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“Surface Treatments for Industrial Applications”

ELECTROPLATING OF HEXAVALENT-CHROMIUM FREE BLACK COATINGS FOR FLAT SOLAR THERMAL COLLECTOR

Supervisor: Prof. V. Palmieri	Student: Vlada Pastushenko
Assistant supervisor: Dr. V. Rampazzo	Matr.№: 1023745

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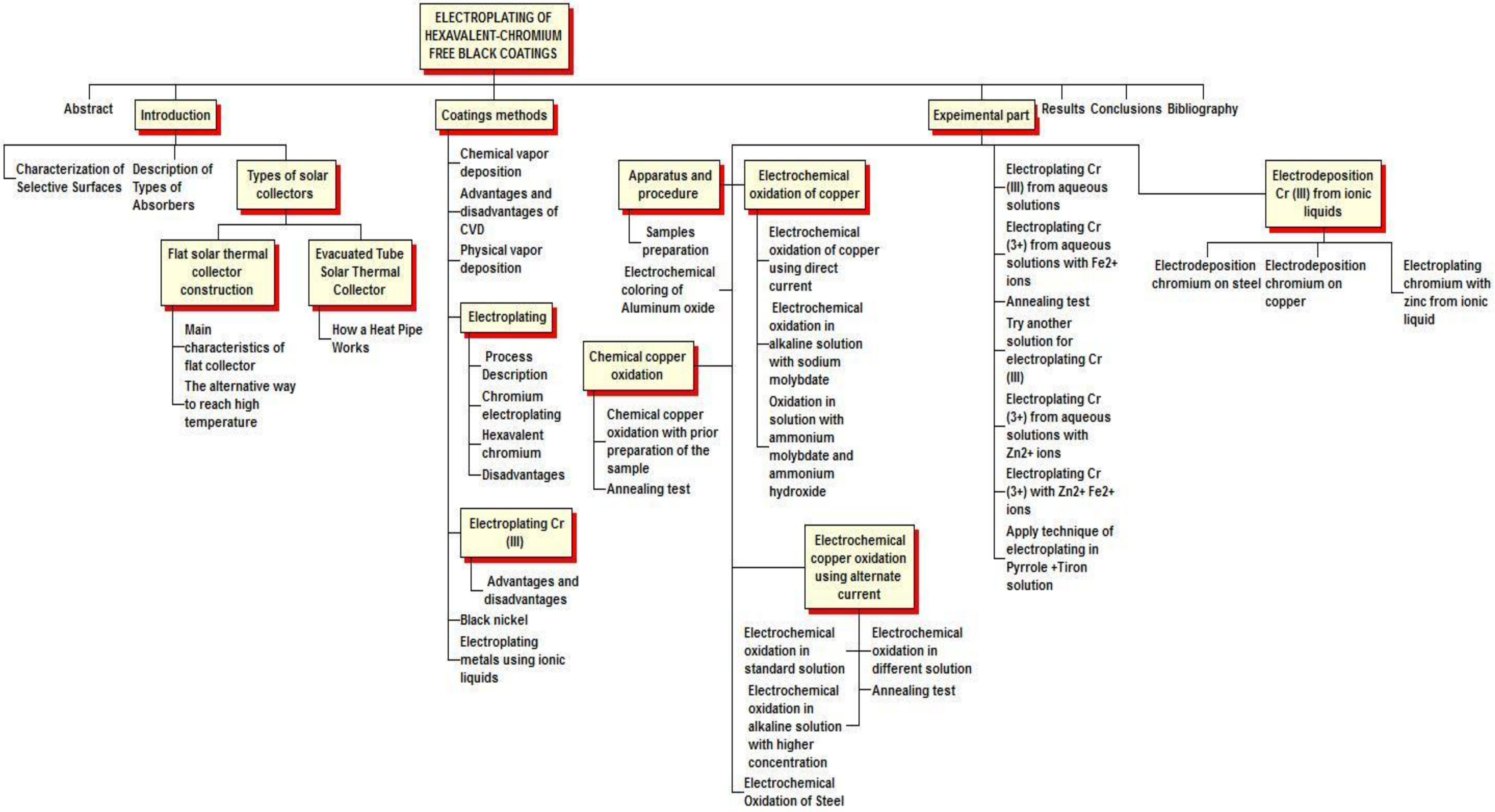
Contest

Scheme of master thesis



Abstract

A solar collector is an apparatus that collects the sunlight energy, and then alters this energy into a more usable or storable energy form. The absorber surface used in thermal solar collectors requires high absorptance in the solar spectrum and low emittance. Several techniques, such as vacuum techniques, are currently used to produce solar absorber surfaces. However, the desired characteristics of the solar absorber coating may be better controlled by direct electrodeposition. Other electrodeposition advantages are basically rapidity, low cost, free from porosity and industrial applicability. Copper substrate was chosen due to its use in a large variety of domestic and industrial piping as a thermal and electrical conductor.

Black chromium is an important coating material used in solar thermal systems as a spectrally selective surface. This coating is usually obtained by electrodeposition from sulphate free chromium (VI) aqueous solutions which represent a health and environmental hazard due to the presence of Cr (VI), a known toxic and carcinogenic agent. Recent developments in green chemistry have shown that ionic liquids can be used as electrolytes, allowing the deposition of a wide range of materials with negligible environmental and health impacts.

1. Introduction

A **solar thermal collector** is a solar collector designed to collect heat by absorbing sunlight. The term is applied to solar hot water panels, but may also be used to denote more complex installations such as solar parabolic, solar trough and solar towers or simpler installations such as solar air heat. The more complex collectors are generally used in solar power plants where solar heat is used to generate electricity by heating water to produce steam which drives a turbine connected to an electrical generator. The simpler collectors are typically used for supplemental space heating in residential and commercial buildings. A collector is a device for converting the energy in solar radiation into a more usable or storable form. The energy in sunlight is in the form of electromagnetic radiation from the infrared (long) to the ultraviolet (short) wavelengths. The solar energy striking the Earth's surface depends on weather conditions, as well as location and orientation of the surface, but overall, it averages about 1,000 watts per square meter under clear skies with the surface directly perpendicular to the sun's rays.

Concentrating solar power (CSP) systems use solar absorbers to convert sunlight to thermal electric power. The CSP program is working to reduce the cost of parabolic trough solar power technology. One of the approaches is to increase the operating temperature of the solar field from approximately 400°C to 500°C (or higher). To accomplish this, new more efficient selective coatings are needed that have both high solar absorptance and low thermal emittance at 500°C. Although designs are likely to use coating in evacuated environments, the coatings need to be stable in the vacuum at temperature $\geq$ 400°C. Current coatings do not have the stability and performance desired for moving to high operating temperatures. For efficient photothermal conversion solar absorber surfaces must have high solar absorptance (α) and a low thermal emittance (ε) at the operational temperature. A low reflectance ($\rho \approx 0$) at wavelengths (λ) $\leq 3\mu m$ and a high reflectance ($\rho \approx 1$) at $\lambda \geq 3\mu m$ characterize spectrally selective surfaces, as shown in Figure.1. The operational temperature ranges of these materials for solar applications can be categorized as low temperature (T<100ºC), mid temperature (100ºC<T<400ºC), and high temperature (T>400ºC). CSP systems operate at high-and mid-temperatures. The ideal spectrally selective surface would be low-cost and easy to manufacture, chemically and thermally stable in air at elevated temperatures (T $\geq$ 500ºC), and have a solar absorptance $\geq$ 0.98 and a thermal emittance $\leq$ 0.05 at 500ºC. However, a high temperature coating may require tradeoffs in performance as the high solar absorption and low emittance may be mutually exclusive [1].

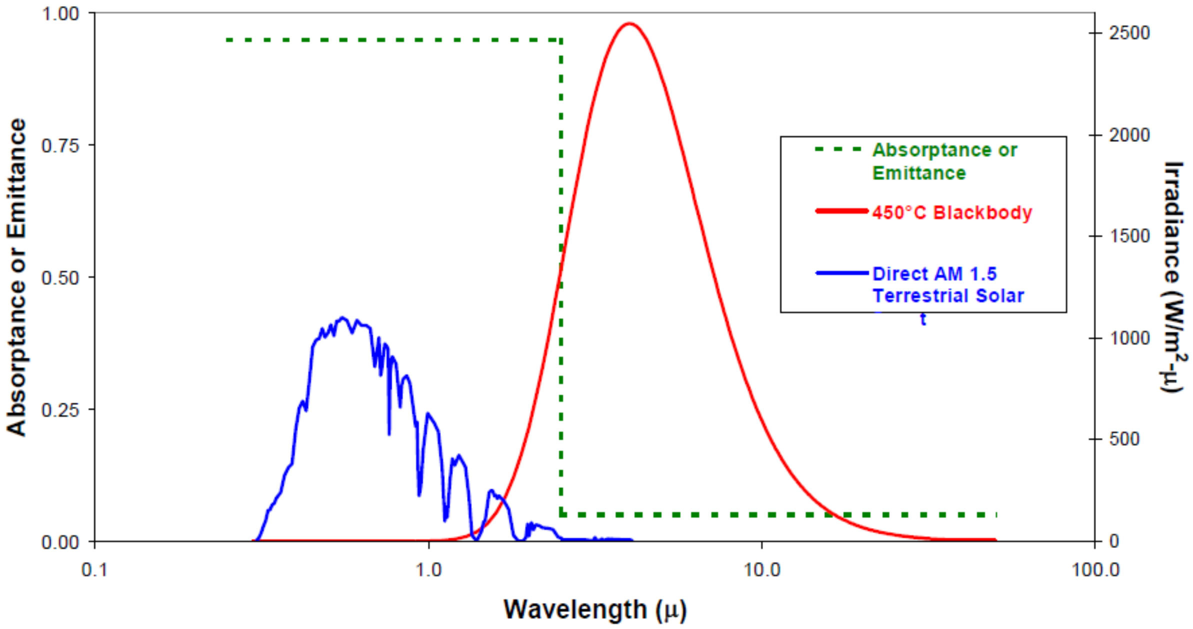


Figure.1.1. *Spectral performance of an ideal selective solar absorber*

1.1. Characterization of Selective Surfaces

The emissivity of a material (usually written ε or *e*) is the relative ability of its surface to emit energy by radiation. It is the ratio of energy radiated by a particular material to energy radiated by a black body at the same temperature. A true black body would have a ε = 1 while any real object would have ε < 1. Emissivity is a dimensionless quantity. In general, the duller and blacker a material is, the closer its emissivity is to 1. The more reflective a material is, the lower its emissivity. Highly polished silver has an emissivity of about 0.02

Absorptance (usually written α) is a measure of the ability of an object to absorb radiation, equal to the ratio of the absorbed radiant flux to the incident flux. For a layer of material the ratio of the flux absorbed between the entry and exit surfaces of the layer to the flux leaving the entry surface is the internal absorptance

The performance of a candidate solar absorber can be characterized by its solar absorptance and thermal emittance. Using Kirchhoff's law, spectral absorptance can be expressed in terms of total reflectance ρ (λ, θ) for opaque materials,

$$\alpha\ (\lambda,\theta) = 1-\rho\ (\lambda,\theta)\ (1)\ \text{and}$$

$$\varepsilon(\lambda,T) = \alpha(\lambda,T) \, , (2)$$

Where $\rho(\lambda, \theta)$ is the sum of both collimated and diffuse reflectance, λ is the wavelength, θ is the incidence angle of light, and T is the given temperature. Development of spectrally selective materials depends on reliable characterization of their optical properties. Using standard spectrophotometers, solar reflectance is usually measured in the 0.3-2.5 μm wavelength range at near-normal $\theta=0$ angle of incidence. The normal practice, this leads to unrealistic predictions of high efficiencies at high temperatures because the emittance is systematically underestimated. Emittance is typically measured at room temperature, though it can be measured at other temperatures.

Emittance is a surface property and depends on the surface condition of the material; including the surface roughness, superficial films, and oxide layers [2] Coatings typically replicate to some degree the roughness of the substrate. Therefore to facilitate development, it is important to measure the emittance of each coating-substrate combination as well as the uncoated substrate when developing a solar selective coating. Furthermore, selective coatings can degrade at high temperatures because of thermal load (oxidation), high humidity or water condensation on the absorber surface (hydratization and hydrolysis), atmospheric corrosion (pollution), diffusion processes (interlayer substitution), chemical reactions, and poor interlayer adhesion [3, 4].

Calculating the emittance from spectral data taken at room temperature assumes that the spectral characteristics do not change with increasing temperature. This is only valid if the material is invariant and does not undergo a phase change (as do some titanium containing materials), breakdown or undergo oxidation (as do paints and some oxide coatings) at higher temperatures. It is important before using high-temperature emittance calculated from room temperature data, that the calculated data is verified with high-temperature emittance measurements for each selective coating. The key for high-temperature usage is a low ε, because the thermal radioactive losses of the absorbers increase proportionally by the fourth power of temperature; therefore, it is important to measure the emittance at the operating temperatures and conditions [5].

1.2. Description of Types of Absorbers

Selective absorber surface coatings can be categorized into six distinct types:

a) intrinsic,

b) semiconductor-metal tandems,

c) multilayer absorbers,

d) multi-dielectric composite coatings,

e) textured surfaces,

f) selectively solar-transmitting coating on a blackbody-like absorber.

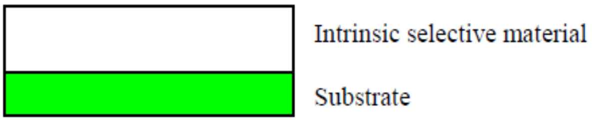
Intrinsic absorbers use a material having intrinsic properties that result in the desired spectral selectivity.

Semiconductor-metal tandems absorb short wavelength radiation because of the semiconductor bandgap and have low thermal emittance as a result of the metal layer. Multilayer absorbers use multiple reflections between layers to absorb light and can be tailored to be efficient selective absorbers.

Metal-dielectric composites – cermets - consist of fine metal particles in a dielectric or ceramic host material.

Textured surfaces can produce high solar absorptance by multiple reflections among needle-like, dendritic, or porous microstructure.

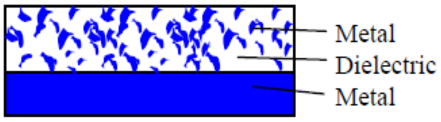
Additionally, selectively solar-transmitting coatings on a blackbody-like absorber are also used but are typically used in low-temperature applications. These constructions are shown schematically in Figures1.2, respectively [1].



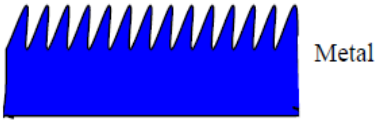
a) Intrinsic absorber

b) Semiconductor-metal tandems

c) Multilayer absorbers



d) Metal-dielectric composite



e) Surface texturing

f) Solar-transmitting coating/blackbody-like absorber

Figure.1.2. *Schematic designs of six types of coatings and surface treatments for selective absorption of energy*

1.3. Types of solar collectors

We all know the sun’s energy can be converted into heat; just get into your car on a summer’s day after it has been left in the sun. The principal of a solar thermal collector is very similar. It takes the light energy from the sun and converts it to useful energy in the form of hot water. To do this, the collector is mounted on high roof in a southerly direction. It needs to be out of the shade as much as possible to collect the maximum amount of sunlight.

Solar collectors fall into two general categories: non-concentrating and concentrating. In the non-concentrating type, the collector area (i.e. the area that intercepts the solar radiation) is the same as the absorber area (i.e., the area absorbing the radiation). In these types the whole solar panel absorbs the light. Flat plate and evacuated tube solar collectors are used to collect heat for space heating or domestic hot water.

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1.3.1. Flat solar thermal collector construction

Flat plate collectors, developed by Hottel and Whillier in the 1950s, are the most common type. They consist of a dark flat-plate absorber of solar energy, a transparent cover that allows solar energy to pass through but reduces heat losses, a heat-transport fluid (air, antifreeze or water) to remove heat from the absorber, and a heat insulating backing.

The absorber consists of a thin absorber sheet (of thermally stable polymers, aluminum, steel or copper, to which a matte black or selective coating is applied) often backed by a grid or coil of fluid tubing placed in an insulated casing with a glass or polycarbonate cover. In water heat panels, fluid is usually circulated through tubing to transfer heat from the absorber to an insulated water tank.

This may be achieved directly or through a heat exchanger. Most air heat fabricates, and some water heat manufacturers have a completely flooded absorber consisting of two sheets of metal which the fluid passes between. Because the heat exchange area is greater they may be marginally more efficient than traditional absorbers [6].

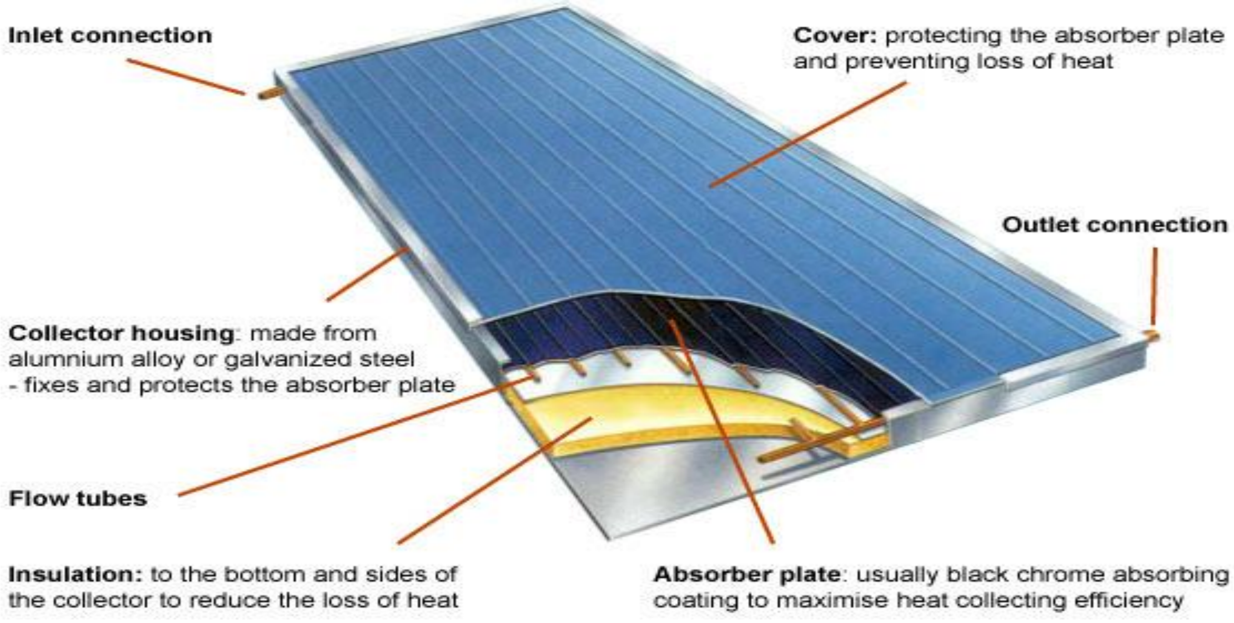

Figure.1.3. *Flat thermal solar absorber*

It is commonly understood that high temperatures on thermosolar energy can only be reached through very high concentration, and flat collectors are always used in low temperature applications because of the low stagnation temperatures. Parabolic and tower technologies have had a significant growth during the last years, but SRB has chosen a different road to reach high temperature which is having a very good isolation by reaching a 10-9 torr vacuum. This quality of vacuum joined to the flat geometry allows the collector to get also the diffuse light. This boost of energy allows the collector with concentrations never bigger than 8:1 reach stagnation temperatures over 450 °C.

