ELECTROPLATING

INTRODUCTION

Electroplating is a branch of electrochemistry concerned with the deposition of metals on the surfaces from the solutions (plating). The role of metal coatings is i.e., corrosion protection, adjusting properties of a surface, decorative purposes, and a slight change of the dimensions of an item.

Corrosion protection

Corrosion is a spontaneous process of deterioration of any material due to its interaction with the environment. The environment consists of many factors, including the presence of water, the presence and concentration of ions (e.g., Cl⁻), polarity/non-polarity of a medium, pH, temperature, and time.

Electrochemical corrosion protection mitigates corrosion by shifting the potential of the corroding material/environment interface into the safe range. To achieve this, we can use:
- corrosion inhibitors (anodic and cathodic) to the environment,
- anodic and cathodic corrosion protection of a material.

In **cathodic protection**, the protected material has a higher potential than the other material. Hence, the protected material is a cathode, while the protector an anode. Cathodic protection encompasses the following methods:
- shifting potential of the protected material in the negative direction (impressed current cathodic protection),
- using a sacrificial anode, which dissolves (corrodes) instead of the protected material (e.g., zinc coatings on steel, magnesium bars on ships).

When a protected material is an anode (has a lower potential) it is called **anodic protection**. Anodic protection includes:
- shifting the potential of the protected material in the positive direction using an external power supply to reach a passive state,
- adding alloying additives (e.g., nickel, chromium, titanium, platinum) during the production of a protected metal/alloy,
- plating metal coatings, that exhibit higher potential (cathodes) than the protected material (e.g., copper coating on a steel surface).

Galvanic coatings

In terms of metal plating, the coatings can be divided into the following groups:

1. **Protective coatings** - applied in order to protect the surface of a metal against corrosion.

The anodic coating has a lower potential (it is an anode) than the protected metal (cathode). It means that an anodic coating is a method of cathodic protection. It protects the metal both mechanically and electrochemically against the influence of the environment. If the coating is damaged and the substrate metal becomes exposed, it is the coating (anode) that will dissolve into the environment instead of the substrate. An example is the zinc coating on steel. The zinc coating, when intact, prevents corrosive substances from reaching the underlying steel or iron. In the case the underlying metal becomes exposed, protection continues as long as there is zinc close enough to be electrically coupled. After all of the zinc in the immediate area is consumed, localized corrosion of the base metal can occur:
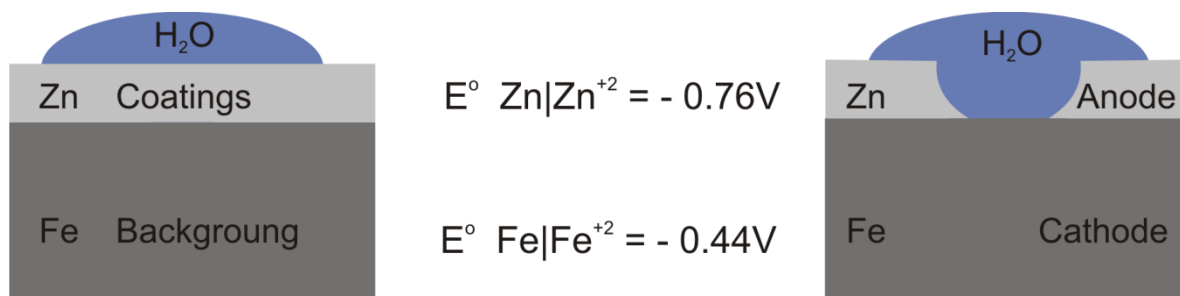
Figure 1. Cathodic protection. The protected metal has a relatively higher potential.

The most common situation is to apply the metal protective layer of higher electrochemical potential (cathode) than the potential of the protected metal (anode). This case is a **cathodic coating** (anodic protection). An example is the nickel layer on steel, which can be a decorative layer and provide corrosion resistance at the same time. However, in case of damage to the surface, the protected metal starts corroding:
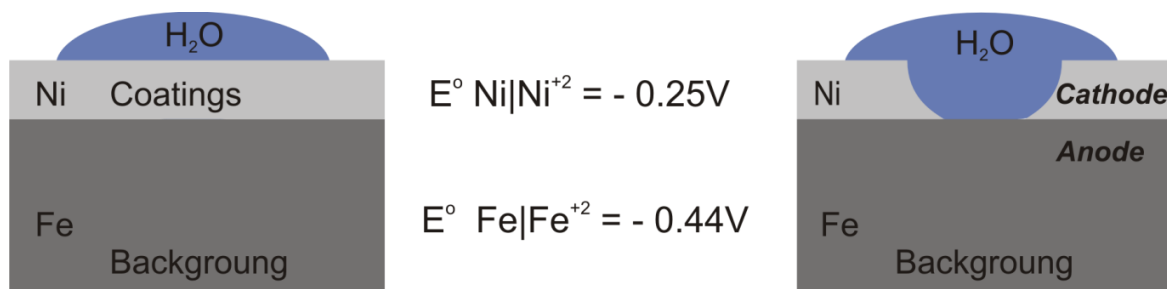

Figure 2. Nickel protective layer. The protected metal has a relatively lower potential.

