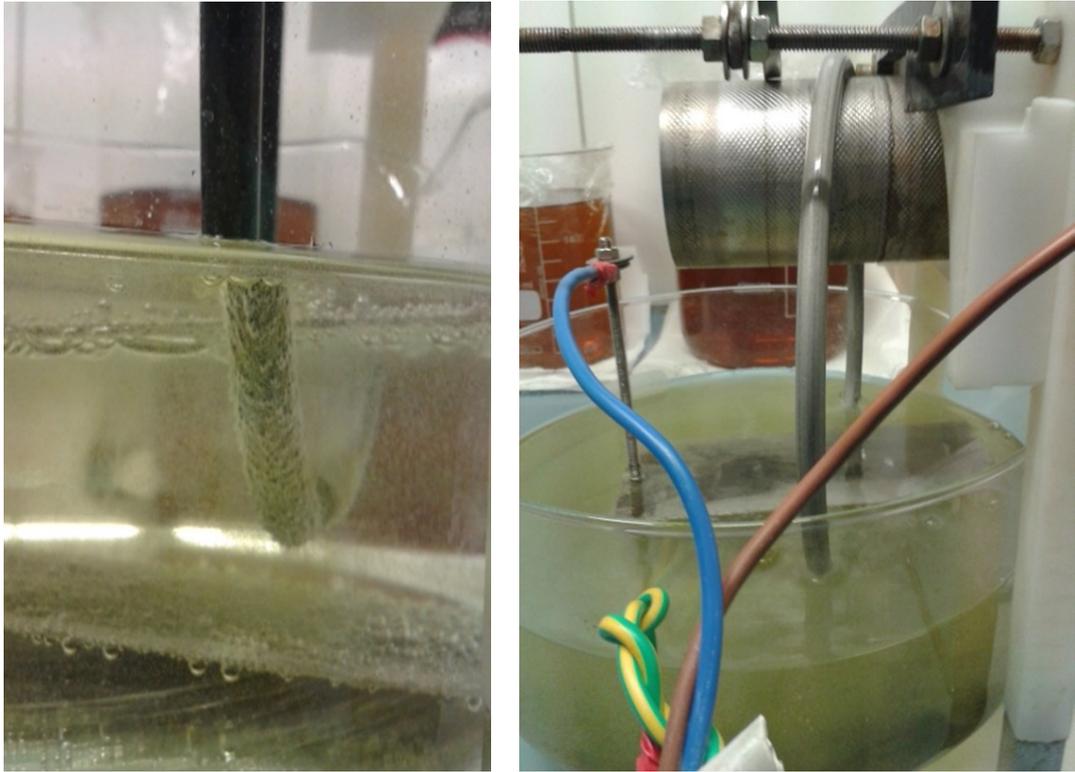


Figure 8.6: Electrolytic descaling of wire rod in Solution “S”.



Figure 8.7: Result of electrolytic descaling in Solution “S”.

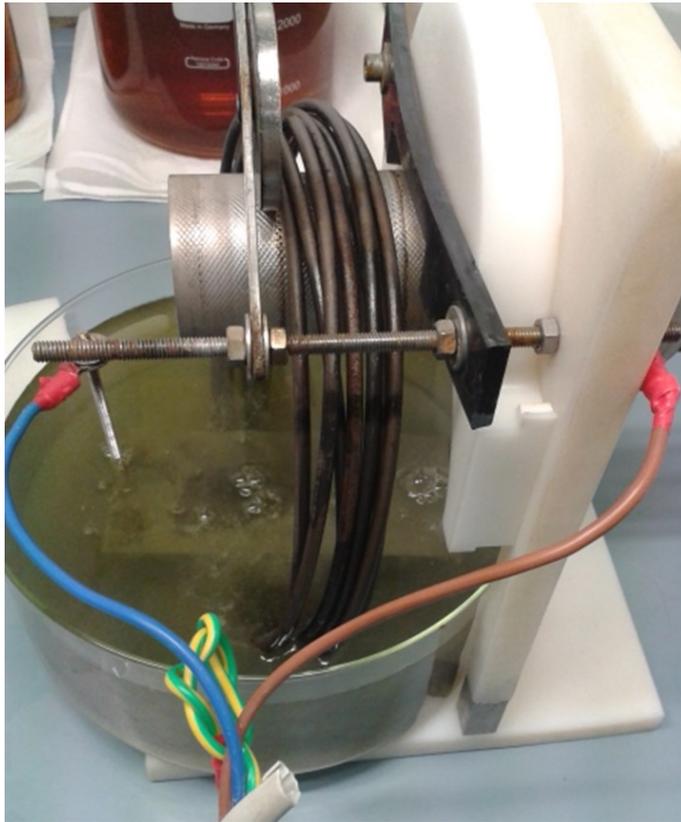


Figure 8.8: System for partially immersing electropolishing.