Also due to the flat geometry of the collector, different concentrators have been designed to reach different stagnation temperatures. It is intended to meet the requirements of temperature and cost of other different markets, than traditional generation of electricity through turbines or hot water for the domestic use.

1.3.1.1 Main characteristics of flat collector

The main properties of the collector are:

1. It is under the Ultra High Vacuum
2. It captures the diffuse light
3. Different concentration geometries can be used depending on the target temperature and application

4. It has a built in getter pump to maintain the vacuum throughout the collectorrs life

The characteristics of SRB collector:

- Ultra High Vacuum (UHV) until 10^{-9} Torr.
- Getter Pump to support the vacuum during 25 years.
- At 300º C, High Absorbency (>90%) and low emittance (<0.07 per side).

Figure.1.4. *SRB thermal solar collector*

In general it’s assumed that:

- The flat collectors are only suitable for low temperature applications.
- The high temperatures are reached by a high index of solar concentration through mirrors (parabolic (satellite dish) and tower technologies)

1.3.1.2 The alternative way to reach high temperatures

The SRB Collector achieves that thanks to:

- High vacuum level.
- Selective treatment of high absorbency and low emittance.

- It’s for all this that reaches stagnation temperatures higher than 320ºC without concentration.
- Its taken advantage of a high percentage of the diffuse light with concentration, due to the collector’s flat geometry (the parabolic (satellite dish) and tower technologies don’t take advantage of it).
- The advantage of the diffuse light makes the use of the panel suitable in regions of low direct radiation like many countries of central and north Europe.

1.3.2 Evacuated Tube Solar Thermal Collector

An evacuated tube collector uses a series of glass tubes with a special coated copper plate inside to collect the energy from the sunlight. The sun shines through the glass, hits the collector plate and is transformed into thermal energy. This energy is used to warm a water-glycol mixture that is flowing through a manifold above the tubes. As in the previous case, the key to the efficiency of evacuated tubes is the vacuum. Hot water running through the collector will be cooled by the outside air on a cold day and thus lose energy to the environment. The vacuum in the tubes works to keep the water warm.

1.3.2.1 How a Heat Pipe Works

The solar thermal collectors use a heat pipe to transfer the heat from the evacuated tube to the manifold. This is a second sealed system that allows for dry connections at the manifold and a limiting device. Inside the evacuated tube, there is a copper pipe that is welded to the collector plate. Inside this pipe there is a small amount of water. When the sun strikes the collector plate, it heats the copper tube that then warms up the water at the bottom of the tube. The temperature gets so high that the water boils and water vapor evaporates and is carried upwards because it is lighter than the air in the tube. At the top, the tube is pushed into the manifold, where water is flowing over the end of the tube. The water vapor hits the end of the tube which is colder, causing its condensing. The heat is transferred to the antifreeze mixture in the manifold and the water flows back down to the bottom of the tube to be boiled again.

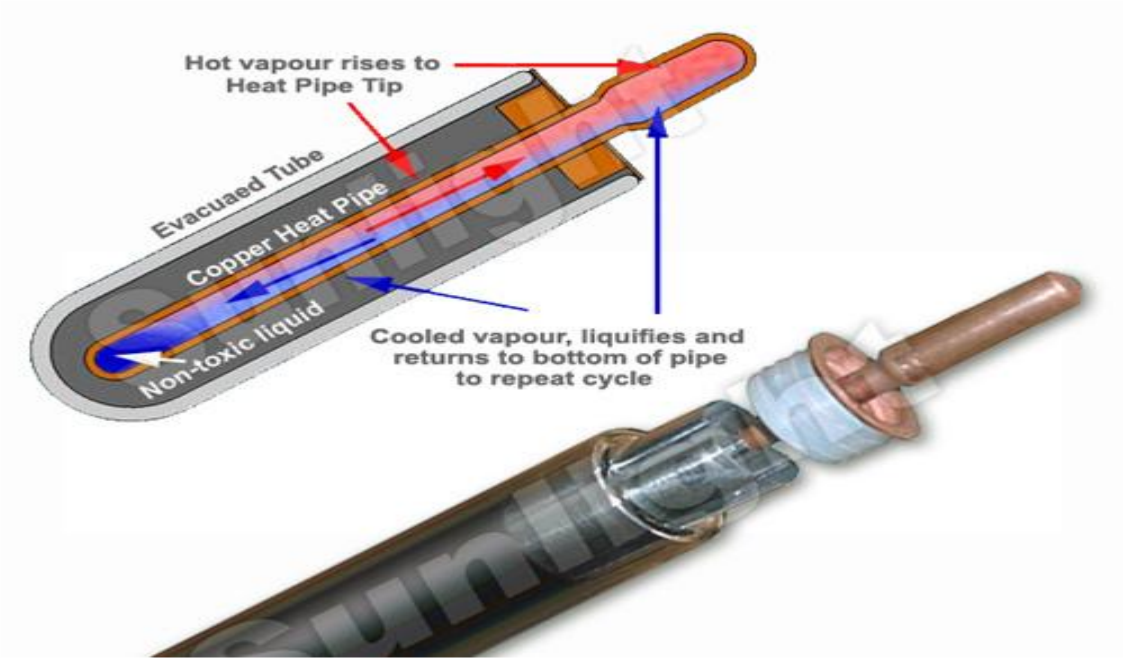

Figure .1.5. *Picture of Heat Pipe for solar collector*

2. Coating methods

2.1. Chemical vapor deposition

Chemical vapor deposition (CVD) is a versatile process that can be used to deposit layers of nearly any metal, as well as nonmetallic elements, such as carbon and silicon. Compounds such as carbides, nitrides, oxides, intermetallics, and many others also can be deposited. This technology has become very important in these applications:

1. Semiconductor and other electronic component manufacturing processes
2. Coatings on tools, bearings, and other wear-resistant parts
3. Optical, opto-electronic, and corrosion-resisting products
4. Monolithic parts, ultrafine powders, and high-strength fibers

The CVD process can be defined as the deposition of a solid on a heated surface via a chemical reaction from the vapor or gas phase. It belongs to the class of vapor-transport processes that are atomistic in nature, that is, the deposition species are atoms or molecules, or a combination thereof. Some metals (notably aluminum and copper) are seldom or never deposited by CVD. As of 2010, a commercially cost effective, viable CVD process for copper did not exist, though copper formate, Cu(II) ethyl acetoacetate, and other precursors have been used. Copper deposition of the metal has been done mostly by electroplating, in order to reduce the cost. Aluminum can be deposited from tri-isobutyl aluminum (TIBAL), triethyl/methyl aluminum (TEA, TMA), or dimethylaluminum hydride (DMAH), but physical vapor deposition methods are usually preferred.

However, CVD processes for molybdenum, tantalum, titanium, nickel, and tungsten are widely used. These metals can form useful silicides when deposited onto silicon. Mo, Ta and Ti are deposited by LPCVD, from their pentachlorides. Nickel, molybdenum, and tungsten can be deposited at low temperatures from their carbonyl precursors. In general, for an arbitrary metal *M*, the reaction is as follows:

$$2\ MCl5 + 5\ H2 \rightarrow 2\ M + 10\ HCl$$

The usual source for tungsten is tungsten hexafluoride, which may be deposited in two ways:

$$WF6 \rightarrow W + 3\ F2$$

$$WF6 + 3\ H2 \rightarrow W + 6\ HF$$

2.1.1. Advantages and Disadvantages of CVD

The CVD process has a number of important advantages that often make it the preferred method when producing hard, tribological, and high-temperature coatings and free-standing structures:

1. Refractory materials can be deposited at temperatures far below their melting point or sintering temperatures.
2. Near-theoretical density is readily achieved.
3. Preferred grain orientation and grain size can be controlled.
4. Processing at atmospheric pressure is possible.
5. Good bonding to a substrate is generally obtained.

Furthermore, the process is not restricted to line-of-sight deposition, as it is for most PVD processes. Deep recesses, high aspect- ratio holes, and other difficult three-dimensional configurations can usually be coated with relative ease. In addition, the deposition rate is high and thick coatings can be readily obtained (in some cases, centimeters thick). The process also is generally competitive and, sometimes, even more economical than other coating processes. Finally, the equipment is relatively simple, does not require ultrahigh vacuum, and generally can be adapted to many process variations. Its flexibility allows many composition changes during deposition, and the codeposition of compounds is readily achieved.

However, the CVD process is not the universal coating panacea. Because it is most versatile at a temperature of 600 °C (1110 °F) or higher, its applications are limited to substrates that are thermally stable at such a temperature. (The development of the plasma and metal-organic CVD processes partially offsets this problem.)

A second problem is that some chemical precursors are hazardous or extremely toxic, which necessitates a closed system.

A third problem is that many reactions either leave solid byproducts or generate solid byproducts with neutralizing solutions. These byproducts can be toxic and corrosive, which necessities the careful consideration of disposal procedures and incurs additional costs. The Environmental Protection Agency (EPA) has been very active, even stringent, in this regard, as have the state regulators of the EPA and Occupational Safety and Health Administration.

A fourth problem is that energy requirements can be high, especially when high deposition temperatures are required.

Finally, the efficiency of the process is sometimes low, resulting in high costs.

2.2. Physical vapor deposition

Physical vapor deposition (**PVD**) is a variety of vacuum deposition and is a general term used to describe any of a variety of methods to deposit thin films by the condensation of a vaporized form of the desired film material onto various workpiece surfaces (e.g., onto semiconductor wafers). The coating method involves purely physical processes such as high temperature vacuum evaporation with subsequent condensation, or plasma sputter bombardment rather than involving a chemical reaction at the surface to be coated as in chemical vapor deposition.

In the vacuum deposition process, elements, alloys, or compounds are vaporized and deposited in a vacuum. The process is carried out at pressures of less than 0.1 Pa (1 mtorr) and usually in vacuum levels of 10 to 0.1 mPa (100 to 1 torr). The substrate temperature typically ranges from ambient to 500 °C (930 °F). Vacuum deposition is commonly used to deposit pure metals (for example, aluminum, silver, gold, nickel, chromium, titanium, molybdenum, and tungsten), some alloys (for example, stainless steel, nickel-chromium, lead-tin, and M-Cr-Al-Y), and selected compounds (for example, Al2O3, TiC, and TiB2).

2.3. Electroplating

2.3.1. Process Description

Electroplating is the process of applying a metallic coating to a sample by passing an electric current through an electrolyte in contact with the piece, thereby forming a surface having properties or dimensions different from previous substrate. Essentially any electrically conductive surface can be electroplated. Special techniques, such as coating with metallic-loaded paints or silver-reduced spray, can be used to make nonconductive surfaces, such as plastic, electrically conductive for electroplating.

The metals and alloy substrates electroplated on a commercial scale are cadmium, chromium, cobalt, copper, gold, indium, iron, lead, nickel, platinum group metals, silver, tin, zinc, brass, bronze, many gold alloys, lead-tin, nickel-iron, nickel-cobalt, nickel-phosphorus, tin-nickel, tin-zinc, zinc-nickel, zinc-cobalt, and zinc-iron. Electroplated materials are generally used for a specific property or function, although there may be some overlap, e. g., a material may be electroplated for decorative use as well as for corrosion resistance [7-10].

The essential components of an electroplating process are an electrode to be plated (the cathode or substrate), a second electrode to complete the circuit (the anode), an electrolyte containing the metal ions to be deposited, and a direct current power source. The electrodes are immersed in the electrolyte with the anode connected to the positive leg of the power supply and the cathode to the negative leg. As the current is increased from zero, a point is reached where metal plating begins to occur on the cathode.

The plating tank is either made of or coated with totally inert materials. Anodes can be either soluble or insoluble, with most electroplating baths using one or the other type. The majority of power supplies are solid-state silicon rectifiers, which may have a variety of modifications, such as stepless controls, constant current and constant voltage. Plate thickness is dependent on the cathode efficiency of a particular plating solution, the current density, and the amount of plating time.

2.3.2. Chromium electroplating

Chromium and chromium oxides are important coating materials. Chromium is widely used as a decorative or functional coating, depending on its thickness. Decorative chromium is up to 0.8 μm thick and is usually applied over a nickel undercoat to increase corrosion resistance. Thicker chromium coatings, up to 500 μm, also called hard-chromium, are applied in wear resistant surfaces in aerospace, oil and gas, heavy equipment and a range of general industrial applications [11].

Another type of chromium-based coating is black chromium, a mixture of metallic chromium and its oxides, which has its main application as absorbing coating in solar thermal panels.

2.3.2.1. Hexavalent chromium

Hexavalent chromium plating, also known as hex-chrome, Cr+6, and chrome (VI) plating, uses chromic anhydride, also known as chromium trioxide, as the main ingredient. Hexavalent chromium plating solution is used for decorative and hard plating, along with bright dipping of copper alloys, chromic acid anodizing, and chromate conversion coating. Usually, chromium coatings are electrodeposited from aqueous solutions. Cr (VI) poses serious health and environmental concerns: it is sharply irritating to the mucous membranes of the nose and throat and potentially carcinogenic, so contact with these solutions as well as inhalation of the mist formed during electrodeposition must be avoided. Moreover, due to its toxicity, treatment of waste waters before disposal is mandatory [12].

Recipe 1	Recipe 2
CrO_3 - 300 g/l $NaNO_3$ -5g/l $(CH3COO)_2Ba$ – 7 g/l Boric acid - 15 g/l T = 20-40 °C I =40-80 A/dm^2	**CrO_3** - 250 g/l CH_3COOH – 6 ml/l T = 20-40 °C I = 50 A/dm^2

Table.2.1. *Different recipes for electroplating Cr (6+)* [13]

2.3.2.2. Disadvantages

One functional disadvantage of hexavalent chromium plating is the low cathode efficiency, which results in weak throwing power. This means it leaves a non-uniform coating, with more on edges and less in inside corners and holes. To overcome this problem the part may be over-plated and ground to size, or auxiliary anodes are used around the hard-to-plate areas. From a health standpoint, hexavalent chromium is the most toxic form of chromium.

Water and hexavalent chromium is released from the bath, which is toxic. To control these emissions wet scrubbers are used. The discharge from the wet scrubbers is then treated to precipitate the chromium from the solution, because absolutely it cannot be discarded in the waste water.

Chromium and chromium oxides are important coating materials. Metallic chromium is widely used in decorative and functional wear and corrosion resistant coatings. On the other hand, black chromium thin films (a mixture of metallic chromium and chromium oxides with an amorphous or a nana crystalline structure) present interesting optical properties and are extensively used as spectrally selective coatings for solar energy thermal conversion systems. Independently of their constitution and properties, chromium coatings are usually electrodeposited from hexavalent chromium (Cr6+) aqueous solutions, but Cr6+ poses serious health and environmental concerns and is currently other strict regulations. These restrictions are particularly severe in the aerospace and automotive industries. The most obvious alternative are aqueous electrolytes based on the less toxic trivalent chromium (Cr3+), and electrolytes of this type have been extensively studied, but there formulation is quite complex due to the high stability of Cr3+ complexes in water , which hinder or even prevent the electrodeposition of chromium. More promising are ionic liquid based electrolytes.

2.3. Electroplating Cr (III)

Trivalent chromium plating, also known as tri-chrome, Cr+3, and chrome (III) plating, uses chromium sulfate or chromium chloride as the main ingredient. Trivalent chromium plating is an alternative to hexavalent chromium in certain applications and thicknesses (e.g. decorative plating).

A trivalent chromium plating process is similar to the hexavalent chromium plating process except for the bath chemistry and anode composition. There are three main types of trivalent chromium bath configurations:

- A chloride- or sulfate-based electrolyte bath using graphite or composite anodes, plus additives to prevent the oxidation of trivalent chromium to the anodes.
- A sulfate-based bath that uses lead anodes that are surrounded by boxes filled with sulfuric acid (known as shielded anodes), which keeps the trivalent chromium from oxidizing at the anodes.
- A sulfate-based bath that uses insoluble catalytic anodes, which maintains an electrode potential that prevents oxidation.

The trivalent chromium plating process plates workpieces at a similar temperature, rate and hardness, as compared to hexavalent chromium.