**2. Decorative coatings** are applied to improve the appearance of the surface of the substrate.

The most important requirements for decorative metal coatings include permanent colour, lustre, and resistance to colour changes or tarnish. They are often applied to impart a specific colour, but also to create a particular reflective property such as gloss or matt. Chrome, gold, rhodium, palladium, and platinum are the most commonly used metals as decorative coatings. The thickness of these coatings may be very small (in the order of micrometres).

3. Technical coatings - are used to change certain physical and technological properties of the substrate surface, such as increased hardness, wear resistance, changing the coefficient of friction, improving the electrical properties of the surface, improving the ability to connect by soldering, changing the dimensions of the covered part of the regeneration of worn parts, etc.

Metal coatings can be formed by the **electroplating** method or **electroless deposition**.

Electrochemical methods of metal plating are based on current flow through the electrolyte-metal boundary. The externally applied voltage supply is used. In this case, the growth of the metallic layer is easy to control. For

example, during the electrolysis of copper ions from an acid solution, the coating of copper is formed on the substrate surface as a result of the reduction of Cu^{2+} ions:

$$Cu^{2+} + 2e^- \rightarrow Cu^o \qquad \text{(cathode)} \qquad (1)$$
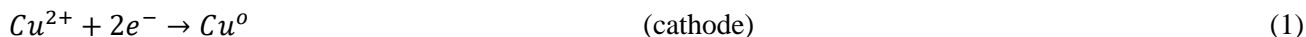
To prevent the concentration loss of Cu^{+2} ion in the solution, the anode is made of plate or copper, so that during the electrolysis it is dissolved:

$$Cu^o \rightarrow Cu^{2+} + 2e^- \qquad \text{(anode)} \qquad (2)$$
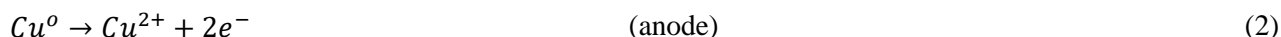
Using a soluble anode allows to maintain the concentration of deposited metal ions at a constant level. Such constructions are used in the majority of electroplating processes. This is not always possible, however. In the case of chromium, anodes are made of lead. During electrolysis, oxygen is deposited on the anode, and therefore the concentration of chromium in the bath decreases so that there is a need to refill its concentration by dissolving the appropriate component.

During the deposition, the current density and thus the thickness and quality of the coatings formed are dependent on the geometry of the system.

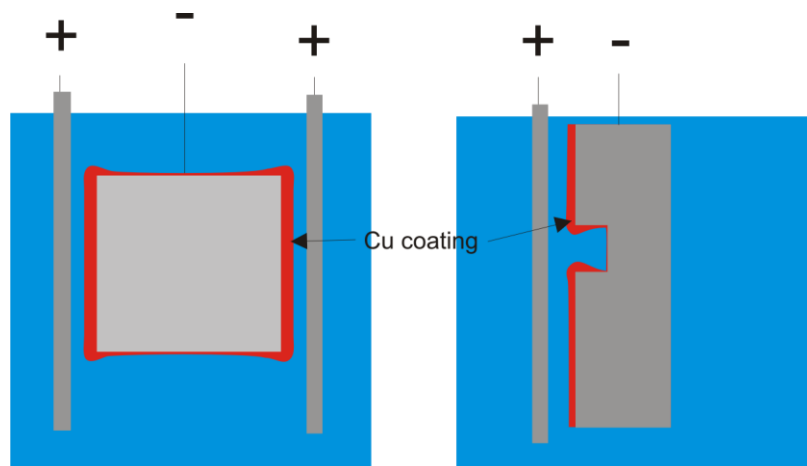To avoid these negative effects, specially selected shapes of anodes and screen shields to cover the corners are used.

Figure 3. The thickness of the metal coatings depends on the electrolyser geometry.

Electroless deposition processes are applied where no current is supplied from an external source**.** A major benefit of this approach over electroplating is that the power sources and plating baths are not needed, reducing the cost of production.