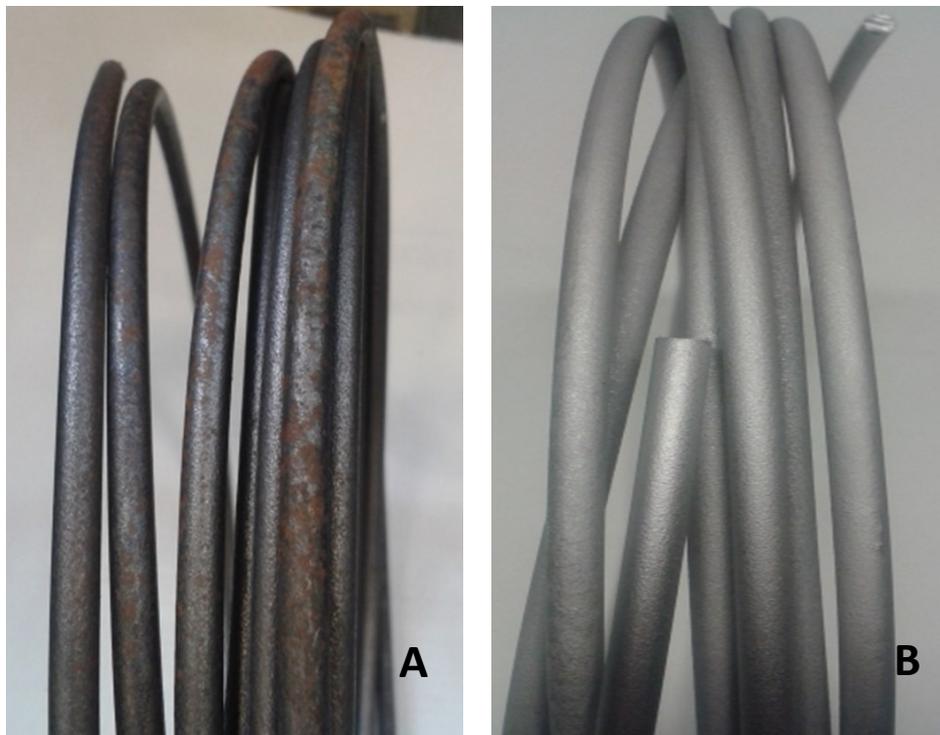


Figure 8.9: Wire rod A - before and B - after the electropolishing in Solution "S".

The result of electropolishing in Solution “S” 20g/l concentration is satisfied. In order to find the optimal parameters we have carried out the test with coils in solution concentration 100g/l. In addition, we have compared the influence of heating (figure 8.10).

Working parameters:

A: Current density – $0,05 \text{ A/cm}^2$; Current – 33,2A; Voltage – 10,5 V; Temperature – 20°C (during the process solution has started to heat by applied current); Time – 110 min.

B: Current density – $0,05 \text{ A/cm}^2$; Current – 30,1A; Voltage – 8,5 V; Temperature – 70°C ; Time – 90 min.

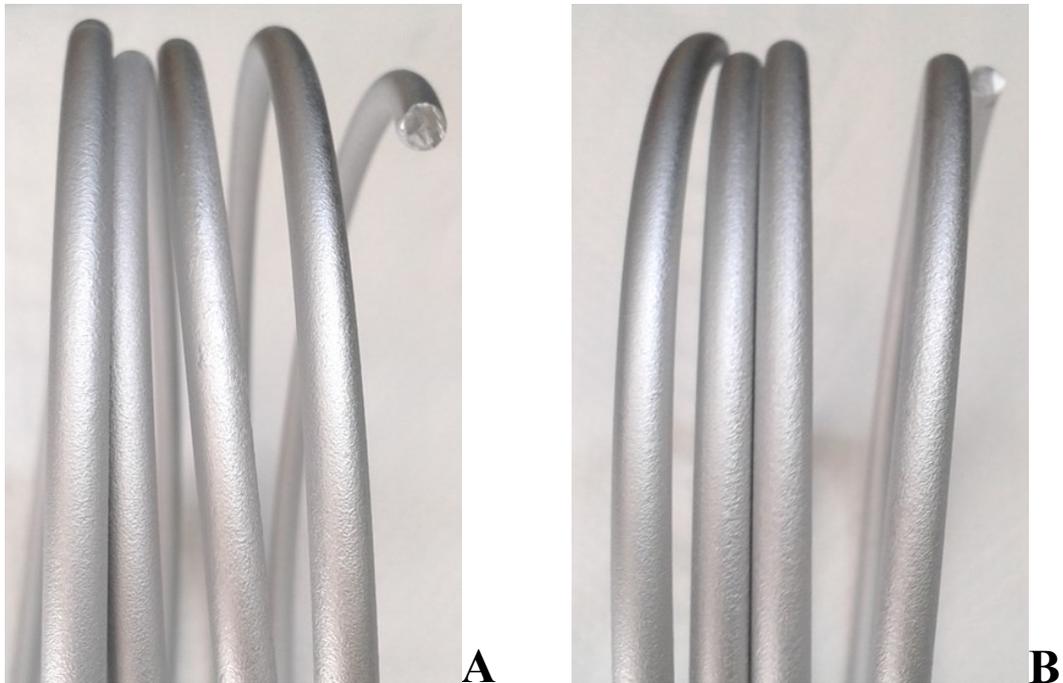


Figure 8.10: The steel coils after electropolishing in 100g/l Solution “S”: A - at ambient temperature, B – at 70°C .