Recipe 1	Recipe 2
$Cr_2(SO_4)_3$ – 200 g/l $(NH_4)_2SO_4$ – 335g/l Fe – 1 g/l pH – 2,3-2,7 i_k – 8-10 A/dm^2 T - 40°C	$Cr(SO_3NH_2)_3$ – 500 g/l $NH_4SO_3NH_2$ – 700 g/l pH – 1,2-1,5 i_k – 6-18 A/dm^2 T – 40-50°C

Table.2.2. *Standard recipes for electroplating Cr (3+)* [14]

2.3.1. Advantages and disadvantages

The functional advantages of trivalent chromium are higher cathode efficiency and better throwing power. The better throwing power means production rates are greater. Less energy is required because of the lower current densities required. The process is more robust than hexavalent chromium because it can withstand current interruptions. From a health standpoint trivalent chromium is intrinsically less toxic than hexavalent chromium. Because of the lower toxicity it is not regulated as toughly, which reduces overhead costs. There are other secondary health advantages:

- Higher cathode efficiencies lead to less chromium emitted into the air
- Lower concentration levels result in less chromium waste
- The anodes do not decompose

One of the disadvantages when the process was first introduced was that decorative customers disapproved of the color differences; however additives are now used to adjust the color. In hard coating applications, the corrosion resistance of thicker coatings is not quite as good as hexavalent chromium. The cost of the chemicals is greater, however this is usually offset by greater production rates and lower overhead costs. In general, the process must be controlled more closely than in hexavalent chromium plating, especially with respect to metallic impurities. This means processes that are hard to control, such as barrel plating, are much more difficult using a trivalent chromium bath.

2.4 Black nickel

Black nickel plating is a typically plated on brass, bronze, or steel in order to produce a non-reflective surface. This type of plating is used for decorative purposes and does not offer much protection [15].

There are at least two formulations for producing black nickel deposits; these incorporate zinc (Zn) and thiocyanate (CNS-) ions. Table.2.3 gives the composition and operating conditions for a sulfate and a chloride black nickel plating bath. The process was developed for decorative reasons - color matching and blending. The black nickel deposit has little wear or corrosion resistance, and is usually deposited over a layer of nickel deposited from a bright or dull nickel plating solution. It is in commercial use, but limited in its applications.

Black nickel (sulfate)	Black nickel (chloride)
Nickel sulfate, 75g/l Zinc sulfate, 30g/l Ammonium sulfate, 35g/l Sodium thiocyanate, 15g/l pH = 5,6 T = 24-32°C i = 0,15 A/dm^2	Nickel chloride, 75g/l Zinc chloride, 30g/l Ammonium chloride, 30g/l Sodium thiocyanate, 15g/l pH = 5,0 T = 24-32°C i = 0,15-0,6 A/dm^2

Table.2.3. *Recipes for electroplating Black Nickel*

2.5. Electroplating metals using ionic liquids

With over 150 years of experience, the metal finishing industry could be said to be mature. An alternative perspective is that with such a wide range of metals to choose from, the limited amount of systems that are currently commercially available means that the current technology is in urgent need of an overhaul to open new markets and products. The industry also faces key challenges. Its main markets are the deposition of Zn, Ni, Cr, Cu, Ag and Au. Legislation is currently limiting the application of Cr and the Ni plating sector will be affected by toxicity issues and the rising price of metals.

Almost the entire electroplating sector is currently based on aqueous solutions generally (acidic or basic) although some specialist applications use organic solvents [15]. More exotic metals can be deposited using plasma or chemical vapor deposition techniques (PVD and CVD). While this allows coating of a wide range of substrates (metal, plastic, glass, ceramic, etc.) not only with metal but also with alloys or compounds (oxide, nitride, carbide, etc.) the high capital investment and large running costs have limited it to niche markets with high value products.

The key solvent requirements for plating solutions are low cost, non-flammable, high solubility of electrolytes, high conductivities resulting in low ohmic losses and good throwing power, high solubility of metal salts, high rates of mass transfer and high electrochemical stability. Water fulfils all of these roles except the last and as such will remain the main stay of the metal plating industry for the foreseeable future. However, issues exist such as the limited potential windows, gas evolution leading to hydrogen embrittlement, passivation of substrates, electrodes and deposits, and hazardous complexing agents, such as cyanide means that since water must be returned to the environment eventually contamination is inevitable.

Over the last 10 years an alternative fluid has been developed. This is called a “room temperature” ionic liquid which is defined as an ionic material that is liquid below 100°C [16]. Ionic materials have high melting points a wide range of organic salts are available and have, in some cases, melting points down to - 40°C. Ionic liquids have a significant property that makes them ideal for metal processing:

1. wide potential windows
2. high solubility of metal salts
3. avoidance of water and metal/water chemistry
4. high conductivity compared to non-aqueous solvents.

Figure.2.1. *Ionic liquid - just mix two solids to make a liquid!*

The use of ionic liquids heralds not only the ability to electrodeposit metals that have until now been impossible to reduce in aqueous solutions but also the capability to engineer the redox chemistry and control metal nucleation characteristics. It has been estimated that there are more than 10^{18} ionic liquids possible and while this has the obvious advantage of flexibility, it also adds extreme complexity to the optimization. Ionic liquids contain large, non-symmetric ions that have low lattice energy and hence low melting points. The most commonly used cations for metal finishing are imidazolium, pyridinium and choline based [18].

3. Experimental part

Methods	Material of substrates	Measurements	Post treatment	Observation
Electrochemical colouring	Aluminum	Non carried out	Not carried out	- Expensive - not black
Chemical oxidation	Copper	Non carried out	Not carried out	Non uniformly covering
Chemical oxidation with prior preparation of the surface	Copper	Non carried out	- Annealing test on air - Annealing test in vacuum	- Non uniformly covering - Non resist in vacuum
Electrochemical oxidation using DC	Copper	SEM and EDAX instrumentation	Annealing test in air	Non stable coatings
Electrochemical oxidation using AC	Copper	X-ray analysis, SEM instrumentation	- Annealing test on air - Annealing test in vacuum	- Uniform, black deposit - not stable in vacuum
Electrochemical oxidation	Steel	SEM and EDAX instrumentation	- Annealing test on air - Annealing test in vacuum	- Well adherent coatings - Stable in vacuum
Electroplating Cr (III) from ionic liquid	Steel	SEM and EDAX instrumentation	Not carried out	Non uniform deposit
Electroplating Cr (III) from ionic liquid	Copper	SEM and EDAX instrumentation	Not carried out	Non uniform deposit
Electroplating alloy of chromium and zinc from ionic liquid	Copper	SEM and EDAX instrumentation	Not carried out	Non adhesive
Electroplating Cr (III) from aqueous solutions	Copper	SEM and EDAX instrumentation	Annealing test in vacuum	- Uniform covering -Stable in vacuum

Table.3.1.*Methods used in this study*

3.1. Apparatus and procedure

For all experiments we used heater with magnetic stirring. Experiments were done in a beaker with quantity of electrolyte ranging from 100 to 400 ml. Electric power was taken from power supply C.E.A. (0-30V, 0-30A).

For investigation film composition we provide X-Ray analysis. For this purpose we used Philips Xpert Diffractometer with a copper X-Ray tube.

For analysing the surface morphology we used SEM microscopy and a EDAX unit of SEM - Philips XL-30 equipped with a field emission gun at accelerating voltage of 0 - 30 keV.

3.1.1. Samples preparation

Samples were cut from sheets or rods of $5x3cm^2$ size. Specimens were partially immersed inside solution. Cleaning of samples was done in the following order: washing in ultrasonic bath with soap, washing in ultrasonic bath in water, rinsing deionizer water, drying with alcohol or acetone using nitrogen blowing. In some cases it was made special preparation (etching of surface, polishing, electropolishing, and oxidation).

3.2. Electrochemical coloring of Aluminum oxide

Aluminum and its alloys are the most attractive as substrates, due to their lightness and high strength to weight ratio, associated with excellent thermal and electrical conductance, good reflectivity, and low working cost. However, usually they require specific surface preparation procedures for a successful application of a proper adherent subsequent deposit especially when electrochemical techniques are involved [19].

Before the electrochemical treatment, the surface was subjected to a chemical degreasing for 5min at 40–60°C in an alkaline solution containing: 30–50 g/l $Na_3PO_4*12H_2O$ + 30–50 g/l;

$Na_2CO_3*10H_2O$ + 5–10 g/l NaOH, followed by a chemical deoxidizing in HNO_3 1: 1 (vol) for 30–60 s at 25 °C.

Initial anodizing in 1.5 M H_2SO_4, at 1–2 A/dm^2 (15 V_{DC}) for 30 min, at 25–30 °C. Unlike normal conditions this recipe works using AC voltage.

Sample №	Solution	Concentration [g/l]	Voltage [V_{AC}]	Time [min]	Temperature [°C]	cathode material
1	$AgNO_3$ H_2SO_4	2 120	20	5	25	Silver
2	$AgNO_3$ H_2SO_4	6 150	10	5	25	Silver

Table.3.2. *Regime data coloring of aluminum oxide*

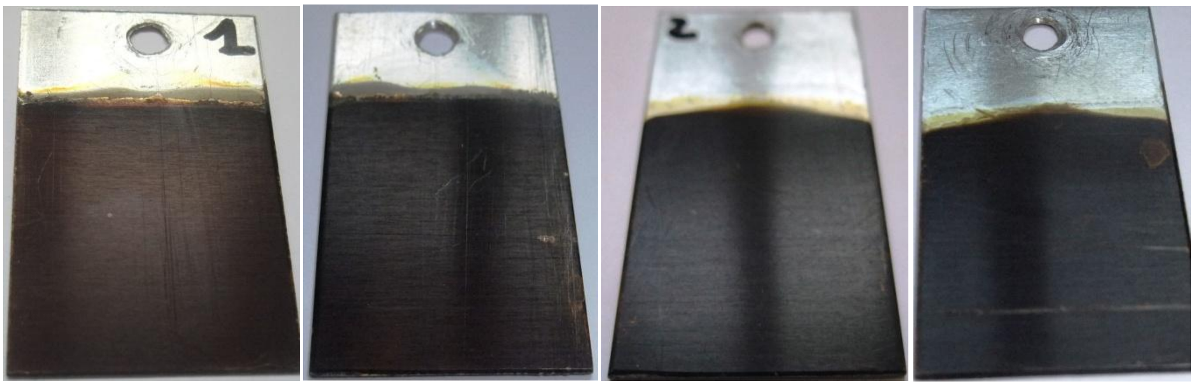

Figure.3.1. *Front and back of aluminum samples*

Applying this method we obtained dark uniform film on aluminum. Changed concentration of silver nitrate (see Table.3.1.) gives more dark color (see Figure.3.1). But the silver use both for component and cathode makes this recipe too expensive.

3.3. Chemical copper oxidation

For this experiment we used standard recipe of chemical copper oxidation:

- NaOH - 9 g/l;
- $(NH_4)_2S_2O_4$ - 3g/l.

All components were added to water and mixed, heated to certain temperature (see Table.3.3). Changing time of treatment we observed different color intensity on samples (see Figure.3.2).

Samples №	Temperature, °C	Time, min
1	70	8
2	90	5
3	80	5
4	80	10
5	80	15

Table.3.3. *Treatment conditions of copper oxidation*

Figure.3.2. *Front and back copper samples treated in oxidation solution*

The optimal result was obtained at a temperature 80°C, treatment time – 10 min.

3.3.1. Chemical copper oxidation with prior preparation of the sample

In order to get better results we introduced a different sample preparation: etching, chemical and electrochemical polishing (see Figure.3.3, Table.3.4).

Figure.3.3. *Front and back of copper samples treated in oxidation solution*

Samples №	Surface preparation	Parameters of chemical oxidation	
		Temperature [°C]	Time [min]
1	Acid-etch in HNO_3 (1:1)	77	10
2	Electropolishing in H_3PO_4:Buthanol(60:40) 2.5 V, 0.3 A , 21°C;	82	10
3	Chemical Polishing in: -Sulfamic acid-5g/l; - Ammonium citrate-1g/l; -Buthanol-50ml/l; -Peroxide-50ml/l ; 5min, 72°C; Then passivation in Sulfamic acid-20g/l, 5min	80	10
4	Chemical polishing + Electrochemical polishing (in the previous solutions)	80	20

Table.3.4. *Chemical oxidation of copper samples with special surface preparing*

All samples that we got have reflective surfaces, this make them unsuitable for our application,

3.3.2. Annealing test

To test our samples - two samples prepared by sandpaper, ultrasonic rinsing. After oxidation in solution: NaOH- 100g/l, $(NH_4)_2S_2O_4$-33/l, T=75°C, τ=25 min; one sample was heating on air at 250°C 24 hours. Another was heating in vacuum till 150°C 2 hours and then to 350°C (see Figure.3.4).

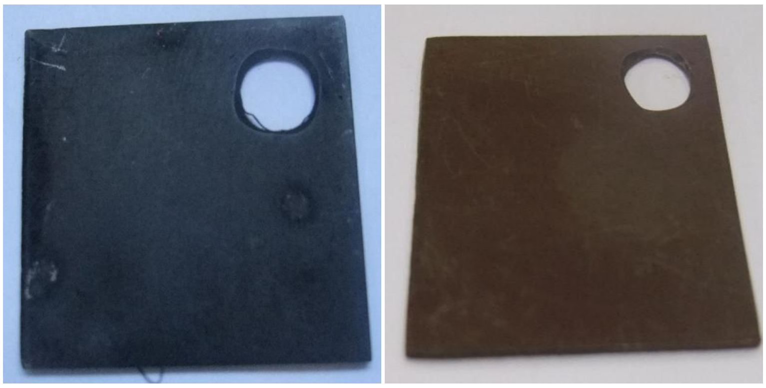

Figure.3.4. *Samples annealed on air (left) and in vacuum (right)*

Conclusion: By chemical copper oxidation we can get black, adhesive, uniform coatings. But it doesn’t stable in vacuum. To improve this disadvantage we provide next step - electrochemical oxidation.

3.4. Electrochemical oxidation of copper

Method	Solution	Post treatment	Measurements	Observations
Electrochemical oxidation of copper using DC	Sodium hydroxide	Non carried out	Non carried out	Non resistant coating
Electrochemical oxidation of copper using DC	Sodium hydroxide with sodium molybdate	Annealing test in vacuum	SEM and EDAX instrumentation	- More intensive color - not resist coating
Electrochemical oxidation of copper using DC	Ammonium molybdate with ammonium hydroxide	Annealing test on air	Non carried out	- Non uniformly - Non adhesive
Electrochemical oxidation of copper using AC	Sodium hydroxide with Ammonium Persulfate	Non carried out	X-ray analysis, SEM instrumentation	Brown coatings
Electrochemical oxidation of copper using AC	Sodium hydroxide	- Annealing test in vacuum - Annealing test on air	Non carried out	Not resistant coating
Electrochemical oxidation of copper using AC	Sodium hydroxide with Ammonium Persulfate and sodium molybdate	Non carried out	Non carried out	Non adhesive
Electrochemical oxidation of copper using A	Copper acetate and sodium acetate	Non carried out	Non carried out	Non adhesive

Teable.3.5. *Elecrtochemical oxidation of copper using different technique*

3.4.1. Electrochemical oxidation of copper using direct current

Electrochemical oxidation on copper using direct current we provide in alkaline solution (NaOH). For preparation we dissolve 80g/l NaOH in water and heated the solution (see Table.3.6). Copper was used as anode, a cathode we tried either steel or cooper.

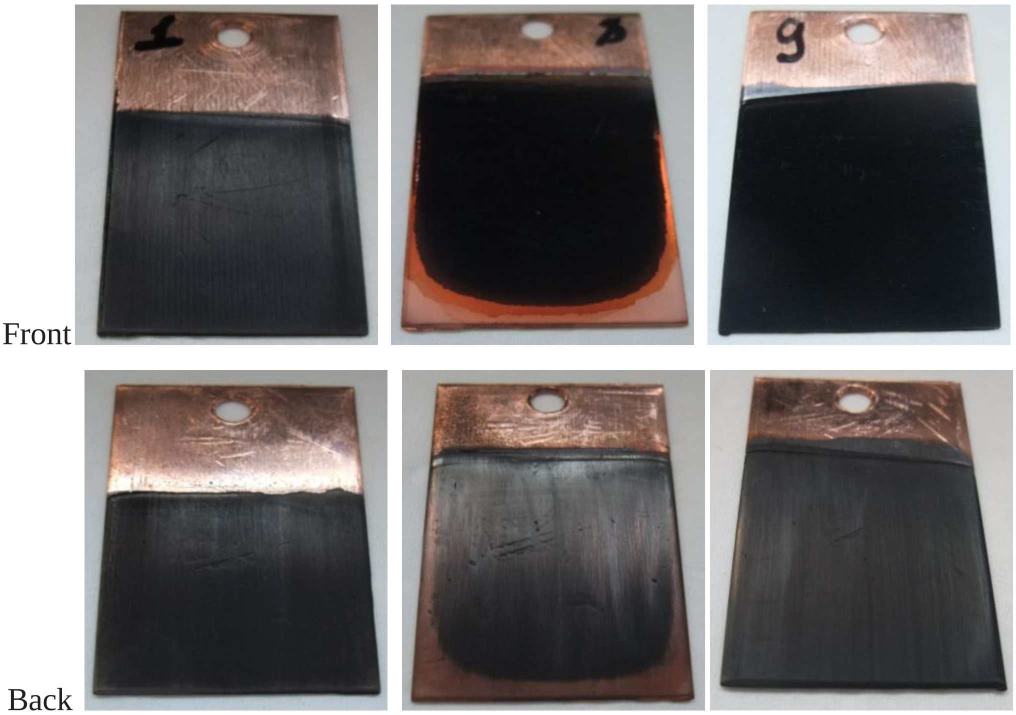

Figure.3.5.*Electrochemical oxidation in alkaline NaOH*

Samples №	Voltage $[V_{DC}]$	Current [A]	Temperature [°C]	Time [min]	Electrodes material	Notes
1	2.0	0.3	80	20	(+)Cu/steel(-)	1min without current, 2 min I - 0.1A
8	2.0→3.2	0.4→0.9 1.6→0.4	20	10	(+)Cu/steel(-)	The film begin dissolve
9	2.3	0.3	78	20	(+)Cu/steel(-)	Electropolished sample

Table.3.6. *Regime parameters of copper electrochemical oxidation*

3.4.2. Electrochemical oxidation in alkaline solution with sodium molybdate

For this experiment we used solution :NaOH- 80 g/l; Na_2MoO_4*$2H_2O$-0.1g; deonized water (see Table.3.7, Figure.3.6).

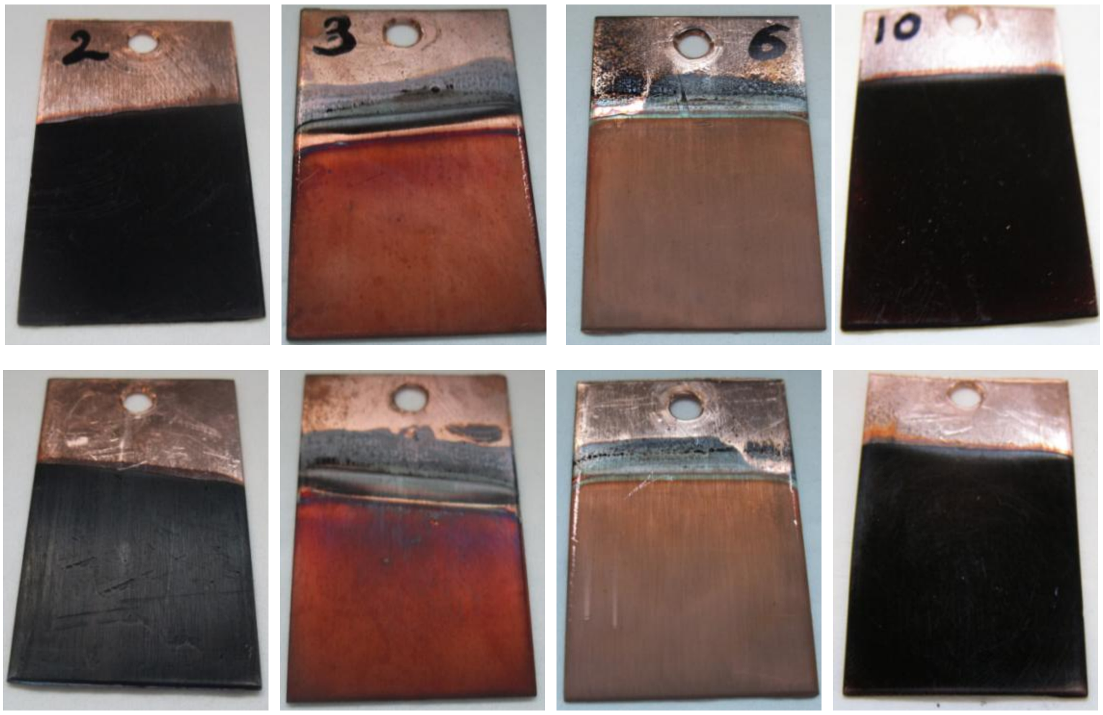

Figure.3.6. *Electrochemical oxidation of copper in alkaline solution with sodium molybdate*

Sample №	Voltage [V $_{DC}$]	Current [A]	Temperature [°C]	Time [min]	Electrode material	Notes
2	2.0	0.4	80	20	(+)Cu/steel(-)	-1min without current -2min I=0.1A
3	2.0→3.0 2.0→1.3	0.4→1.8 →0.3	20	20	(+)Cu/steel(-)	-1min without current -2 min I=0.1A
6	6.0→2,5	1.2	80	20	(+)Cu/steel(-)	-1min without current -2 min I=0.1A -high gas evolution
10	2.0	0.4	80	20	(+)Cu/steel(-)	Sample prepared by sputter-etching

Table.3.7. *Parameters of electrochemical oxidation of copper in alkaline solution with sodium molybdate*

3.4.3.Oxidation in solution with ammonium molybdate and ammonium hydroxide

Prepared new solution with ammonium molybdate and ammonium hydroxide, dissolve all components in water. We tried with different concentration of components; changed voltage and electrode material (see Figure.3.7, Table.3.8).

Figure.3.7. *Electrochemical oxidation in solution with ammonium molybdate and ammonium hydroxide*

Sample № 10 was heated in air up to 350°C, to check behaivour of coating (see Figure.3.8).

Figure.3.8. *Sample annealed on air*

Sample №	Solution	Voltage [V_{DC}]	Current [A]	Temp-re [°C]	Time [min]	Electrode material	Notes
1	$(NH_4)_6Mo_7O_2*4H_2O$ - 20g/l NH_4OH - 10g/l	3.0	0.1	25°C	5	(+)Cu/Cu(-)	Dark grey film
2	$(NH_4)_6Mo_7O_2*4H_2O$ - 20g/l NH_4OH -10g/l	2.6	0.1	25	5	(+)Steel/Cu(-)	Etching in HNO_3
3	$(NH_4)_6Mo_7O_2*4H_2O$ - 20g/l NH_4OH-10g/l	3.0	0.1	25	10	(+)Steel/Cu(-)	Etching in HNO_3
4	$(NH_4)_6Mo_7O_2*4H_2O$ - 20g/l NH_4OH - 20g/l	2.5	0.1	25	20	(+)Steel/Cu(-)	-polishing with sandpaper -etching in HNO_3:H_2SO_4 (1:1) -neutralized in NaOH
18	$(NH_4)_6Mo_7O_24*4H_2O$ - 20g/l NH_4OH - 20g/l	2.5	0.1	45	12	(+)Steel/Cu(-)	- polishing with sandpaper - etching in HNO_3:H_2SO_4 (1:1) - neutralized in NaOH

Table.3.8. *Electrochemical oxidation in solution with ammonium molybdate and ammonium hydroxide*

We carried out SEM and EDAX analysis. From this data we can see that we obtained copper oxide and it has dendritic structure (see Fifure.3.9, 3.10), so it doesn't resist to mechanical stress.

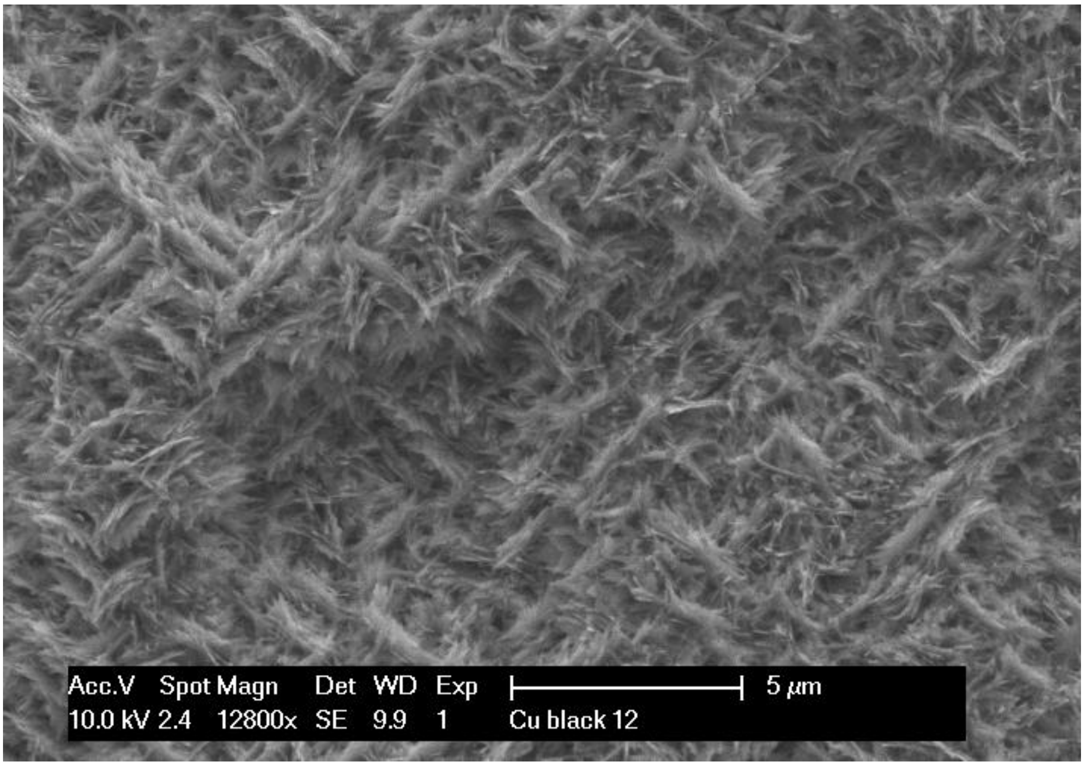

Figure.3.9. *SEM data black film obtained by electrochemical oxidation of copper (sample №4)*

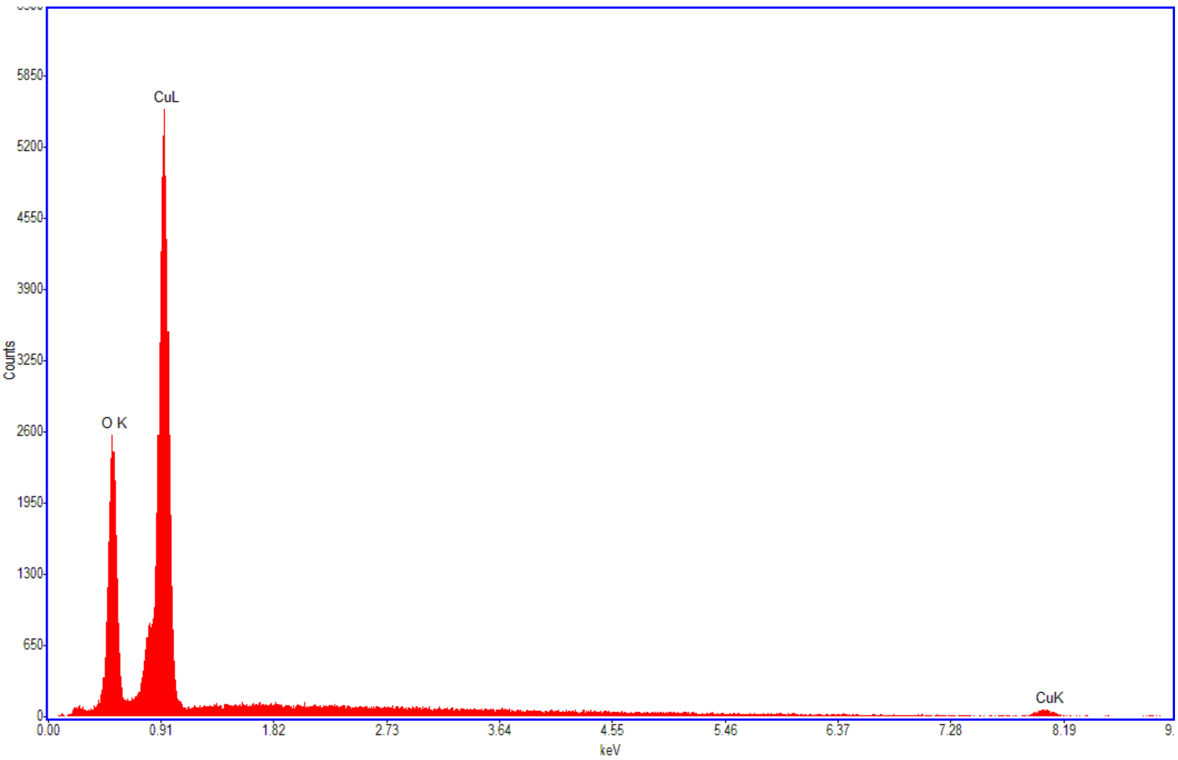

Figure.3.10. *EDAX data black film obtained by electrochemical oxidation of copper (sample №4)*

3.5. Electrochemical copper oxidation using alternate current

3.5.1. Electrochemical oxidation in standard solution

For this experiment we used the previous solution: NaOH - 9 g/l; $(NH_4)_2S_2O_4$ - 3g/l, for oxidation and applied the alternate current (AC). All components were added to water and heated (see Table.3.9).

Figure.3.11. *Electrochemical oxidation of copper with AC*

Samples №	Voltage $[V_{AC}]$	Current [A]	Temperature [°C]	Time [min]	Electrode Material	Notes
5	20→15	8,3	70	5	(+)Cu/Cu(-)	-
6	31→18	10	70	5	(+)Cu/Cu(-)	WE - chemical polished
7	25→18	10,3	80	10	(+)Cu/Cu(-)	WE - chemical polished
8	20	11	80	10	(+)Cu/Cu(-)-	Non uniform film

Table.3.9. *Electrochemical oxidation of copper using AC*

Sample №8 measured on X-Ray diffractometer and on Semi Conductor Microscopy. (see Figure.3.10, 3.11).

X-ray analysis shows pick on copper sulfide that probably means ammonium persulfate began decomposed at high current. Morphology analysis shows compact and uniform deposit.

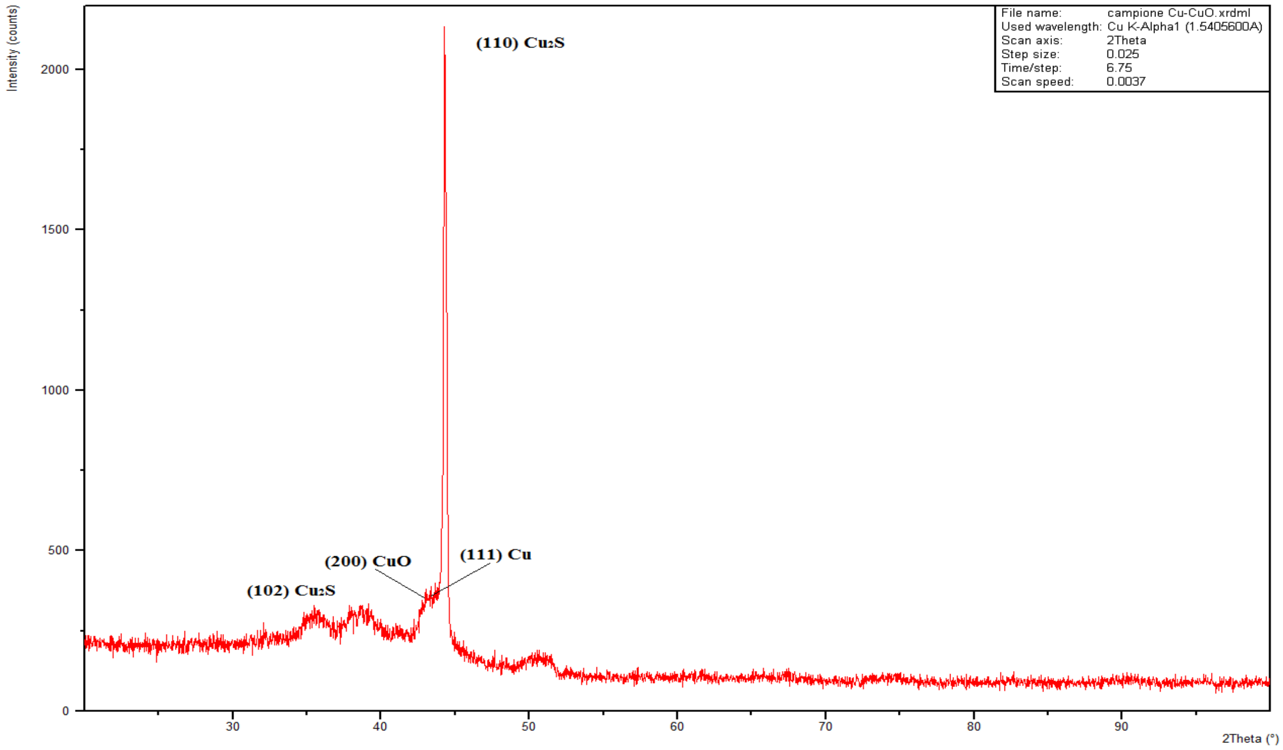

Figure.3.12. *X-ray analysis of film on copper substrate*

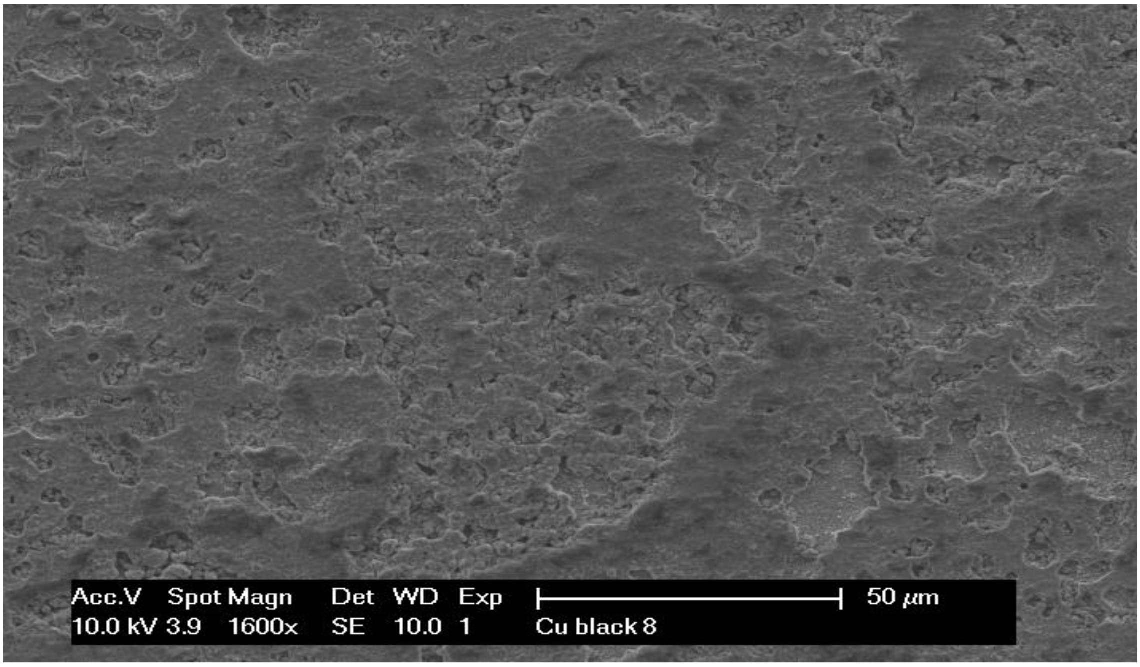

Figure3.13. *SEM data of film on copper substrate*

In order to obtain a more uniform and black film we tried to reduce voltage, change concentration of electrolyte and change electrodes materials (see Figure.3.14, 3.15; Table.3.10).

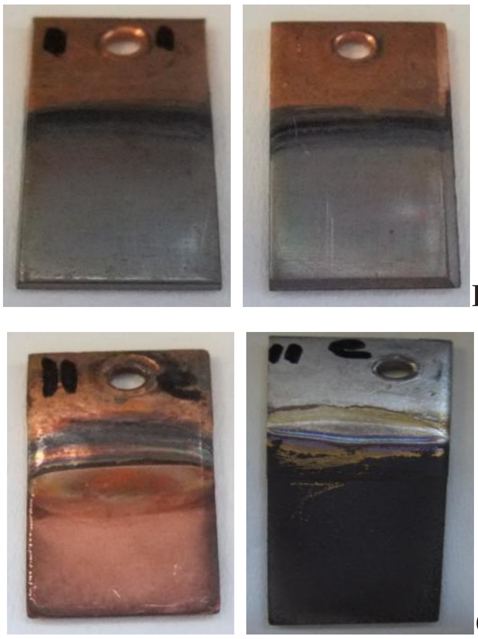

Figure.3.14. *Electrochemical oxidation of copper with AC*

Figure.3.15. *Electrochemical oxidation of copper using Nb-cathode*

Preparation of solution were the same: NaOH - 18 g/l; $(NH_4)_2S_2O_4$ - 6g/l.

Samples №	Voltage [V_{AC}]	Current [A]	Temperature [°C]	Time [min]	Electrode Materials
9	21	18	70	5	(+)Cu/Cu(-)
10	10	5.8	70	20	(+)Cu/Cu(-)
11	DC 5.0→2.5	1.1→0.2	72	15	(+)Cu/Nb(-)
11*	10	2.5	75	10	(+)Cu/Nb(-)

Table.3.10. *Electrochemical oxidation of copper with AC using different electrode*

In conclusions, the AC current application did not give noticeable results. As next step we planned to try to increase the concentration of solutions, special preparation of surface, change parameters of processes.

3.5.2. Electrochemical oxidation in alkaline solution with higher concentration

Figure.3.16. *Electrochemical oxidation of copper using AC in alkaline higher concentration*

Sample №	Solution	Voltage [V_{AC}]	Current [A]	Tem-re [°C]	Time [min]	Electrode material	Notes
14	NaOH- 80 g/l $(NH_4)_2S_2O_4$-6g/l	10	22.6	95	10	(+)Cu/Cu(-)	Etching in HNO_3(1:1) Neutralized in NaOH
15	NaOH- 80 g/l $(NH_4)_2S_2O_4$-6g/l	7.0	15.0	80	20	(+)Cu/Cu(-)	Etching in HNO_3:H_2SO_4(1:1) Neutralized in NaOH
16	NaOH- 80 g/ $(NH_4)_2S_2O_4$-6g/l	5.0	9.9	80	30	(+)Cu/Cu(-)	The same preparation as previous

Table.3.11. *Parameters of electrochemical oxidation of copper using AC in alkaline with higher concentration*

Observed films are black and velvet-like, but not adhesive. So we try to apply the AC technique to solutions with different additives.

3.5.3. Electrochemical oxidation in different solutions

For this experiment we used alkaline solution with sodium molybdate, alkaline solution with sodium molybdate and ammonium persulfate; solution with copper acetate and sodium acetate (see Table.3.12)

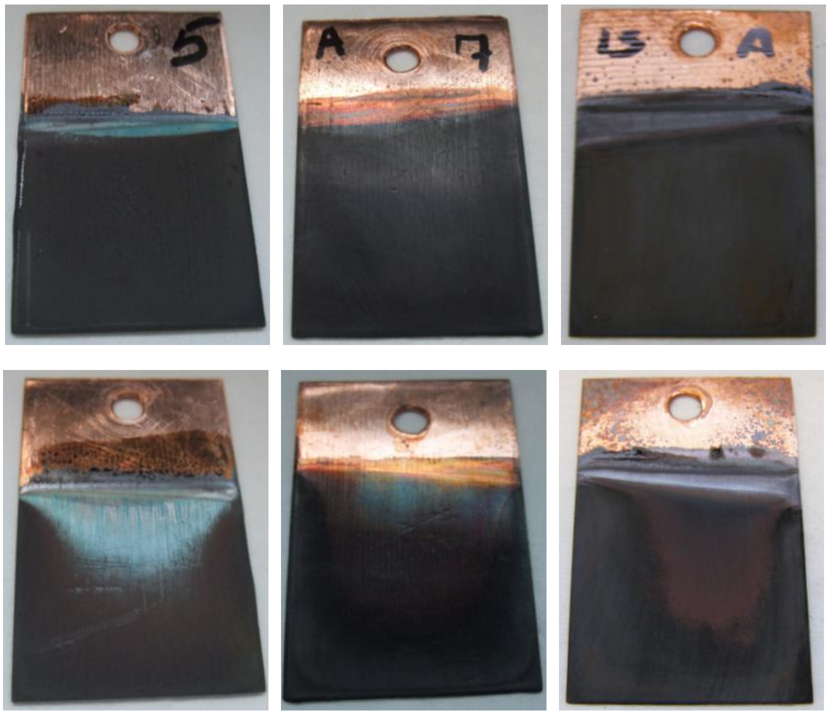

Figure.3.17. *Electrochemical oxidation of cooper in different solutions*

Sample №	Solution	Voltage [V_{AC}]	Current [A]	Tem-re [°C]	Time [min]	Electrode material	Notes
5	NaOH- 80 g/l $Na_2MoO_4*2H_2O$-0.1g	0.1	5.1	80	20	(+)Cu/steel(-)	1min without current, 2min I=0.1A
7	$(CH_3COO)_2Cu$ - 0.1M CH_3COONa - 1M	20	1.2	80	10	(+)Cu/steel(-)	Thin brown film
13	NaOH - 80 g/l $Na_2MoO_4*2H_2O$ - 0.1g $(NH_4)_2S_2O_4$ - 6g/l	5.0	16.5	85	10	(+)Cu/Cu(-)	Etching in HNO_3(1:1) Neutralized in NaOH

Table.3.12. *Parameters of electrochemical copper oxidation*

3.5.4. Annealing test

To check the resistance of the coatings we prepared two samples in alkaline solution using alternate current. After we annealed one of them on air, another in vacuum, till 350°C.

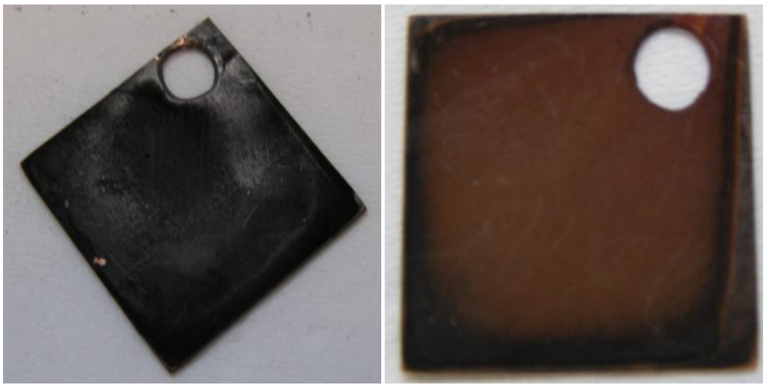

Figure.3.18. *Samples annealed on air (left) and in vacuum (right)*

Conclusion: electrochemical oxidation of copper with the use of direct or alternating current gives a uniform, black velvet deposits. Analysis showed that we have received copper oxide, but it is not stable when heating in vacuum, which makes them unsuitable for application for thermodynamic panels.

3.6. Electrochemical Oxidation of Steel

Another black coating applied onto metal surface involved conducting polymers, respectively, the anodic polymerization of Pyrrole (see Figure.3.20) using Tiron (see Figure 3.19) as mediator. For preparing solution we dissolved Pyrrole and Tiron in water in different molar concentration (see Table 3.13)

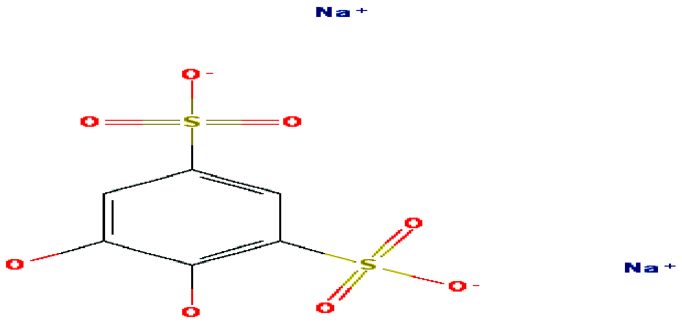

Figure.3.19. *Tyron - 4, 5-Dihydrox-1, 3-benzenedisulfonic acid disodium salt monohydrate*

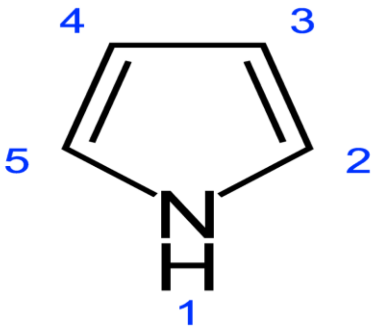

Figure.3.20. *Pyrrole (C4H5N)*

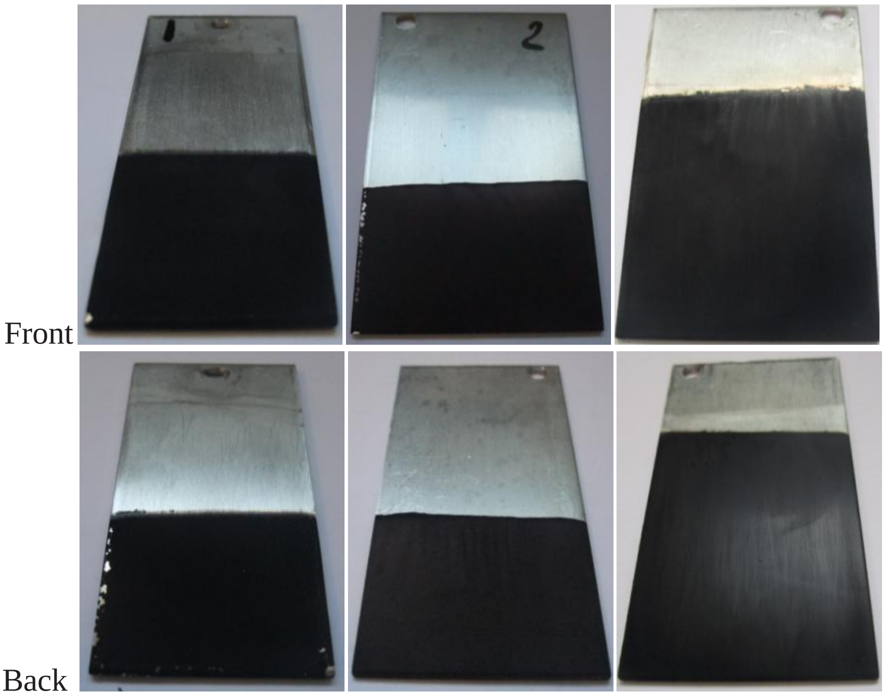

Figure3.21. *Electrochemical Oxidation of steel*

Sample №	Solution	Voltage [V_{DC}]	Current [A]	Temp-re [°C]	Time [min]	Electrodes	Preparation
1	Tyrone 0,2 M Pyrrole 0,1M	2.0	0.1	20	10	(-)Cu/St.Steel(+)	-by sandpaper -washed in ultrasonic
2	Tyrone 0,2 M Pyrrole 0,2M	2.0	0.1	20	10	(-)Cu/St.Steel(+)	- by sandpaper -washed in ultrasonic
3	Tyrone 0,5 M Pyrrole 0,2M	2.0	0.2	20	10	(-)Cu/St.Steel(+)	-etched in HCl 20% for 2min -in H_2SO_4 20% 3min

Table.3.13.*Parameters of steel oxidation in Pyrrole + Tiron*

To check resistant of coating we annealed sample in vacuum till up 350° C. It showed good behavior (see Figure.3.22).

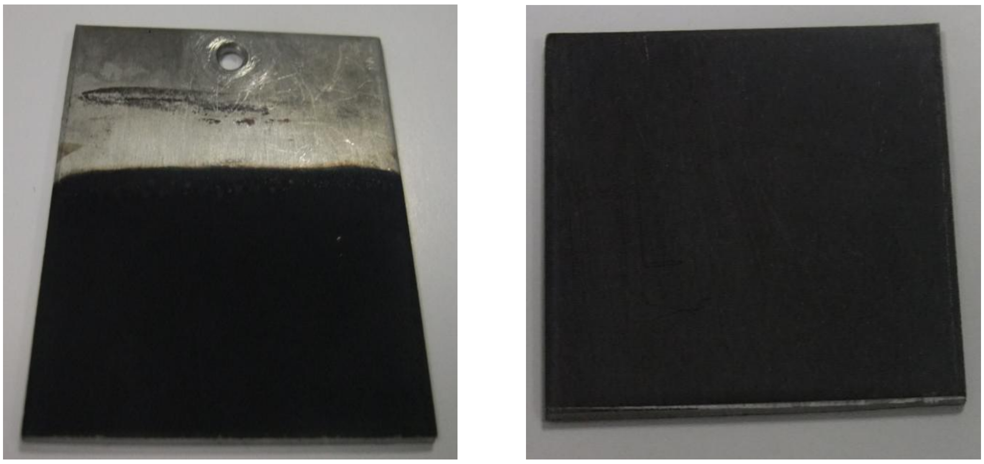

Figure.3.22. *Black film before (right) and after (left) annealing in vacuum at 350°C*

We performed X-ray analisys and investigation the morphology of obtained film (see Figure 3.22; 3.23). Films were obtained dense, well-packaged, and adherent.

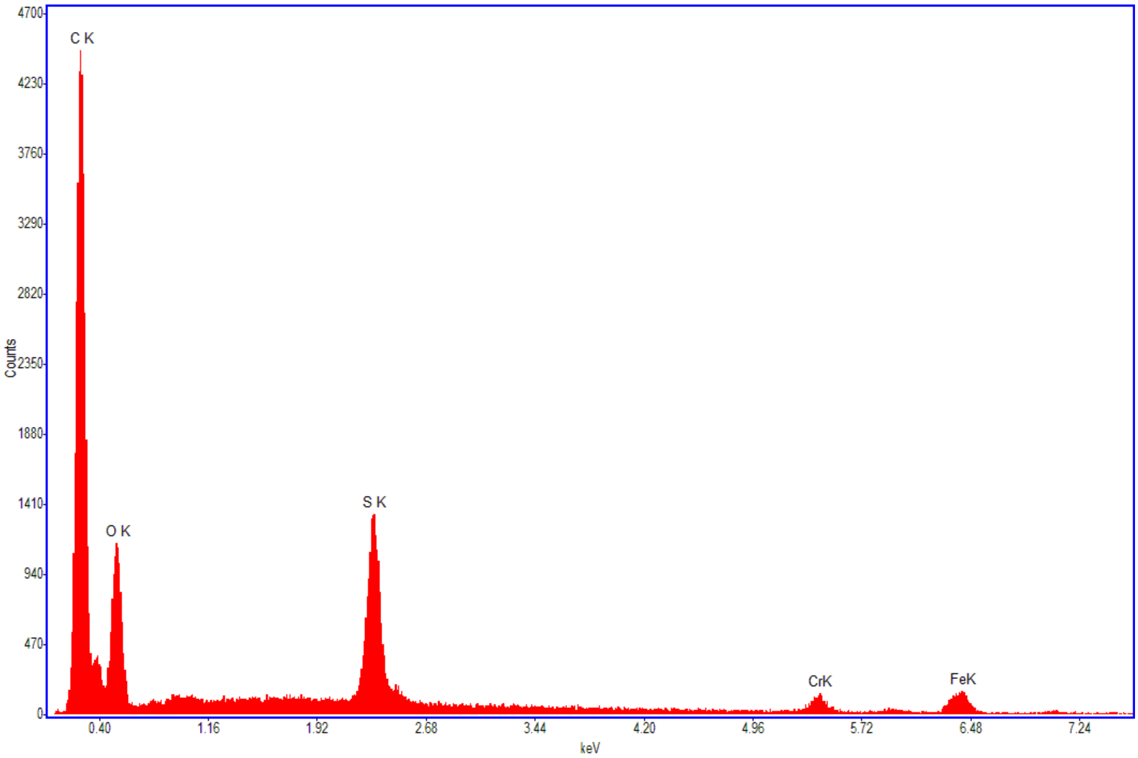

Figure.3.23. *X-Ray analysis of black coating on steel*

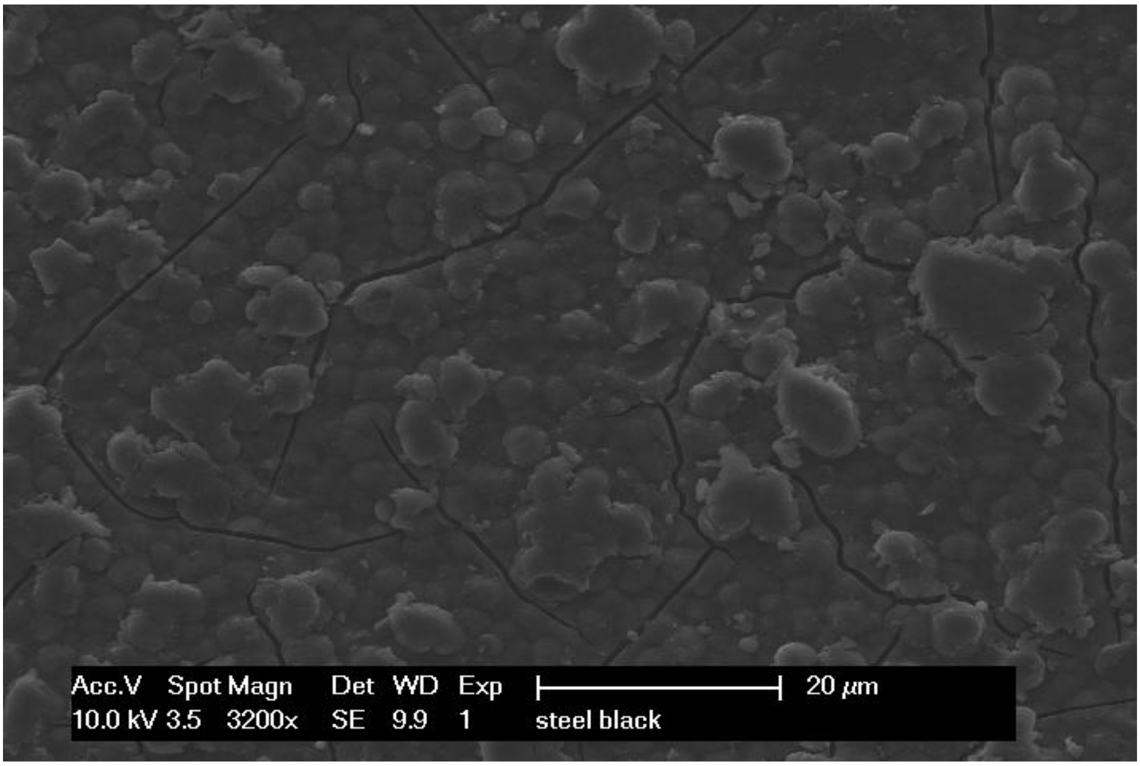

Figure.3.24. *Morphology of black film on steel*

3.7.Electroplating Cr (III) from aqueous solution

	Method	Post treatment	Measurements	Observations
1	Electroplating Cr (3+) from aqueous solution with Fe^{2+} ions	Annealing in vacuum	SEM and EDAX analysis	- Dark, adhesive coating - Stable in vacuum
2	Electroplating Cr (3+) from aqueous solution with Zn^{2+} ions	Not carried out	Not carried out	- More black coating - Not adhesive
3	Electroplating Cr (III) with Zn^{2+} and Fe^{2+} ions	Not carried out	Not carried out	- Nonuniformly - Not adhesive
4	Apply technique of electroplating in Pyrrole + Tiron solution	Not carried out	Not carried out	- Dark gray - Nonuniformly

Table.3.14. *Electroplating Cr (III) from aqueous solutions*

3.7.1. Electroplating Cr (3+) from aqueous solution with Fe^{2+} ions

For electroplating Cr (III) we used following solution: $CrCl_3$ – 200 g/l; NH_4Cl – 80 g/l; H_3BO_3 – 60 g/l; NaH_2PO_2 – 80g/l; $FeCl_2$ – 20 g/l; NaH_2PO_4 – 1 g/l.

Changing the parameters we tried to obtain black, uniform coatings (see Figure.3.25, Table.3.15)

Sample №	Voltage [V]	Current [A]	Temperature [°C]	Time [min]	Electrode material	Notes
2	2,0 ↑2,5	0,1↑0,2	35	5	(-)Cu/Ti_{Pt} (+)	Nothing
	3,6	1,0	40	60	(-)Cu/Ti_{Pt} (+)	- A lot of bubbles - Nonuniformly
3	3,3	0,5	40	15	(-)Cu/Ti_{Pt} (+)	Nothing
	5,0	2,0	40	20	(-)Cu/Ti_{Pt} (+)	Gray film
	8,0	5,0	40	5	(-)Cu/Ti_{Pt} (+)	Surface etched in HNO_3 50%
4	12,3	10	40	5	(-)Cu/Ti_{Pt} (+)	- A lot of bubbles - Non uniformly - Normal surface
5	11,3	10	50	5	(-)Cu/Ti_{Pt} (+)	Etching surface
6	5,2	5	60	30	(-)Cu/Ti_{Pt} (+)	Smooth surface
7	6,9	5	50	30	(-)Cu/Ti_{Pt} (+)	- Rough-finished surface - Easily removed from surface
8	5,0	2,5	20	10	(-)Cu/Ti_{Pt} (+)	Light grey film
	8,2	3,5↑5,0	20↑	10	(-)Cu/Ti_{Pt} (+)	Tried stirring
	8,6	5,0	20	10	(-)Cu/Ti_{Pt} (+)	Add NaF -1g

Table.3.15. *Parameters of electroplating Cr (3+) from aqueous solution with* Fe^{2+} *ions*

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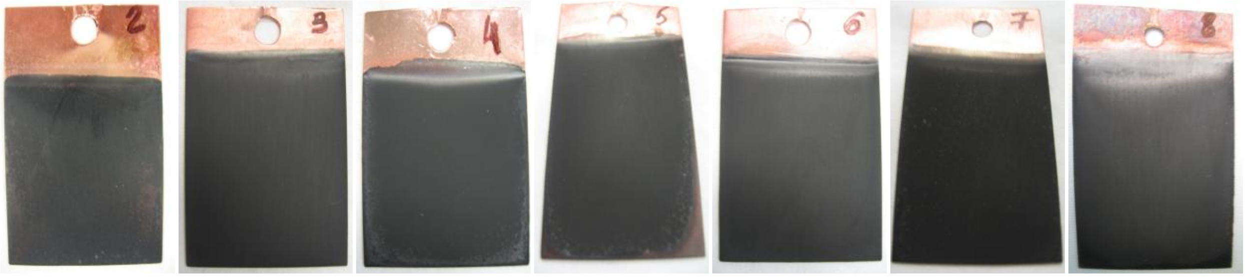

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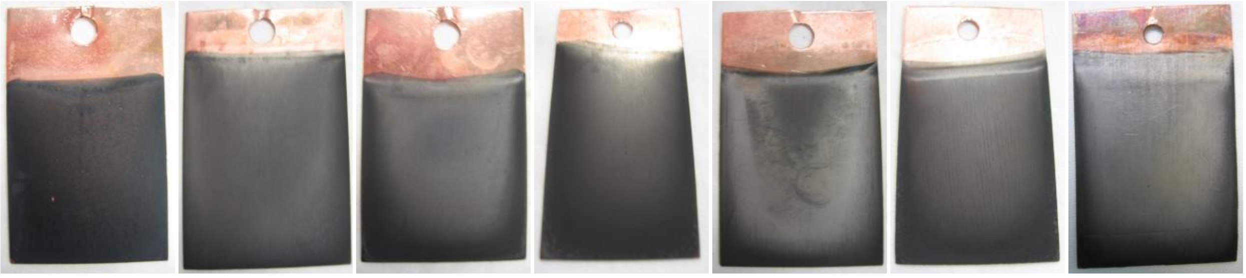


Figure.3.13. *Electroplating Cr (3+) from aqueous solution with* Fe^{2+} *ions*

We performed SEM and EDAX data of black trivalent chromium deposit obtained from aqueous solution (see Figure.3.26, 3.27).

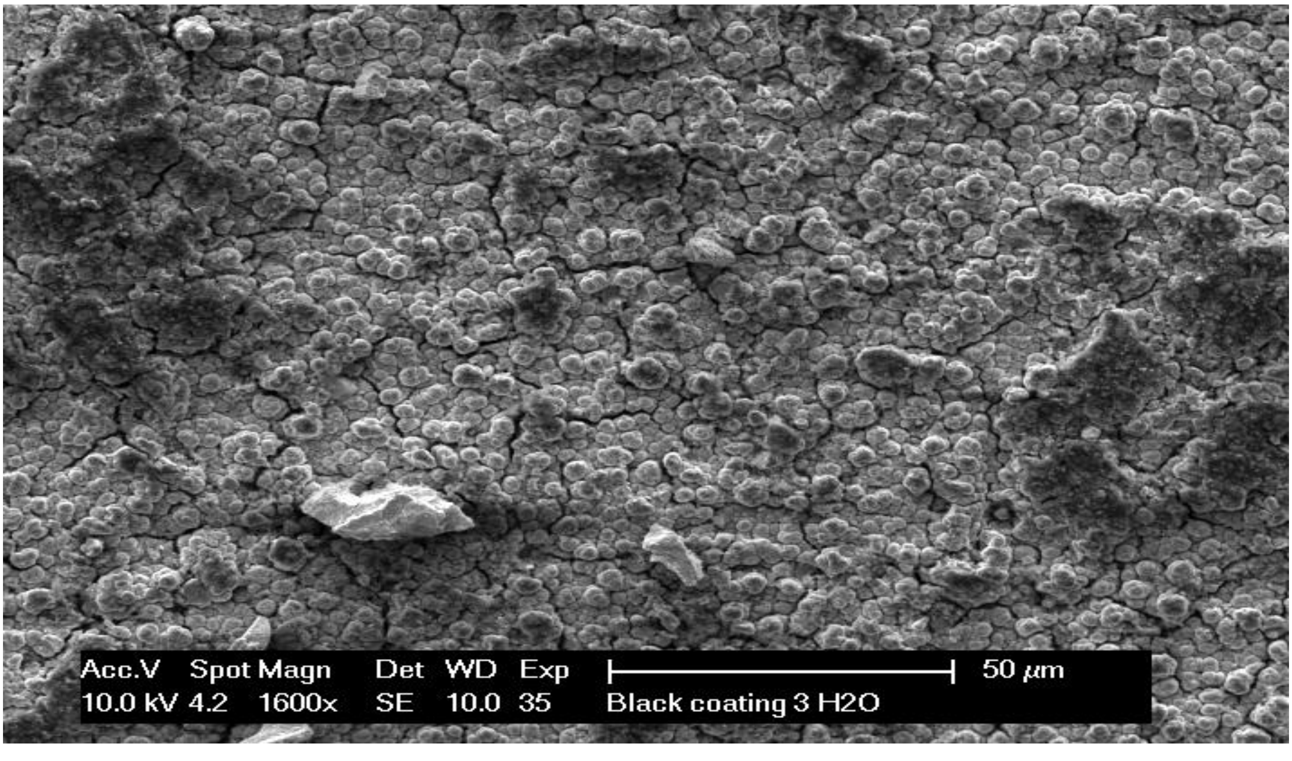


Figure .3.26.*SEM data of black chromium film on copper substrate*

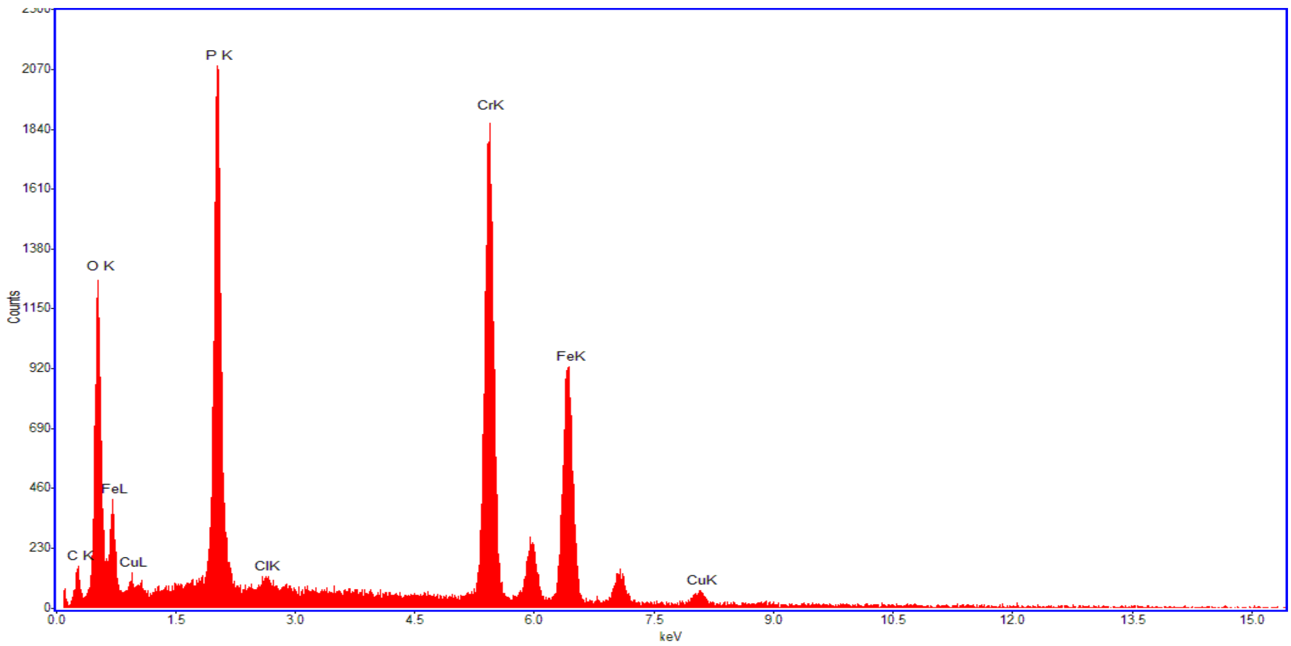
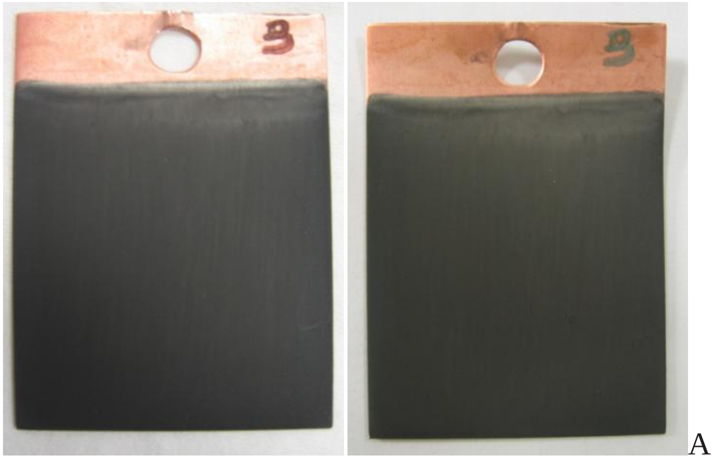


Figure.3.27. *EDAX data of black trivalent chromium film on copper substrate*

3.7.2. Annealing test

To check the resistance of the coating we annealed sample in the vacuum till up 350°C. It showed good behavior (see Figure.3.28).



Before After

Figure.3.28. *Annealing in vacuum*

3.7.3. Try another solution for electroplating Cr (III)

For the next experiment we prepared following solution: $CrCl_3$ – 266 g/l; NaF – 0,5M; NaH_2PO_2 – 80g/l; $FeCl_2$ – 20 g/l; NaH_2PO_4 – 1 g/l.

It didn’t give better result, as previous solution (see Figure.3.29, Table.3.16)

Figure.3.29. *Electroplating Cr(3+) from aqueous solution with* Fe^{2+} *ions on copper*

Sample №	Voltage [V]	Current [A]	Temperature [°C]	Time [min]	Electrode material	Notes
16	11,4	5	22↑35	5	(-)Cu/Ti_{Pt} (+)	Surface etched in HNO3 50%
17	10,2	5	35↑43	5	(-)Cu/Ti_{Pt} (+)	Smooth surface
18	5,0	1,5	20	5	(-)Cu/Ti_{Pt} (+)	Etched surface
	5,0	1,0	20	5		Non uniform
	6,8	2,0	26	10		Not adhesive
	6,3	2,5	26	10		Black-gray

Table.3.16. *the working conditions of electroplating black chromium from aqueous solution*

3.7.4. Electroplating Cr (3+) from aqueous solution with Zn^{2+} ions

Instead of iron ions we tried to use zinc ions to receive more black color of deposits (see Figure3.30). And for this purpose we prepared following solution: $CrCl_3$ – 266 g/l; NaF – 0,5M; NaH_2PO_2 – 0,75M; $ZnCl_2$ – 15 g/l; NaH_2PO_4 – 4 g/l.

Sample №	Voltage [V]	Current [A]	Temperature [°C]	Time [min]	Electrode material	Notes
9	14,6	5	22	5	(-)Cu/Ti_{Pt} (+)	Not adhesive
10	5,0	1,0	32	40	(-)Cu/Ti_{Pt} (+)	Nothing
	8,6	5,0	32	40	(-)Cu/Ti_{Pt} (+)	A lot of gases
11	15	10	52	10	(-)Cu/Ti_{Pt} (+)	Not adhesive
12	14,6	10	40	1	(-)Cu/Ti_{Pt} (+)	Not adhesive

Table.3.17.*The working conditions for electroplating black chromium from aqueous solution with* Zn^{2+} *ions*

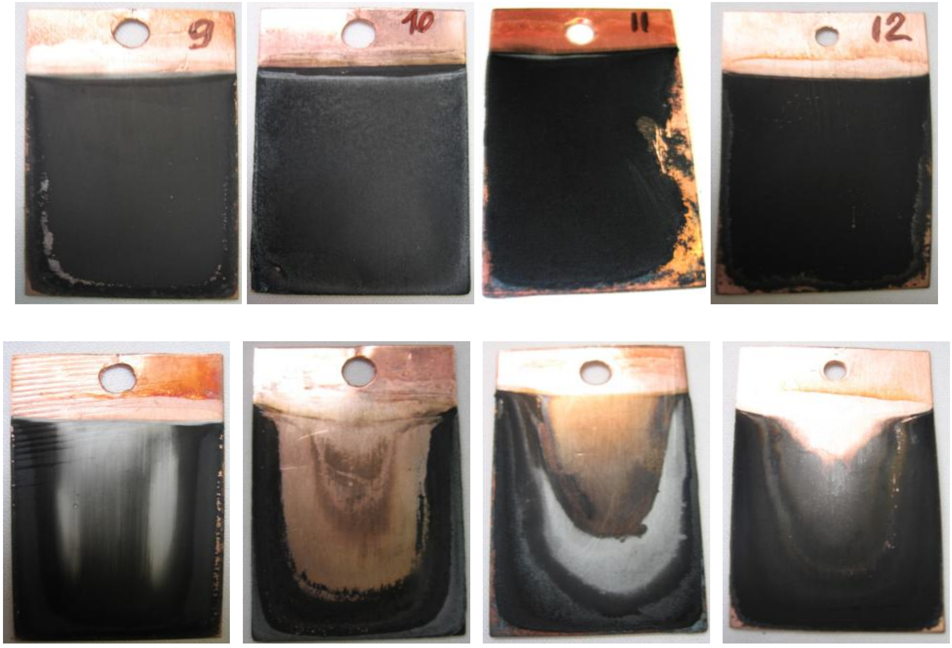


Figure.3.30. *Electroplating black chromium from aqueous solution with* Zn^{2+} *ions*

3.7.5. Electroplating Cr (III) with Zn^{2+} and Fe^{2+} ions

For this experiment we decided to add in solution for electroplating chromium both zinc and iron ions (see Table.3.18). It gave not adhesive coatings (see Figure.3.31).

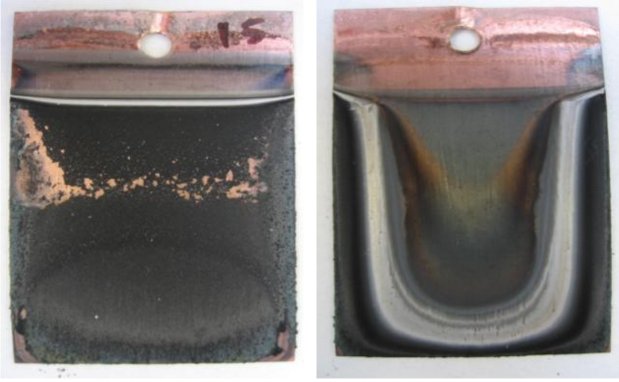


Figure.3.31. *Electroplating black chromium from aqueous solution with* Fe^{2+} *and* Zn^{2+} *ions on copper*

Solution	Voltage [V]	Current [A]	Temperature [°C]	Time [min]	Electrode material	Notes
CrCl3 – 1M; ZnCl2 -15 g/l; FeCl2- 20 g/l; NaH2PO2 – 0,75M; NaF -0,5M; NaH2PO4 -4 g/l	3	1	30	5	(-)Cu/Ti_{Pt} (+)	Nothing
	4,7	2,5	30	5		Nothing
	9,6	5	21	5		Not adhesive

Table.3.18. *Working conditions of electroplating black chromium from aqueous solution with* Zn^{2+} *and* Fe^{2+} *ions*

3.7.6. Apply technique of electroplating in Pyrrole + Tiron solution

We obtained good results in electrodeposition black coatings with solution Pyrrole and Tiron on steel substrate. So we decided to apply this solution on cooper, but covered with chromium (see Table.3.18, Fegure.3.32). For electroplating chromium we prepared following solution: $CrCl_3$ – 266 g/l; NaF – 0,5M; NaH_2PO_2 – 80g/l; $FeCl_2$ – 20 g/l; NaH_2PO_4 – 1 g/l, and for next step: Tyron - 0,5M; Pyrrole – 0,2M.

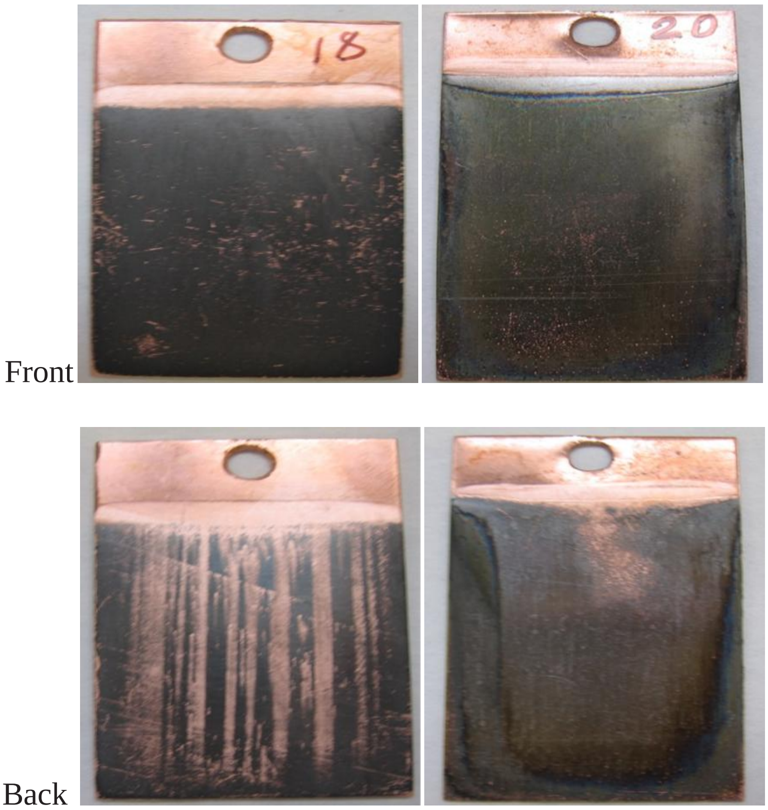


Figure.3.32.*Electroplating in Pyrrole + Tiron solution*

Sample №	Solution	Voltage [V]	Current [A]	Temperature [°C]	Time [min]	Electrode material	Notes
18	Cr(III)	6,6	2,5	41	5	(-)Cu/Ti_{Pt} (+)	-Smooth surface - Got light gray film
	Pyrrole + Tiron	2,0	0,2	18	5		Not adhesive
20	Cr (III)	3,5	1,0	27	5	(-)Cu/Ti_{Pt} (+)	- smooth surface
		5,0	1,5	30	10		- nothing
		5,8	2,0	30	10		-Black-gray spots
		5,4	2,0	30	10		-Not uniform gray film
		5,7	2,0	30	10		-stirring
	Pyrrole + Tiron	2,0	0,1	20	10		-Non uniform -Non adhesive

Table.3.18. *Parameters of electroplating black film on copper*

3.8. Electrodeposition Cr (III) from ionic liquids

Cr (III) chloride hexahydrate and Choline chloride were mixed in a 2:1 molar ratio. The solid mixture was heated at a temperature of around 120°C, with stirring, until no more solids were observed. The product is a liquid which is initially purple in color at 120°C (see Figure.3.33) and a green liquid at 60°C.

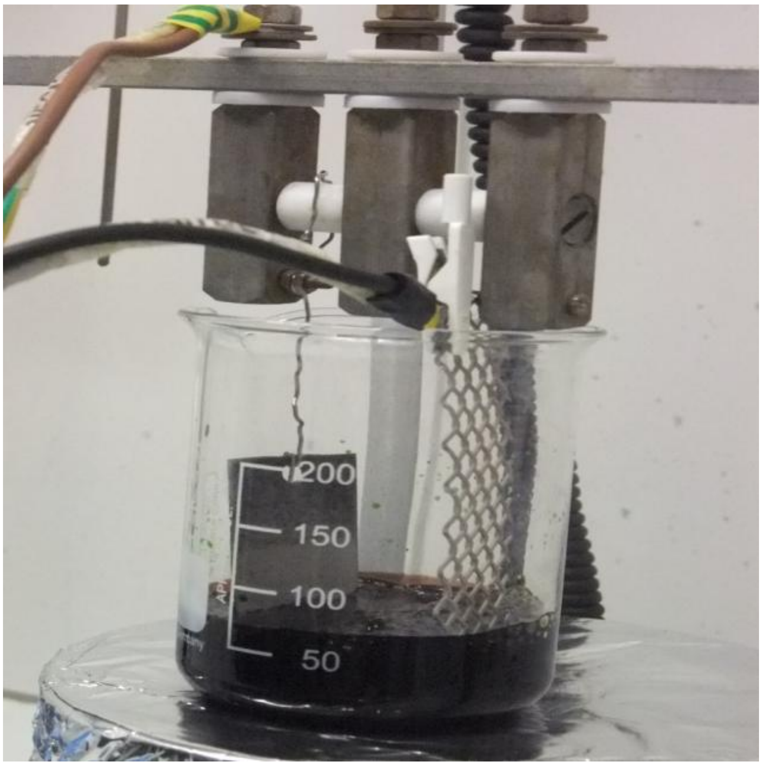


Figure.3.33. *Two electrodes system for electroplating Cr (3+) in ionic liquid*

Platinised titanium plate was applied as anode and connected to the positive terminal of a DC power source, whereas carbon steel was used as the cathode (substrate) and connected to the negative terminal. Prior to introduction into the bath, the substrate plate was cleaned with a soap in ultrasonic bath, washed in ultrasonic with water, dry with ethanol and nitrogen and finally in a 4M HCl aqueous solution. When both plates were connected and introduced into the cell, the voltage difference was to 30 V.

3.8.1. Electrodeposition chromium on steel

We prepared solution as it described in previous part, and got the black coatings on steel substrats (see Figure 3.34).

Figure3.34. *Black chromium on steel substrate from ionic liquid*

Sample №	Voltage [V]	Current [A]	Temp-re [°C]	Time [min]	Electrode material	Notes
43	30	0,2	80	30	(+)Ti(Pt)/steel(-)	High gas evolution
48	30	0,1	110	30	(+)Ti(Pt)/steel(-)	With time solution became more viscous
49	25	0,1	100	30	(+)Ti(Pt)/steel(-)	-
58	30	0,01	110	30	(+)Ti(Pt)/steel(-)	-

Table.3.19. *Parameters of chromium electrodeposition from ionic liquids*

Also we carried out SEM and EDAX measurements. EDAX analysis shows us presence of chromium in our coating (see Figure.3.35). SEM analysis shows that film is well-packed (see Figure.3.36).

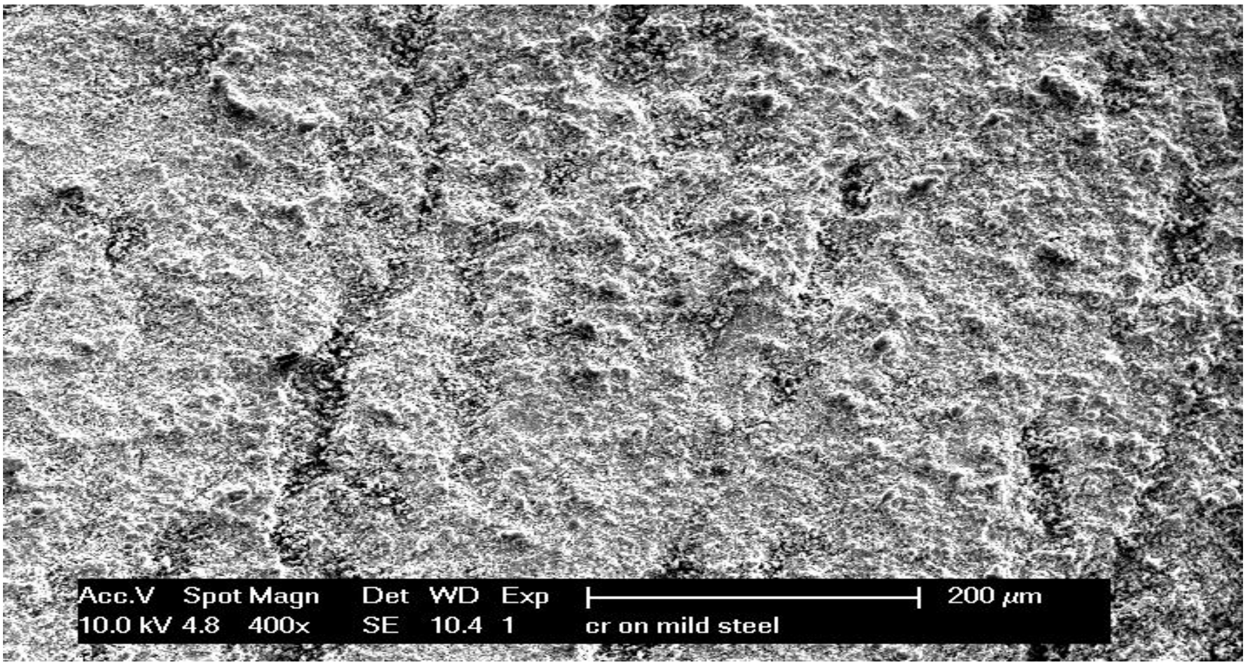


Figure.3.35. *SEM Data of chromium film on steel substrate*

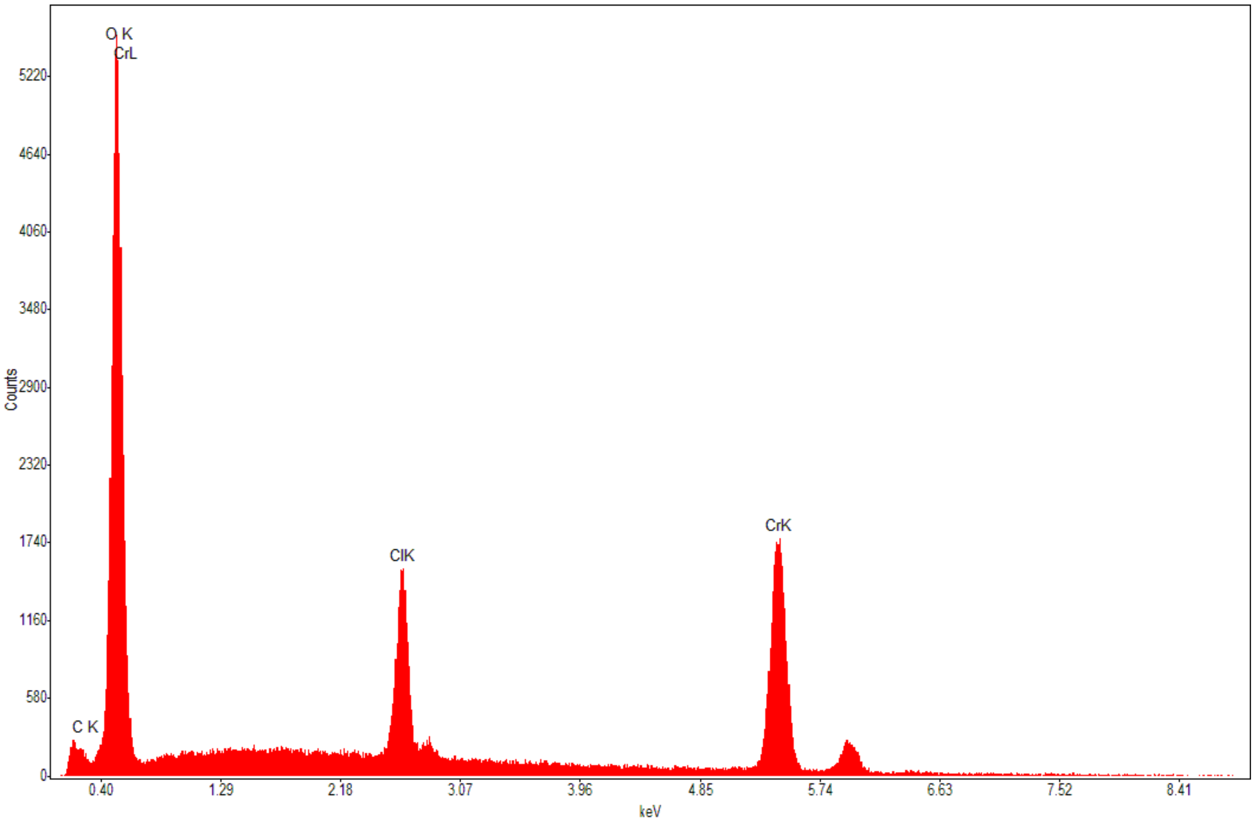


Figure.3.36. *EDAX data of chromium film on steel*

3.8.2. Electrodeposition of chromium on copper

We try to apply the method of electroplating chromium from ionic liquids to copper substrate (see Figure.3.37). For this we prepared samples as usual.

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Figure.3.37. *Electroplating Cr(3+) on copper substrate from ionic liquiud*

Voltage [V]	Current [mA]	Temp-re [°C]	Time [h]	Electrode material	Notes
1.18	2.4	60	2	(+) Ni/Cu (-).	Non uniform

Table.3.20. *Parameters of processe electroplating chromium on copper substrate*

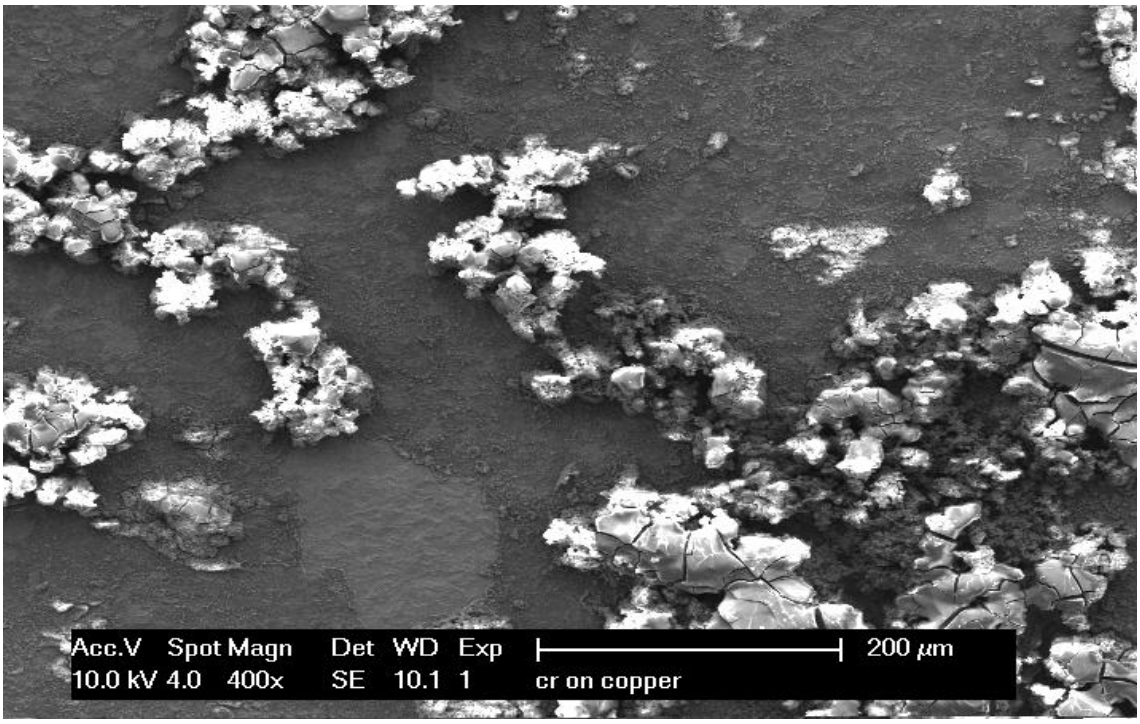

Figure.3.38. *SEM data of chromium film on copper substrate*

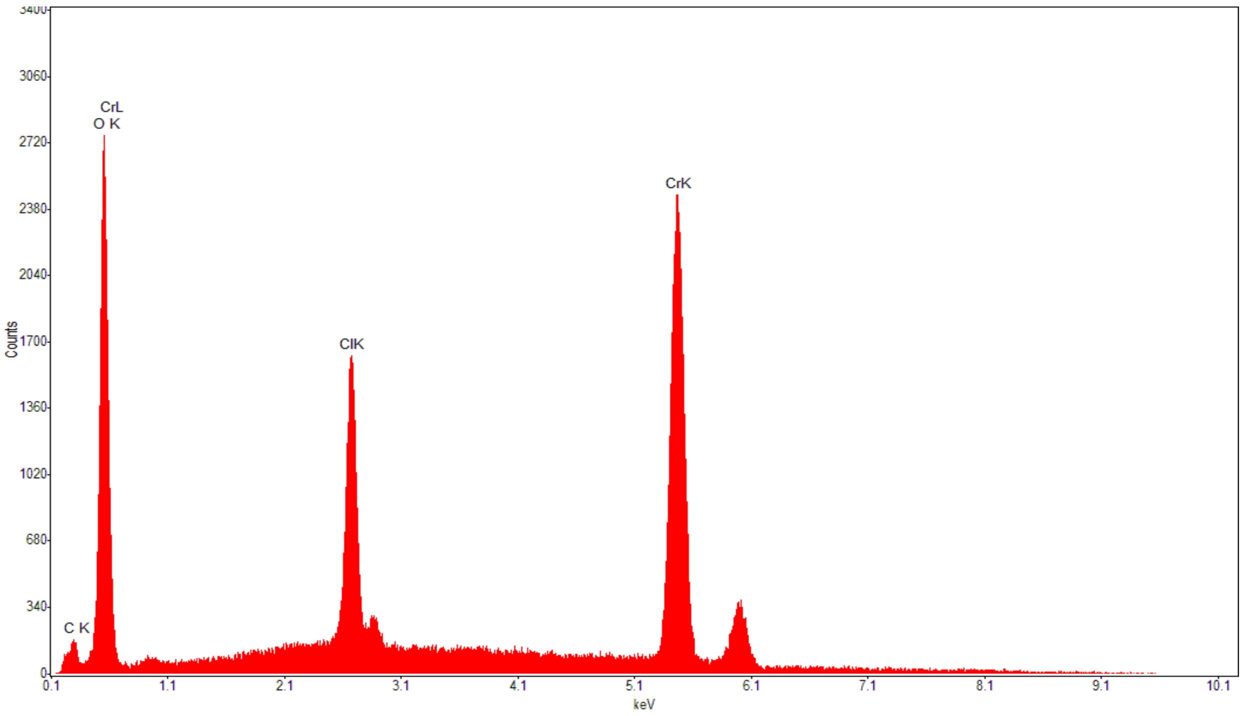

Figure.3.39.*EDAX data of chromium film on copper substrate*

Spectrum analysis shows that we got chromium oxide on copper surface, and as we can see from Figure 3.39. It deposits nonuniformly.

3.8.2.1. Electroplating chromium with zinc from ionic liquid

We try to apply the method of electroplating from ionic liquids to deposit chromium-zinc film on the copper substrate (see Figure.3.40). For this we prepared samples as usual. Solution was prepared in following order: mixed Choline Chloride with chromium chloride and zinc chloride (in molar ratio 1:1:1), heat solution till 80°C (when it became totally liquid).

Sample №	Voltage [V]	Current [A]	Temperature [°C]	Time [min]	Electrode material	Notes
1	27,7	0,2	80	10	(-)Cu/Ti$_{Pt}$ (+)	Nonuniformly
1a	30	0,3	75	30	(-)Cu/Ti$_{Pt}$ (+)	A lot of bubbles
2	30↓22 ↓ 10↑22,3	0,7↑1,4↓0,5	88	60	(-)Cu/Ti$_{Pt}$ (+)	Nonuniformly
2a	19,5	0,2	70	60	(-)Cu/Ti$_{Pt}$ (+)	A lot of bubbles
3	10	0,1	75	2	(-)Cu/Ti$_{Pt}$ (+)	-Nonuniformly -Surface etched in HNO_3

Table.3.21. *Parameters of processe electroplating chromium-zinc film on copper substrate*

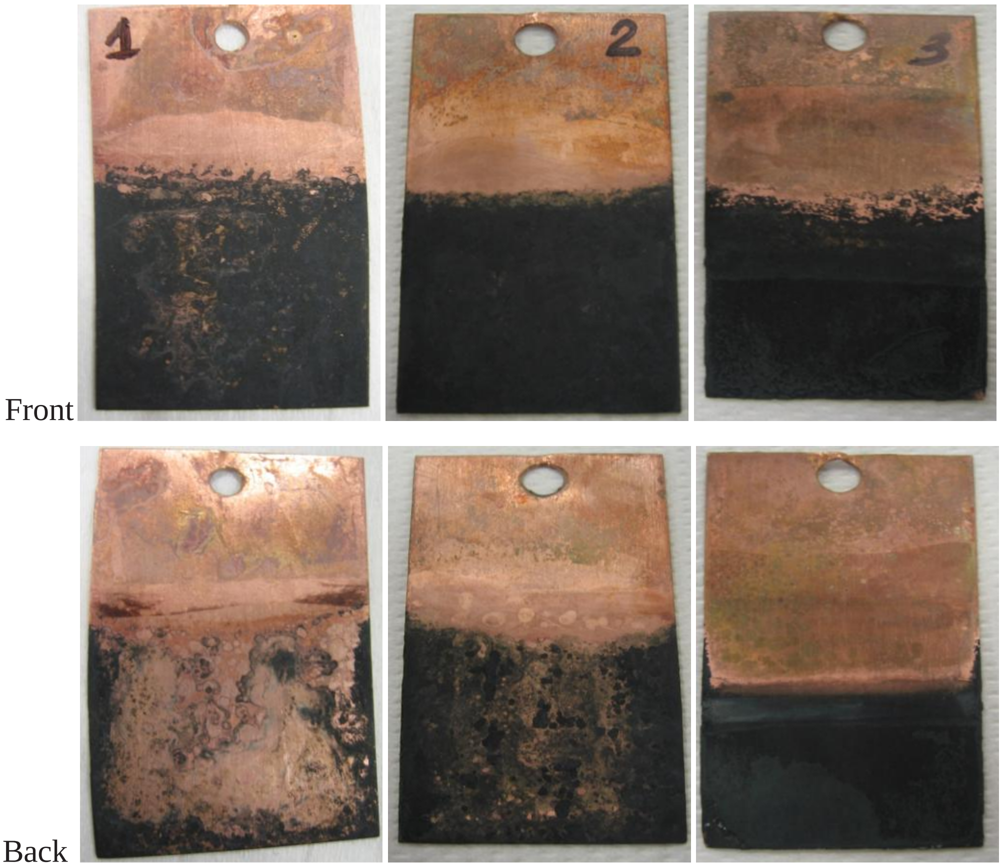

Figure.3.40. *Electroplating chromium-zinc film from ionic liquid*

We carried out SEM and EDAX measurements of chromium-zinc deposit (see Figure.3.41, 3.42). Analysis showed presence both chromium and zinc. The coatings more uniform compare to electrodeposition without presence of zinc ions.

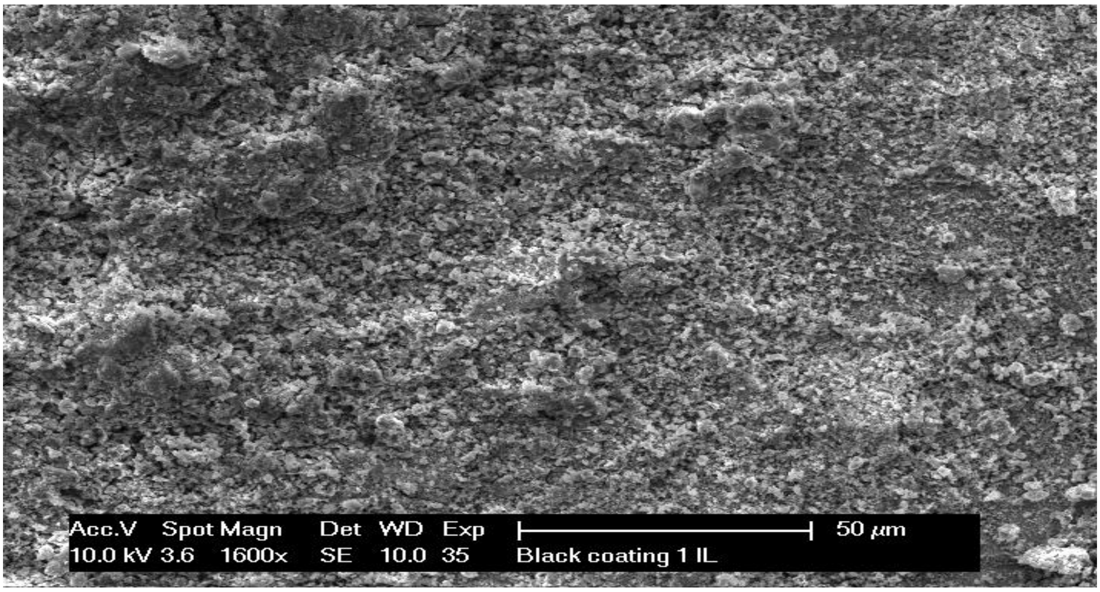

Figure.3.41.*SEM data chromium-zinc film on copper substrate*

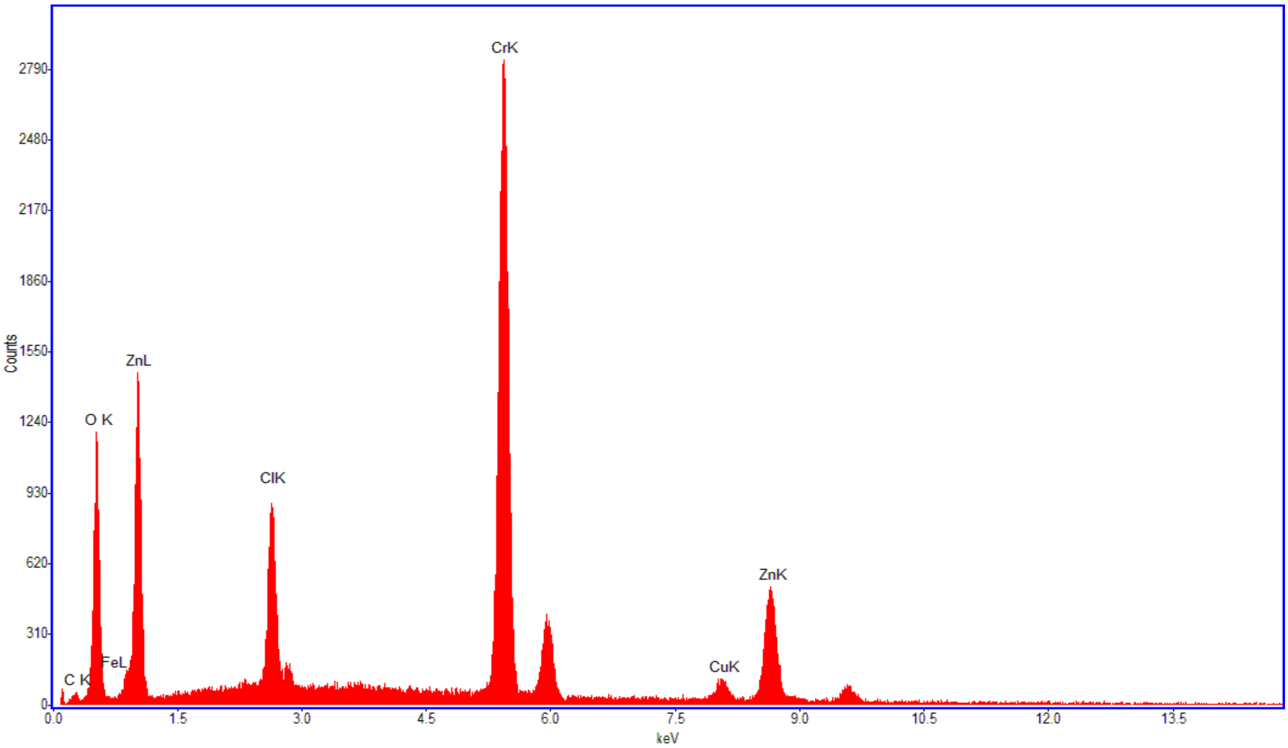

Figure.3.42.*EDAX data chromium-zinc film on copper substrate*

Conclusions:

1. Black Cr films electrodeposited have been electrodeposited in carbon steel and copper.
2. The films are homogeneous and adherent on steel, but not on copper substrate.
3. On copper was electrodeposited black chromium-zinc film, which more dark than chromium deposit.
4. Ionic liquids make it possible to receive the black coatings without using harmful chromium (VI)

4. **Results**

Electroplating Cr (VI) is well-known process. It is quite dangerous, so in this work we try to find alternative recipe. We work with different substrates (aluminum, steel, copper). Used various processes, such as chemical or electrochemical oxidation, and electrochemical deposition. Was made the SEM and X-ray measurements. Shot summary of all recipes which gave useful results for conclusion of work are reported in Table.4.1

Substrate	**Method**	**Results**	**Recommended for further study**
Aluminum	Electrochemical Coloring	- dark brown film -expensive	**Not**
Steel	Electrochemical Oxydation	-black film -stable in vacuum	**Yes**
Steel	Ionic liquids	-black film - adhesive - homogenous	**Yes**
Copper	Chemical oxidation	-black film -not stable in vacuum	**No**
Copper	Electrochemical oxidation	-black film -not stable in vacuum	**No**
Copper	Electrodeposition Cr(III) from aqueous solution	- black film - adhesive - homogenous - stable in vacuum	**Yes**
Copper	Electrodeposition Cr(III) from ionic liquids	- black film - nontoxic solution	**Yes**

Table.4.1.*Recommendation for further study*

Conclusions

In this work several chemical and electrochemical procedures to obtain adherent, black layers onto copper substrate have been proposed. The Coatings have been characterized from morphological and spectrum viewpoints. Potential solutions to electrodeposit black coating for solar absorber surfaces were found.

A textured black copper oxide has been developed by chemical and electrochemical conversion technique (see Table.5.3). From annealing test we obtained that it doesn't resist in vacuum.

Due to the fact black chromium stable in vacuum, we electrodeposited Cr (III) from aqueous solution and from ionic liquids.

The most successful are the recipes for electroplating black coatings resistant in U.H.V. and in air - see Table.5.1, 5.2.

Solution	Substrate	Process parameters	Observations
$CrCl_3$ – 200 g/l; NH_4Cl – 80 g/l; H_3BO_3 – 60 g/l; NaH_2PO_2 – 80g/l; $FeCl_2$ – 20 g/l; NaH_2PO_4 – 1 g/l.	Copper	8,0 V; 5,0 A; 40°C; 5 min; (-)Cu\Ti$_{Pt}$(+)	- Uniform dark film - Stable in vacuum
Tyrone 0,5 M Pyrrole 0,2M	Stainless Steel	2,0 V; 0,2 A; 20°C; 10 min; (-)Cu\St.Steel(+)	- Adherent black film - Stable in vacuum

Table.5.1. *Effective recipes of electroplating black coatings resistant in U.H.V.*

Solution	Substrate	Process parameters	Observations
$AgNO_3$ - 6 g\l; H_2SO_4 - 150g\l	Aluminum	10V; 5min; 25°C	Dark brown film
NaOH – 80 g\l; $(NH_4)_2S_2O_4$ – 6g\l	Copper	5,0 V_{AC}; 9,9 A; 80°C; 30 min	Black, satin deposit
NaOH –9 g\l; $(NH_4)_2S_2O_4$ – 3g\l	Copper	20 V_{AC}; 11 A; 80°C; 10 min	Brown copper sulfide

Table.5.2. *Recipes of electroplating black coatings resistant on air*

Methods	Material of substrates	Obtained coatings	Analysis of coatings	Notes
Electrochemical colouring	Aluminum	Brown aluminum oxide	Not carried out	- Expensive - not black
Chemical oxidation	Copper	Black Copper oxide	Not carried out	Non uniformly covering
Chemical oxidation with prior preparation of the surface	Copper	Copper oxide	- Annealing test on air - Annealing test in vacuum	- Non uniformly covering - Non resist in vacuum
Electrochemical oxidation using DC	Copper	Black copper oxide	-Annealing test in air - SEM and EDAX mesurments	Non stable coatings
Electrochemical oxidation using AC	Copper	Brown copper sulfide	- X-ray analysis - SEM measurment - Annealing test on air - Annealing test in vacuum	- Uniform, black deposit - Not stable in vacuum
Electrochemical oxidation	Steel	Black iron oxide	- SEM and EDAX mesurments - Annealing test on air - Annealing test in vacuum	- Well adherent coatings - Stable in vacuum
Electroplating Cr (III) from ionic liquid	Steel	Black chromium oxide	SEM and EDAX mesurments	Non uniform deposit
Electroplating Cr (III) from ionic liquid	Copper	Black chromium oxide	SEM and EDAX mesurments	Non uniform deposit
Electroplating alloy of chromium and zinc from ionic liquid	Copper	Black deposit	SEM and EDAX mesurments	Non adhesive
Electroplating Cr (III) from aqueous solutions	Copper	Black chromium oxide	- Annealing test in vacuum - SEM and EDAX mesurments	- Uniform covering - Stable in vacuum

Table.5.3 *Summary table of results*

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