There are three basic methods of electroless deposition of metals:

1. Coating by **exchange reaction** - the more noble metal (of higher potential redox) is displaced from the solution by the less noble metal (of lower potential redox). An example is an iron object immersed in a Cu^{2+} solution where a reaction occurs on the surface:

$$Fe + Cu^{2+} \leftrightarrows Cu + Fe^{2+} \qquad (3)$$

Coating takes place until the entire surface of an iron substrate gets covered with copper, and then further reaction will be terminated.

2. **Coating by chemical reduction** – is based on the chemical reduction of metal ions to a metallic state by the redaction agent – a substance present in the solution for electroless deposition. An example of this reaction is so-called 'the silver mirror reaction' (this reaction takes place in an alkaline ammonia solution, and ammonia complex is an intermediate product):

$$Ag^+ + 2NH_4OH \rightarrow [Ag(NH_3)_2]^+ + H_2O$$

$$2[Ag(NH_3)_2]^+ + RCHO + H_2O \rightarrow 2Ag^o + 4NH_3 + ROOH + 2H^+$$

(4)
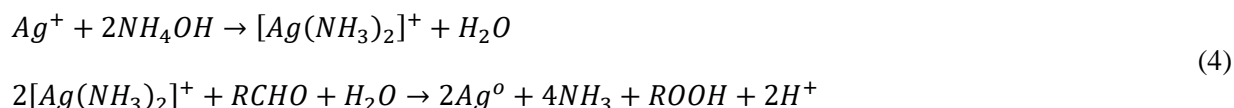
Metallic silver as a product of the reaction settles on the surface of the coated object. However, a reduction reaction takes also place in the bulk of the solution.

3. **Catalytic coating** - is a variation of the chemical reduction, except that the reduction reaction takes place only in the presence of a catalyst. When a catalyst is placed on the surface of the metal or the metal itself is a catalyst, the reduction takes place only on the surface, rather than throughout the entire volume of solution, which leads to savings in the bath solutions.

Widespread nickel covers are formed by the catalytic reduction method.

The reaction involves the reduction of nickel by molecular hydrogen, which is derived from the decomposition reaction in the solution hypophosphite:

$$Ni^{+2} + 8H_2PO_2^- + 2H_2O \rightarrow 2Ni^o(s) + 6H_2PO_3^- + 2H^+ + 2P^o(s) + 3H_2(g)$$

(5)
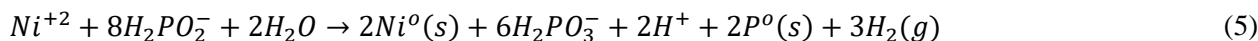
The reaction yields orthophosphate, elemental phosphorus, and protons. The phosphorus is commonly built in the nickel layer. The reaction is catalysed by cobalt, iron, aluminium, and nickel. Thus, the reduction reaction begins spontaneously on the surface of these metals, and, because nickel is also the catalyst, coating takes place until the desired thickness.

Both the current processes and electroless deposition of the metal-coated surface of the object require several preparatory operations:

1. Mechanical grinding (sanding) and polishing
2. Rinsing after grinding
3. Organic solvent degreasing
4. Rinsing after degreasing
5. Etching in dilute acids
6. Rinsing after etching

The quality of the galvanized coating depends on several factors:

1. Bath temperature
2. Concentration of bath components
3. Bath pH
4. Current density
5. Applied voltage
6. Geometry of the counter electrode (anode)
7. Bath purity

OBJECTIVE OF THE TASK

The purpose of this exercise is to cover the steel washers for bolts with a layer of copper, a nickel layer, and a layer of nickel-copper.

APPARATUS

- DC power supply
- Microscope for observation in reflected light
- Tray for copper plating
- Copper wire hanger
- Thermostat U-10
- Cables – 3 pcs

LAB GLASS

- $25 \, cm^3$ beakers - 5 pcs.
- $800 \, cm^3$ beaker – 1 pc
- Petri dish -1 pc
- Self-adhesive tape
- Scissors
- Forceps
- Sandpaper

CHEMICALS

- Nickel plating bath (per $1000 \, cm^3$):
  - Nickel chloride, $NiCl_2 \cdot 6H_2O$ - 30g
  - Sodium hypophosphite, NaH_2PO_2 - 12g
  - Sodium acetate, CH_3COONa - 10g
  - Distilled water   - up to $1000 \, cm^3$
- Copper plating bath (per $1000 \, cm^3$)|
  - Copper sulphate, $CuSO_4 \cdot 5H_2O$ - 200g
  - Sulphuric acid, H_2SO_4 - 75g
  - Distilled water   - up to $1000 \, cm^3$
- Organic solvent for degreasing (chloroform)
- Sulphuric acid for etching (10% H_2SO_4)
- Carbon steel washers