8.5.1. Comparison of the applicability aqueous solutions for treatment stainless steel

We have also tried the aqueous solutions as an alternative treatment for stainless steel. Some of them have shown very good results, and quality of the surface is comparable with industrial etching. In table 8.8, we present brief comparison of aqueous solutions for the treatment. Pulse reverse finishing has

shown the ability to remove scale, but the processing time is longer. The Solution “S” works with DC power supply and pulse reverse power supply. The DC-mode works faster, and we will choose for further construction of electrochemical plant this power supply.

Table 8.8: Comparison of alternative aqueous solutions for treatment stainless steel.

Solution	Observation
Solution “C”	Not suitable, does not clean surface
Solution “C” + additive “A”	Works only pulse reverse finishing, clean and satin surface
Cl ions contained solution	Does not clean enough, not suitable
Solution”S”	Works with DC-mode, pulse reverse finishing; in both cases gives clean and satin surface

8.6. Selecting the best parameters for electropolishing in alternative solution.

The electrochemical process is more costly compare to the chemical etching. We have carried out tests of chemical descaling of steel in 100 g/l solution of the Solution “S”. We have tried at different parameters, and the best result is presented on figure 8.11. We compare the obtained result with electropolished samples, descaled with different concentration. For the chemical treatment, we need high concentration and maximum high temperature. The electropolishing can give us accelerating of the process and uniform clean surface.

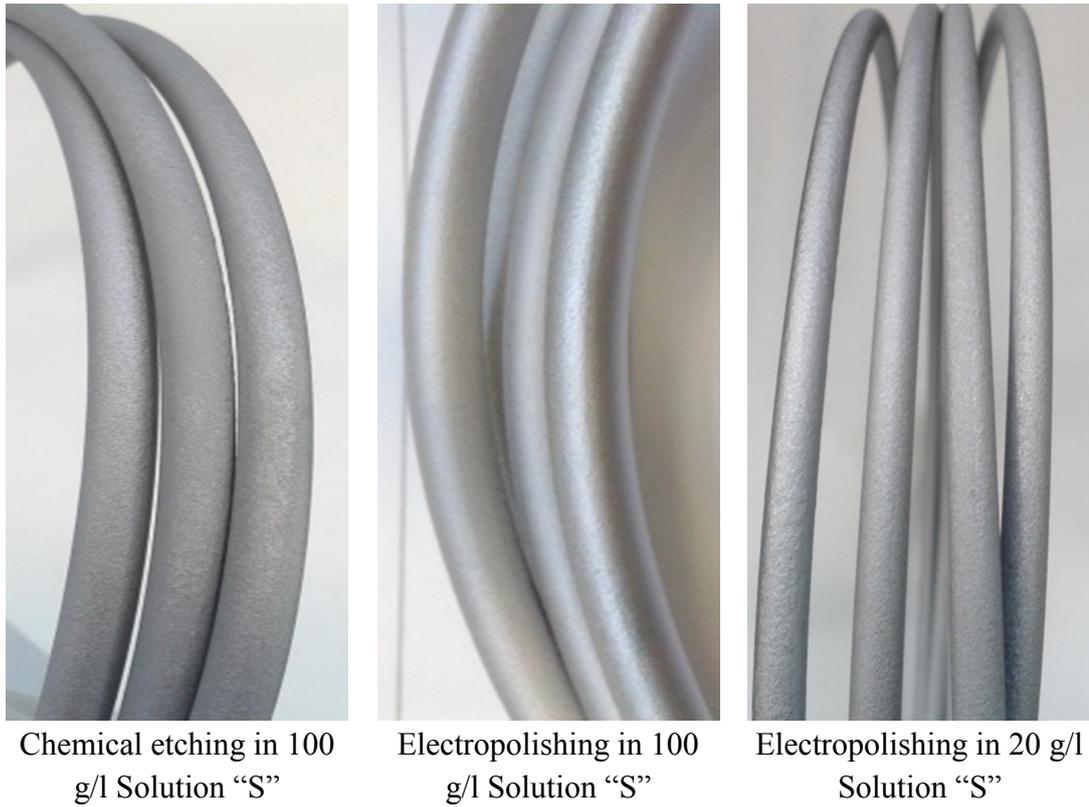


Figure 8.11: Comparison of the different etching.

We have also suggested to reduce the cost of the process by using chemical etching with electropolishing. We have carried out the process in such sequence – main time is chemical etching and only at the end apply current for short period.

Process conditions:

Chemical etching - 90 min;

EP – 10 min (at Current – 36,8 A; and Voltage – 9,5 V); Temperature – 70°C.



Electropolishing



Chemical etching + EP

Figure 8.12: The comparison of EP full time and chemical etching with additional EP

In conclusion: we have carried on the tests with different concentrations: 20g/l, 30g/l, 50 g/l and 100 g/l Solution “S”. The solution 100 g/l concentration gave the better result than the rest. As we can see, the 100g/l concentration solution is the best in our conditions. Also, we obtained that high temperature is influenced on the appearance of the surface, time of the process and quantity of the dissolved metal. However, we do not need to heat the solution because it heats during the electrochemical process by current. Moreover, to avoid evaporation or high gas evolution we decided to keep working temperature 40°C.

9. The design of technological demonstrator for the wire rods descaling.

The final treatment will be done on the wire rod of AISL304/304L stainless steel (see figure 9.1). The weight of the wire rod is 1253 kg the diameter is 31 mm. For preliminary calculations, we have cut the piece of wire 6 cm length (see figure 9.2) and polished it in Solution “S” at the following working parameters:

Concentration = 100 g/l;

Current density = 0,1 A/cm²;

Voltage = 6,8 V;

Current = 11,3 A;

Total time = 60 min;

Temperature = 40 °C.



Figure 9.1: The wire rod of AISL 304/304L stainless steel before electropolishing.



Figure 9.2: The stainless steel sample A- before and B- after electrochemical polishing

The solution completely cleans stainless steel. We have described in paragraph 6.6 the idea is to imitate a washing machine for industrial treatment of the wire rods. It gives us an advantage in organizing work only in the single tank that is presented in figure 9.3. The tank will be filled and emptied with the electrolyte or water by pumps. The wire rod will be completely immersed in the solution. The main bath is connected to the external tanks for recirculation of the electrolyte and water for rinsing. During the process, the bath will be linked to the aspiration system. On figure 9.4, we can see the schematic view of the electrochemical plant for descaling the wire rods.

The process step will be the following:

1. Insert the wire rod inside the process tank by the crane;
2. Shut down and start up the aspiration;
3. Fill the tank with the electrolyte;
4. Check the connection to the power supply;
5. Set working parameters and start the process of electropolishing;
6. At the end of the electropolishing process, the electrolyte is drained from the working tank to the external container;
7. Rinse the wire rod with water, pumped inside working tank;

8. Pump out the wastewater;
9. Fill the tank with the passivating solution (if it is needed);
10. Remove the passivating solution and rinse the wire rod with water (if it is needed);
11. Remove the wastewater;
12. Shut down of the aspirator and displace the wire rod outside from the process tank;
13. Remove the clean wire rod and dry;
14. Check the quality of descaling and if it is needed repeat the procedure.



Figure 9.3: The working bath, made of stainless steel.

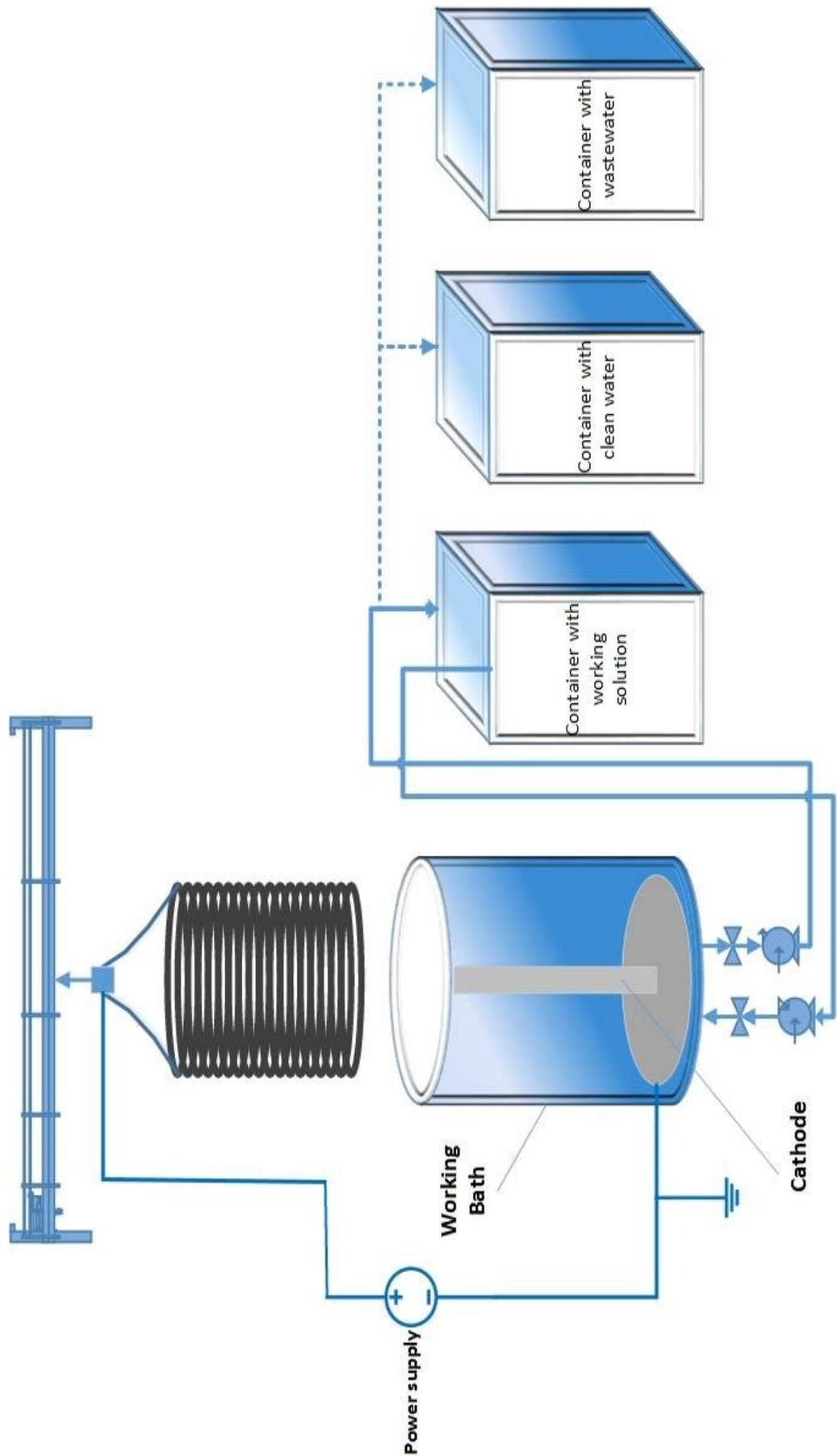


Figure 9.4: The Schematic view of electrochemical plant for descaling wire rods.

Conclusions

This work describes surface treatments applied to the operation of removing the scale:

- Removing the scale using high-pressure water rinsing;
- The “dry ice” blasting;
- Electropolishing with ionic liquids;
- Electropolishing in aqueous solutions;
- Chemical etching.

The water at high pressure (300 bar) can be an effective treatment for pre-finishing when used with the sandblasting only. The treatment is very quick because it is possible to get a good finish in just 2 minutes. However, apart from the shortest execution time of the treatment we do not see the advantage of replacing the current blasting performed by Valbruna.

The jet "dry ice" blasting has not yielded the expected results, since it removes the scale at the points where the thickness of scale presents fractures and are not compact.

The good results in electropolishing with ionic liquids is the considerable success of the research. It was developed a "green recipe", based on Vitamin B4 (Choline Chloride), removes the scale and gives a clean, satiny surface. The ionic liquid solution is comparable with the standard solution of hydrofluoric and nitric acids.

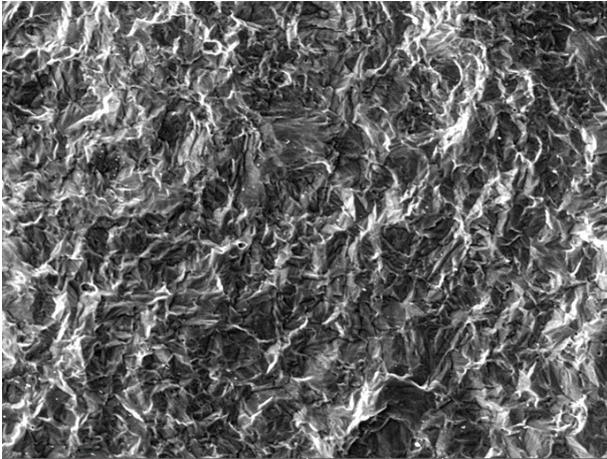
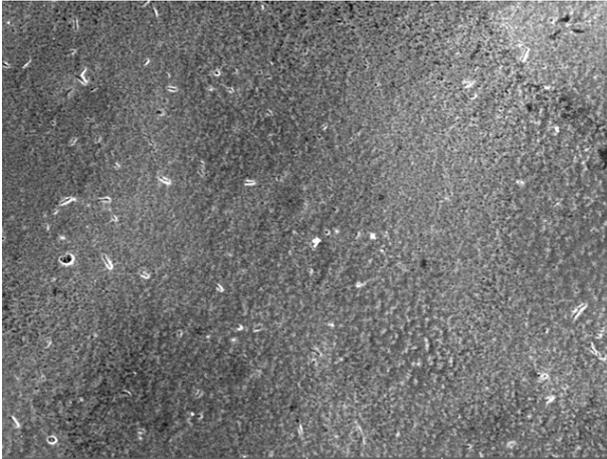
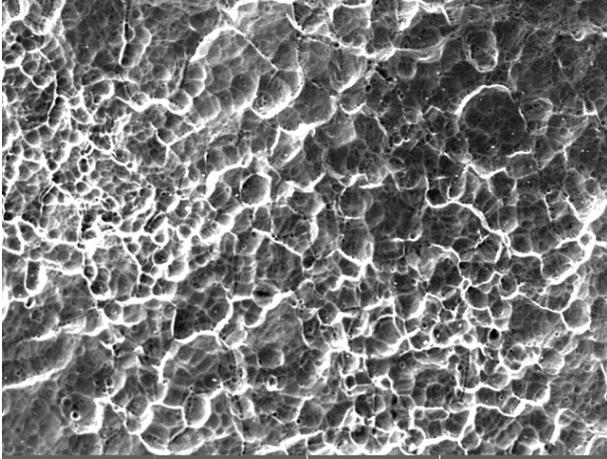
The lifetime of the solution is lower than a standard solution. However, the main advantage is possibility to recycle the solution and not only one time.

The filtered solution works as good as the fresh electrolyte.

The aqueous solutions have also shown good ability to remove the scale. We have found the best result based on Solution “S” contained inorganic acid that is much less dangerous than standard acids for descaling.

In table 9.1, we compare the best solution that we found in this study with the industrial treatment. As we can see, the electropolishing in aqueous solution gives the similar surface appearance to industrial etching.

Table 10.1: Comparison SEM micrographs and samples surfaces after treatment in the best solutions.

Description	SEM micrographs and samples	
<p style="text-align: center;">Industrial etching</p>	 <p>SEM HV: 20.0 kV WD: 11.95 mm VEGA3 TESCAN SEM MAG: 1.23 kx Det: SE 50 μm View field: 224 μm Date(m/d/y): 04/23/14 Performance in nanospace</p>	
<p style="text-align: center;">EP in Eutectic “O”</p>	 <p>SEM HV: 20.0 kV WD: 11.87 mm VEGA3 TESCAN SEM MAG: 1.23 kx Det: SE 50 μm View field: 225 μm Date(m/d/y): 04/24/14 Performance in nanospace</p>	
<p style="text-align: center;">EP in Solution “S”</p>	 <p>SEM HV: 20.0 kV WD: 11.91 mm VEGA3 TESCAN SEM MAG: 1.21 kx Det: SE 50 μm View field: 229 μm Date(m/d/y): 04/23/14 Performance in nanospace</p>	

This project served to define the configuration of the prototype for the electropolishing of the wire rods. The various lines of the project have been focused on the industrialization of the process and have led to a lot of information and improvements of the standard process. The main aspects are summarized below:

- We have designed and successfully tested a revolutionary system for electropolishing, which consists of treating a wire rod only partially immersed in the solution and, due to the rotation, removing the scale from the entire surface.

- It was shown that the rotating system could remove the scale, even in areas in which the coils are overlapped.

- We have designed a very compact system, a single tank, instead of electrochemical line for treatment.

List of figures

<i>Figure 1.1: Production of the steel from the iron ore in basic-oxygen furnace.</i>	11
<i>Figure 1.2: Flow diagram showing the principal process steps involved in converting raw materials into the major product forms, excluding coated products.</i>	12
<i>Figure 1.3: Fe-Fe₃C phase diagram</i>	14
<i>Figure 1.4: Typical microstructures of different stainless steel grades.</i>	16
<i>Figure 1.5: The hot rolled rod coil.</i>	18
<i>Figure 1.6: Mixed-acid pickling line.</i>	21
<i>Figure 1.7: Typical electropolishing setup and surface profiles.</i>	24
<i>Figure 1.8: A microscopic view of the same surface before and after electropolishing shows that the process produce clean metallic surface.</i>	26
<i>Figure 2.1: Eutectic phase diagram.</i>	29
<i>Figure 2.2: Freezing point of choline chloride with phenylpropionic and phenylacetic acids as function of composition.</i>	30
<i>Figure 2.3: Atomic force microscopy images (3D left and 2D right) of stainless steel 316 grade Hull cell plate etched in 1 ChCl:2 EG mixture at 7.0V for 10 min at 45°C showing the boundary between a region protected with acrylic resin and a polished region.</i>	32
<i>Figure 3.1: Self-repair mechanism of stainless steel.</i>	33
<i>Figure 3.2: The anodic polarization curve.</i>	35
<i>Figure 4.1: SEM micrographs of the austenitic bar from both side.</i>	38
<i>Figure 4.2: SEM micrographs of the martensitic bar from both side.</i>	38
<i>Figure 4.3: EDX spectroscopy - rough surface - sandblasted - cleaned with standard chemical etching.</i>	39
<i>Figure 4.4: SEM micrograph rough surface (A) sandblasted (B), cleaned with standard chemical etching (C).</i>	39
<i>Figure 4.5: SEM micrographs of the raw bar, arranged with increasing magnification.</i>	41
<i>Figure 4.6: EDX spectrum of the raw bar.</i>	42
<i>Figure 4.7: SEM micrographs of the bar 50 AISL sandblasted, arranged with increasing magnification.</i>	43
<i>Figure 4.8: EDX spectrum of the bar 50 AISL sandblasted.</i>	44

<i>Figure 4.9: SEM micrographs of the bar AU 1882 / P 51 (doped with sulphur), arranged with increasing magnification.</i>	45
<i>Figure 4.10: EDX spectrum of the bar AU 1882 / P 51 (doped with sulphur).</i>	46
<i>Figure 4.11: SEM micrographs of the bar VAL 1C martensitic, arranged with increasing magnification.</i>	47
<i>Figure 4.12: EDAX spectrum of the bar VAL 1C martensitic.</i>	48
<i>Figure 4.13: SEM micrographs of the raw rod, arranged with increasing magnification.</i>	49
<i>Figure 4.14: EDAX spectrum of the raw rod.</i>	50
<i>Figure 4.15: SEM micrographs of the raw hexagonal rod, arranged with increasing magnification.</i>	51
<i>Figure 4.16: EDAX spectrum of the raw hexagonal bar.</i>	52
<i>Figure 4.17: SEM micrographs of the raw square bar, arranged with increasing magnification</i>	53
<i>Figure 4.18: EDAX spectrum of the raw square bar.</i>	54
<i>Figure 4.19: SEM micrographs of the raw wire rod, arranged with increasing magnification.</i>	55
<i>Figure 4.20: EDAX spectrum of the raw wire rod.</i>	56
<i>Figure 4.21: Untreated samples raw and sandblasted.</i>	62
<i>Figure 4.22: Sandblasting at 200 bar with hot water and sand.</i>	63
<i>Figure 4.23: Sandblasting at 300 bar with hot water and river sand</i>	63
<i>Figure 5.1: SEM micrographs of the bar pickled with standard industrial recipe, arranged with increasing magnification.</i>	69
<i>Figure 5.2: EDX spectrum of the bar after etching in standard industrial solution.</i>	70
<i>Figure 5.3: Performance of the potential function of the distance cathode-anode with constant current (250 mA / cm²).</i>	72
<i>Figure 5.4: Samples after electropolishing, front from 1 to 10.</i>	76
<i>Figure 5.5: Samples after electropolishing, back from 1 to 10.</i>	76
<i>Figure 5.6: Samples after electropolishing, front from 11 to 18.</i>	77
<i>Figure 5.7: Samples after electropolishing, back from 11 to 18</i>	77
<i>Figure 5.8: Samples after electropolishing, front from 34 to 36 and “dry ice” blasted.</i>	77
<i>Figure 5.9: Samples after electropolishing, back from 34 to 36 and “dry ice” blasted.</i>	77

<i>Figure 5.10: Samples after electropolishing, front from 41 to 46 (without 42).</i>	78
<i>Figure 5.11: Samples after electropolishing, back from 41 to 46 (without 42).</i>	78
<i>Figure 5.12: Samples after electropolishing, front from 19 to 26.</i>	79
<i>Figure 5.13: Samples after electropolishing, back from 19 to 26</i>	80
<i>Figure 5.14: Samples after electropolishing in Eutectic “C”, front and back (27 and 29).</i>	81
<i>Figure 5.15: Samples after electropolishing, front 30-40.</i>	82
<i>Figure 5.16: Samples after electropolishing, back 30-40.</i>	82
<i>Figure 5.17: Comparison between samples electropolished with or without ultrasonic bath, with different process times.</i>	83
<i>Figure 5.18: EDX spectrum, comparison after treatment in eutectic 1:2 ChChl: urea and the standard recipe.</i>	87
<i>Figure 5.19: EDX spectrum, comparison after treatment in Eutectic “O” and the standard recipe.</i>	87
<i>Figure 5.20: Graphic dependence erosion rate on time.</i>	89
<i>Figure 5.21: Degradation of the ionic liquid solution after A – 0 min; B – 30 min; C – 60 min.</i>	89
<i>Figure 5.22: Degradation of the ionic liquid solution after D – 180 min; E – 500 min; F – 2000 min.</i>	90
<i>Figure 5.23: Sample of the sulphur doped steel after electropolishing</i>	91
<i>Figure 5.24: Sample of the martensitic steel after electropolishing</i>	92
<i>Figure 5.25: Comparison between the samples obtained in solutions technical grade and pure grade, after 4 min.</i>	93
<i>Figure 5.26: The samples after 90 minutes of treatment with the two different solutions.</i>	94
<i>Figure 5.27: Samples after different pre-treatment and half electropolishing process.</i>	95
<i>Figure 5.28: Separation (A) and filtration (B) of the solution after the addition of water.</i>	108
<i>Figure 5.29: The change of sample mass with time in fresh solution.</i>	109
<i>Figure 5.30: The change of sample mass with time in recycled solution.</i>	111
<i>Figure 5.31: Typical rectification curves: half-wave rectification; full-wave, single-phase rectification; full-wave, three-phase rectification.</i>	112
<i>Figure 5.32: Appearance of parts during the test with rectifier.</i>	114
<i>Figure 6.1: System for the electropolishing of a coil in ionic liquid solution.</i>	114

<i>Figure 6.2: Coil before (A) and after (B) the electropolishing</i>	114
<i>Figure 6.3: System for electropolishing in ionic liquid with steel tank.</i>	115
<i>Figure 6.4: System in scale with polyethylene tank.</i>	116
<i>Figure 6.5: The rod 12 turns side by side A - before electropolishing; B - after electropolishing.</i>	117
<i>Figure 6.6: The rod with overlapped coils A- before and B- after electropolishing.</i>	117
<i>Figure 6.7: The electrochemical plant for descaling stainless steel wire rod.</i>	119
<i>Figure 6.8: The electrochemical plant during the cleaning process</i>	119
<i>Figure 6.9: The front panel “Ametek” Sorensen SGI power supply.</i>	120
<i>Figure 6.10: The wire rod 5mm diameter before treatment.</i>	121
<i>Figure 6.11: The wire rods 5mm diameter after treatment</i>	121
<i>Figure 6.12: The squared rod 23 x 23 mm A – before and B- after treatment.</i>	122
<i>Figure 6.13: The tubes diameter A – 40 mm, B -130 mm, before treatment.</i>	123
<i>Figure 7.1: Samples passivated in different solutions.</i>	125
<i>Figure 7.2: EDAX spectrum and SEM micrograph of the sample without passivation</i>	126
<i>Figure 7.3: EDAX spectrum and SEM micrograph of the sample passivated in solution-1.</i>	126
<i>Figure 7.4: EDAX spectrum and SEM micrograph of the sample passivated in solution-2.</i>	126
<i>Figure 7.5: Samples passivated and left outside for 30 days.</i>	127
<i>Figure 7.6: Graph of the anodic polarization for non-passivated sample.</i>	129
<i>Figure 7.7: Graph of the anodic polarization for the sample passivated in solution-1.</i>	130
<i>Figure 7.8: Graph of the anodic polarization for the sample passivated in solution-3.</i>	130
<i>Figure 7.9: Graph of the anodic polarization for the sample passivated in solution-2.</i>	131
<i>Figure 7.10: The seawater test.</i>	132
<i>Figure 7.11: Atmospheric corrosion test.</i>	134
<i>Figure 8.1. A typical pulse reverse waveform.</i>	140

<i>Figure 8.2: Pulse reverse electropolishing settings.</i>	141
<i>Figure 8.3: Actual current and voltage waveform of pulse reverse electropolishing.</i>	142
<i>Figure 8.4: The wire rod A - before and B - after the pulse reverse finishing in Solution "C".</i>	144
<i>Figure 8.5: Electropolishing of stainless steel with ultrasound.</i>	147
<i>Figure 8.6: Electrolytic descaling of wire rod in Solution "S".</i>	149
<i>Figure 8.7: Result of electrolytic descaling in Solution "S".</i>	149
<i>Figure 8.8: System for partially immersing electropolishing.</i>	150
<i>Figure 8.9: Wire rod A - before and B - after the electropolishing in Solution "S".</i>	150
<i>Figure 8.10: The steel coils after electropolishing in 100g/l Solution "S" A - at ambient temperature, B – at 70°C.</i>	151
<i>Figure 8.11: Comparison of the different etching.</i>	153
<i>Figure 8.12: The comparison of EP full time and chemical etching with additional EP</i>	154
<i>Figure 9.1: The wire rod of AISL 304/304L stainless steel before electropolishing.</i>	155
<i>Figure 9.2: The stainless steel sample A- before and B- after electrochemical polishing</i>	156
<i>Figure 9.3: The working bath, made from stainless steel.</i>	157
<i>Figure 9.4: The Schematic view of electrochemical plant for descaling wire rods.</i>	158

List of tables

<i>Table 1.1: The pickling solutions for stainless steel.</i>	23
<i>Table 1.2: The recipes for electropolishing steel.</i>	27
<i>Table 4.1: Samples used for the characterization of the scale surface layer.</i>	40
<i>Table 4.2: The raw samples after treatment with HPWR at different pressures.</i>	58
<i>Table 4.3: Sandblasted samples after treatment with HPWR at different pressures.</i>	59
<i>Table 4.4: The raw samples after HPWR with the nozzle blade at different pressures.</i>	60
<i>Table 4.5: The sandblasted samples after HPWR with nozzle blade at different pressures.</i>	61
<i>Table 4.6: The raw steel samples after “dry ice”-blasting at different pressures.</i>	65
<i>Table 4.7: The sandblasted samples after “dry ice”-blasting at different pressures.</i>	67
<i>Table 4.8: Summary of the pre-treatment study.</i>	68
<i>Table 5.1: Melting Points (° C) of some alkyl halides</i>	71
<i>Table 5.2: Electropolishing with ionic liquid choline chloride – urea.</i>	74
<i>Table 5.3: The parameters of electropolishing in choline chloride and ethylene glycol.</i>	79
<i>Table 5.4: The parameters of electropolishing in Eutectic “C”.</i>	80
<i>Table 5.5: The parameters of electropolishing in Eutectic “O”.</i>	81
<i>Table 5.6: Analyses wastewater solution of Eutectic “O”.</i>	84
<i>Table 5.7: Analyses wastewater solution of choline chloride – urea.</i>	84
<i>Table 5.8: Comparison of SEM micrographs after polishing in ionic liquids and the standard recipe.</i>	86
<i>Table 5.9: Test at different temperatures Eutectic “O”.</i>	97

<i>Table 5.10: Tests at different concentration ratios Choline Chloride-Carboxylic Acid</i>	98
<i>Table 5.11: Result of electropolishing in Eutectic “O” with additives.</i>	100
<i>Table 5.12: Influence of water on electropolishing in ionic liquid.</i>	102
<i>Table 5.13: Research alternative Choline Chloride-based ionic liquids.</i>	104
<i>Table 5.14: Summary of the ionic liquids mixtures, applicable to the electropolishing of stainless steel.</i>	107
<i>Table 5.15: Test of the recycled solution.</i>	108
<i>Table 5.16: Comparison result of electropolishing with different power supplies.</i>	112
<i>Table 6.1: The working parameters for electropolishing the coil in ionic liquid.</i>	114
<i>Table 6.2. The working conditions for electropolishing coil with 12 turns.</i>	117
<i>Table 6.3: The process conditions for polishing the rod with overlapped coils.</i>	118
<i>Table 7.1: Result after different passivation and obtained potential.</i>	128
<i>Table 7.2: The average values of breakingdown potential for different passivation.</i>	129
<i>Table 7.3: Result after 40 hours in seawater.</i>	133
<i>Table 7.4: Result after 5 weeks in outdoors environment.</i>	135
<i>Table 8.1: The result of etching in ammonium citrate based solutions.</i>	138
<i>Table 8.2: Result after electropolishing in Solution “C”.</i>	139
<i>Table 8.3: Result of pulse reverse electropolishing in aqueous solutions.</i>	142
<i>Table 8.4: Samples after pulse reverse electropolishing in Solution”C”.</i>	144
<i>Table 8.5: Samples after electropolishing in Solution “S”.</i>	145
<i>Table 8.6: Influence of the current density on the electropolishing of stainless steel.</i>	146
<i>Table 8.7: The influence of the concentration and additional treatment.</i>	148

Table 8.8: Comparison of alternative aqueous solutions for treatment stainless steel. 152

Table 10.1: Comparison SEM micrographs and samples surfaces after treatment in the best solutions. 160

Bibliography

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