EXPERIMENTAL PROCEDURES

1. In this exercise, steel washers for bolts should be coated according to the list below (7 washers should be prepared):
   - (Fe) – 1 pcs remain as reference (after cleaning procedure)
   - (Cu) – 1 pcs covered by Cu in electroless deposition (chemical exchange reaction)
   - (Cu) – 1 psc covered by Cu in the electroplating process by the use of a current of 0.1 A
   - (Cu) – 1 psc covered by Cu in the electroplating process by the use of a current of 0.01 A
   - (Ni) – 3 pcs covered by electroless deposition of Ni (catalytic reduction)
     - (Ni - Cu): electroplating of Cu on steel washers previously covered by Ni at 0.1A
     - (Ni - Cu): electroplating of Cu on steel washers previously covered by Ni at 0.01A

2. Pre-treatment of steel washers to cover the metallic coatings:

   7 steel washers must be cleaned with sandpaper. Then steel washers should be washed with distilled water and placed in a 25 cm³ beaker containing an organic solvent. After 2-3 minutes, move the washers **using tweezers** to the second beaker with distilled water. After 2-3 minutes, transfer them into a beaker filled with sulphuric acid and etching for about 30 seconds. Place the etched steel washers in another beaker of water. After being washed, the washers are prepared for coating.

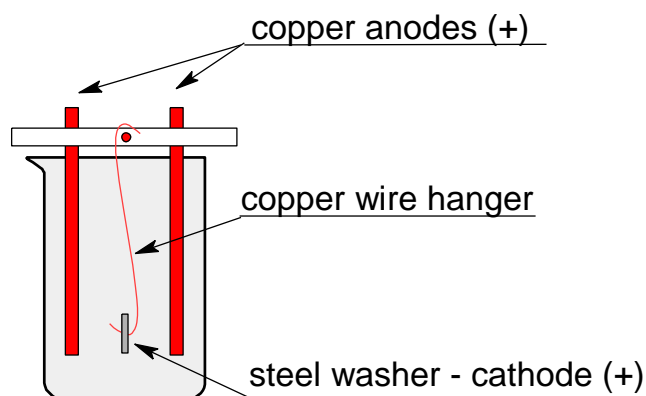3. Copper coating processes are carried out in a vessel presented in Figure 4.

Figure 4. Beaker system to copper plating.

4. Hang the washer on a hook and dip in the bath. After a while (1-2 min), take it out and note the observation. Subsequently, connect the electrodes to the power supply, set the appropriate value of the current, and hang a new washer (do not turn on the power supply by yourself, follow the teacher's instructions). Copper coating time is 10-15 minutes. The copper washers should be rinsed thoroughly with tap water and then with distilled water.
5. For nickel coating (3 pieces), place washers in a 25 cm³ beaker filled with a solution containing the nickel plating bath in an amount sufficient to cover the bottom of the underlying plates. Then place the beaker in a thermostat chamber for 20-30 minutes, at 70°C. After that, rinse them with tap water and then with distilled water.
6. The quality of coatings is evaluated visually under a microscope.

W a r n i n g !
1. The number of washers is given per 1 student performing the exercise.
2. Solution for copper plating after work should be poured back into the reagent bottle.

PREPARATION OF A REPORT

1. After completing the observations, the steel washers with various coatings should be fixed with adhesive tape to the report. Describe the results of observation and compare the properties such as layer thickness, adhesion of the layers with the substrate, and resistance to scratching.

2. Based on the performed experiments, propose the optimum conditions for copper plating.

Template of the table and draft of the study

……………………….. *Faculty* ………………………….. *Field of study* *Full-time/ part-time studies*	…………………………………… *Name and surname*	…………………………….... *Date:*
Group no.: ……………… Team no.: ………………	………..……………… *Exercise no.:*	………………………………….. *Instructor:*

……………………….. *Wydział* ………………………….. *Kierunek* *Studia stacjonarne/niestacjonarne*	…………………………………… *Imię i Nazwisko studenta*	…………………………….... *Data wykonywania ćwiczenia:*
Nr grupy: ……………….. Nr zespołu: ………………..	………..……………… *Nr ćwiczenia:*	………………………………….. *Nazwisko Prowadzącego:*

1. Temat ćwiczenia
2. Cel ćwiczenia:
3. Wstęp teoretyczny:
4. Pomiary:
5. Obliczenia:
6. Wykresy:
7. Wnioski

1. Exercise title:
2. The aim of the exercise:
3. Theoretical introduction:
4. Results:
5. Calculations:
6. Graphs:
7. Conclusions: