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Experiments

COATING METALS WITH ZINC AND METHOD FOR MEASURING THE THICKNESS OF THE LAYER

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Abstract. When a copper coin is immersed with zinc into a solution of a zinc salt ($ZnSO_4, ZnCl_2$, etc.) an electrochemical reaction occurs in the mixture. As a result, a thin layer of zinc appears on the surface of the copper which gives the impression for silver color. The purposes of this project are: to explain the phenomenon and to investigate relevant parameters; to measure the thickness of the zinc layer; to determine which metals can be covered with zinc in such experiments. Method for measuring the thickness of the zinc layer was obtained by using dimension properties of the coin – radius, height and mass. The advantage of this method is the fact that it can be applied for all metals whose form has an integrable volume. The thickness of the layer was determined to be in the order of 1 $\mu m \mu m$. The relationship between the thickness of the zinc and the time at which the coin has spent in the solution was also studied and an exponential tendency was observed. It was proved that only metals after hydrogen in the Reactivity series can be plated with zinc with this setup.

Keywords: zinc layer; electroplating and electroless plating; redox reactions; Reactivity series of metals

1. Plating reactions

Plating is a surface coating technique, which has been used for hundreds of years, in which a metal is being deposited on a conductive surface. In particular, zinc metal has the characteristic to be corrosion protective coating for iron and steel substrates. Zinc coatings prevent oxidation of the protected metal. Its oxide is a white powder that does not cause a breakdown of the substrate's surface coherence (zinc is also used for the plating of most of the hardware parts). In the industry, these reactions can used to prevent the further oxidation of the corroding metals. There are several plating methods – electroplating, electroless plating, vacuum deposition, vapor deposition, etc.[1),2)]

1.1. Electroplating

Electroplating represents the processes which result in metal coating through redox reactions by applying a direct electric current. In this scenario, the substrate acts as the cathode, the anode is the piece of the metal, and the electrolyte is a solution of a salt of the metal to be coated.[3)]

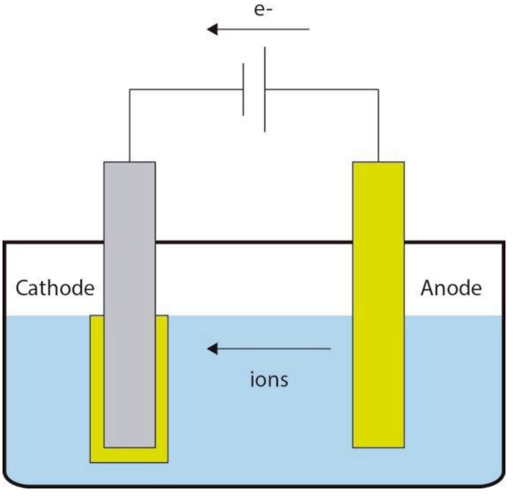

Figure 1. General scheme for electroplating in a liquid bath[4)]

1.2. Electroless plating

Electroless plating is a set of chemical processes that happen spontaneously in a liquid bath (there is no need of electric current to drive the plating which differentiates the electroless plating from electroplating)[5)]. For example, when zinc granules or powder are immersed in a solution of zinc chloride the metal starts to dissolve and two electrons are released and are strictly connected to the surface of the granule (the zinc has the role of an electrode). The dissolving process is reversible (Varbanova et al. 2020).

$$Zn_{(s)} \leftrightarrow Zn^{2+}_{(aq)} + 2e^{-}$$

Eq.1. Redox reaction of zinc metal

On the phase boundary between the metal and the solution electric double layer occurs and subsequently a potential difference (in our case called electrode potential). The electrode potential is the driving force of the reactions (Varbanova et al. 2020).

When we add the copper coin in the reaction mixture and when we ensure that there is a direct contact between the coin and the zinc granules, the electrons that were released through the electrochemical reaction will transfer onto the surface of the coin. Thus, the reduction of the zinc cations will happen onto the copper.[6)]

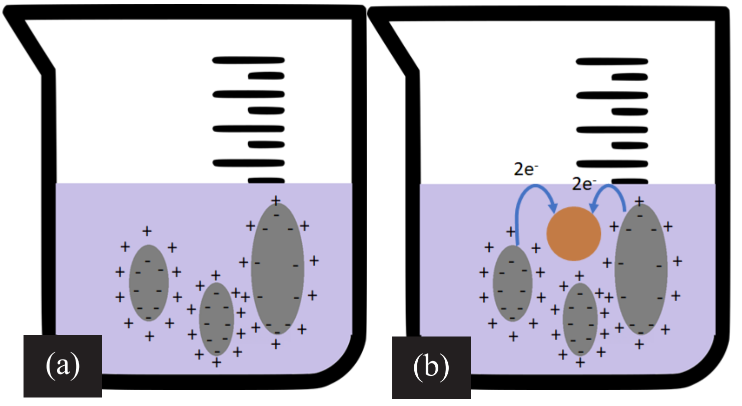

Figure 2. (a) Solution of zinc salt with zinc granules, electrode potential between the coin and the solution; (b) Immersion of copper coin, transfer of electrons to the copper surface, reduction of zinc ions

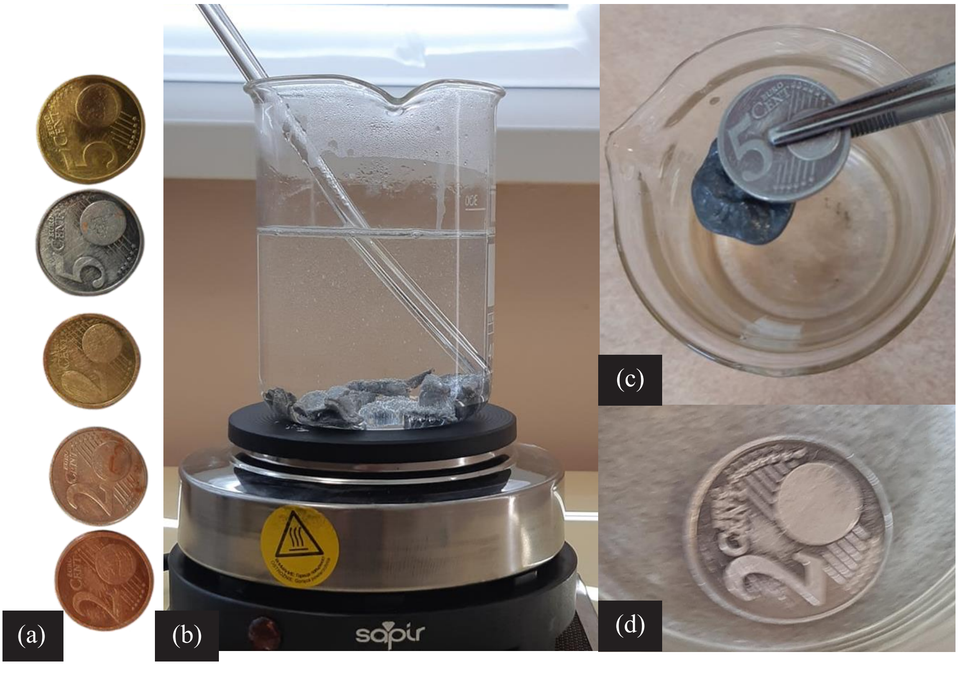

Figure 3. (a) Demonstration of plated and brass coins; (b) Preparing the reaction mixture; (c) and (d) Removing the coins from the solution and cooling them in cold water

2. Theoretical model for measuring the thickness of the layer

The coin can be approximated as a cylinder with radius rr and thickness (height) $h.h$. We can determine the volume of the coin with the following formula:

$$V_1 = \pi r^2 h$$

Eq.2. Initial volume of the coin

After the plating reaction we obtain another cylindrical coin with radius $r_1 = r + d$, height $h_1 = h + 2d$, where d is the thickness of the zinc layer. We can determine the volume of the coin one more time:

$$V_2 = \pi(r + d)^2(h + 2d) = \pi hr^2 + 2\pi hrd + \pi hd^2 + 2\pi r^2 d +$$

Eq.3. Volume of the coin after the plating

The difference between the two volumes will give us the volume of the zinc metal which can be estimated using the mass of the zinc and its density.

$$V_2 - V_1 = 2\pi d^3 + \pi(h + 4r)d^2 + 2\pi(hr + r^2)d = \frac{m_{Zn}}{\rho_{Zn}}$$

Eq.4. Difference between the volumes of the coins

Finally, we have obtained the following third-degree equation for the unknown d:

$$2d^3 + (h + 4r)d^2 + 2(hr + r^2)d - \frac{m_{Zn}}{\pi\rho_{Zn}} = 0$$

Eq.5. Third-degree equation of d

This equation can be solved analytically by dividing the equation with the leading coefficient (in this case 2), obtaining the normalized cubic equation and removing the square member with substitution. Thus, the canonical form of the cubic equation is derived ($x^3 + px + q = 0$) which is then resolved with Cardano's formula. However, in this project numerical method – Newton's method – is presented.

Newton's method is a root-finding algorithm which produces approximation of the roots of a real-valued function. The idea of the algorithm is to start with an initial guess which is significantly close to the real root, then to approximate the function by its tangent line at this guess and finally to estimate the x-intercept of the tangent line. [7)]

Let's define the real-value function $f: f \rightarrow R$ and let's have a current approximation x_n. Then the x-intercept of the tangent line at the point $(x_n, f(x_n))$ is

$x_{n+1}x_{n+1}$. Let us now observe the triangle with sides the tangent line, $f(x_n)$ and $|x_{n+1} - x_n|$. We can derive the following expression (look at fig.4):

$$tg\theta = \frac{f(x_n)}{x_n - x_{n+1}} = f'(x_n) \Rightarrow$$

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$$

Eq.6. Newton's iterations

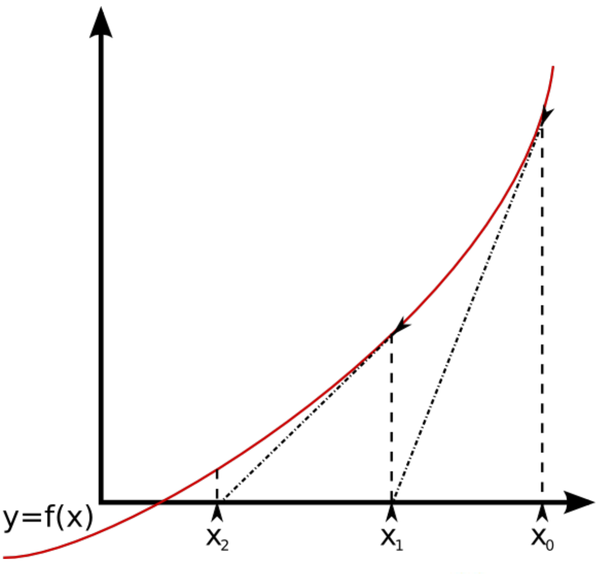

Figure 4. Newton's root-finding algorithm, the angle $\theta\theta$ in the described triangle

3. Properties of the coins

To solve the equation described above we should first determine the values of the radius and the thickness of the coin and the mass of the coated zinc. For this project we have used 5- and 2-euro cents which are copper-coated steel coins (makes them perfect for the purposes of the task).[8),9)] Thus, we can get the values of its dimensions (diameter and height) from the website of the European Central Bank (look at Table 1).

For measuring the mass of the coin, we should follow the **procedure**: First, the oxide layer is removed off the coin's surface by using an abrasive material (the rough part of the sponge is perfect for this aim). To remove any traces of fats or other organic compounds the coin is cleaned with both acetic acid and acetone. The coin is let to dry well and after that is measured with analytical balance (KERN, 0.001g accuracy). The solution of $ZnCl_2$ and Zn is prepared (300ml water, 10g salt, 10g zinc) and is heated to 88.6°C or until the water starts boiling. The coin is immersed, let to spend some time in the solution, then removed and cooled in cold water. The mass of the coin is measured one more time.

It is important to note that this setup is not fully precise, and it is possible that the zinc is not distributed equally to the whole surface. So, after obtaining the value of d, this will not be the actual thickness of the layer but the average value of the thicknesses of the layer of all different spots on the coin.

Table 1. Some quantities of the coin[10)]

coin	diameter	thickness
5-euro cents	21.25 mm	1.67 mm
2-euro cents	18.75 mm	1.67 mm
1-euro cent	16.25 mm	1.67 mm

4. Procedure for estimating d

Excel worksheet is generated. The first two cells from the second row are filled with the coefficients of the second and first degree of d and the third cell – with the free-standing coefficient, the next two cells are for the iterations of the root and the function.

Table 2. The thickness of 5-euro cents which spent 10 min in the solution

***h* + 4*r*, mm**	***2hr* + 2*r*², mm²**	***m*/(πp),mm³**	***x*, μm**	***f* (*x*), mm³**
44.17	261.27	0.31	1000	306.13
			131.82	34.90
			3.96	0.73
			1.19	**≈0**

To ensure that there are no more roots the graph of the function can be observed (fig. 5a).

On Figure 5a, the y-axis corresponds to the value of the function $f(d) = 2d^3 + (h + 4r)d^2 + 2(hr + r^2)d - \frac{m_{Zn}}{\pi \rho_{Zn}}$. Obviously, the graph has 3 intercepts of the x-axis. However, only one of them is positive. From fig. 5b it can be seen that the positive root is approximately 0.0012 mm which corresponds to our estimations for the thickness of the layer.

This procedure is done also for 2-euro cents coin.

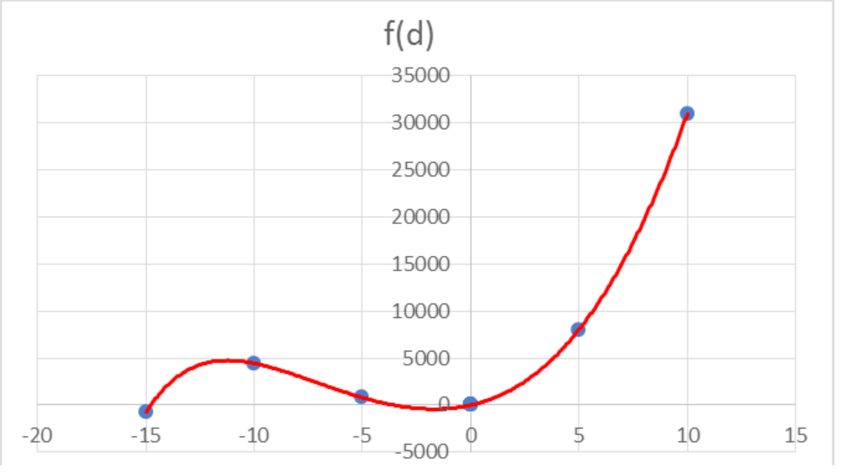

Figure 5. (a) Graph of $f(d)$ for $[-15, 10]$

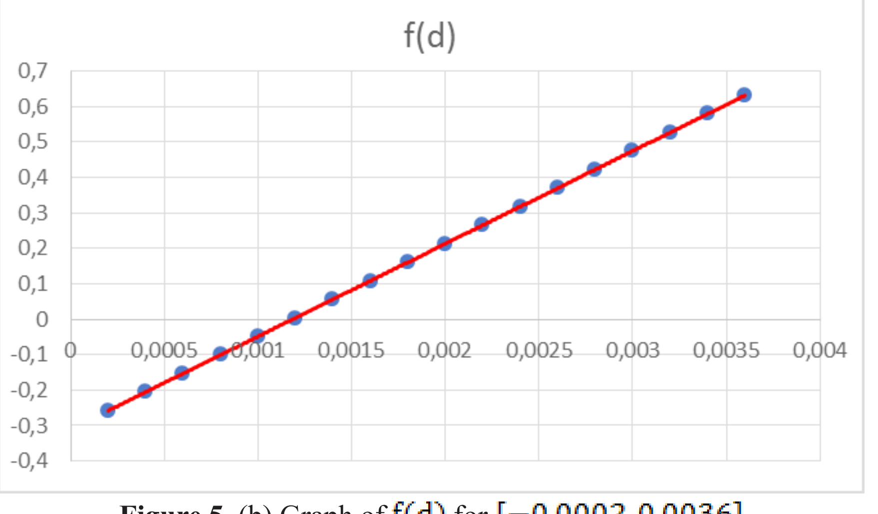

Figure 5. (b) Graph of $f(d)$ for $[-0.0002, 0.0036]$

5. Results

After spending in the solution 10 minutes the 5-euro cents coin obtained zinc layer with thickness of 1.19 μm. As for the 2-euro cents, 1.47 μm were calculated. Also, for both the calculations 3 iterations of the algorithm were necessary. The thickness of the layer was examined at different times at which the coin has spent in the mixture. We have predicted the following trend:

$$d(t) = d_{\infty}(1 - e^{-kt})$$

Eq.7. Exponential relationship between d and t

Here, d_{∞} is the thickness after a considerable amount of time and k is a constant. The results are presented in the graphs:

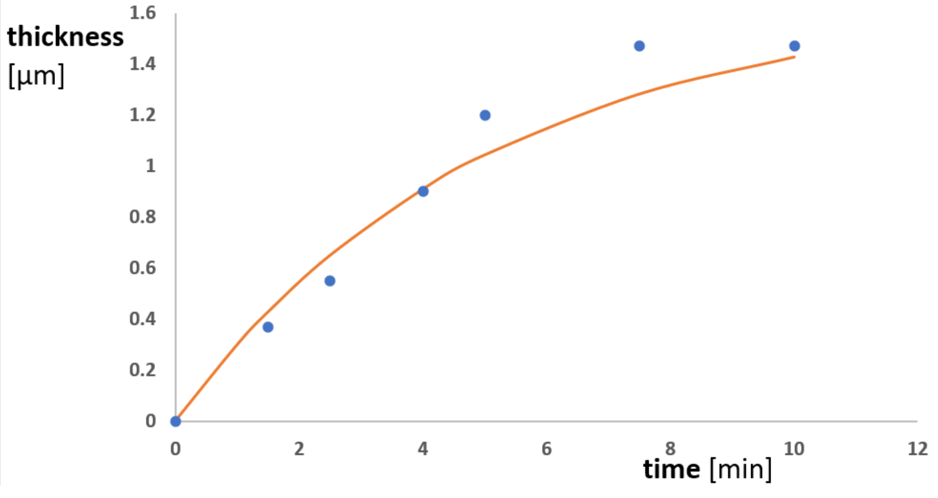

Figure 6. (a) 2 euro cents trend line, $\boldsymbol{d(t) = 1.65(1 - e^{-0.2t})}$

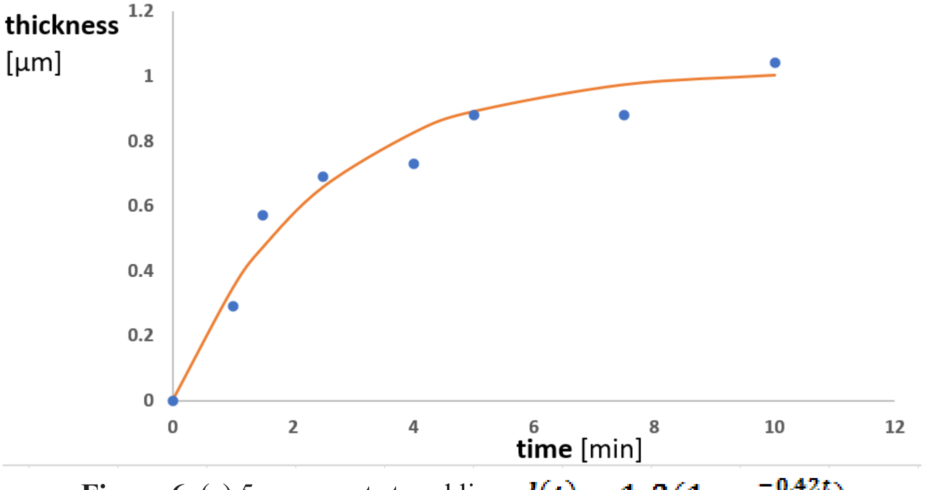

Figure 6. (a) 5-euro cents trend line, $\boldsymbol{d(t) = 1.2(1 - e^{-0.42t})}$

Criteria for metals that can be plated with zinc

The dissolving of metals is a reversible process and for some metals (due to their nature, those who stand after the hydrogen in the Reactivity series) the backward reaction starts with higher rate. That is also the case for the copper. Its dissolving equilibrium can be expressed with the equation:

$$Cu^{2+}_{(aq)} + 2e^{-} \leftrightarrow Cu_{(s)}$$

Eq.8. Dissolving of copper

However, in the reaction mixture there are only zinc cations and there are not any copper cations so the copper cannot dissolve, and the plating occurs. As a conclusion, all metals that stand after the hydrogen in the Reactivity series of metals (they cannot start dissolving) can be plated with zinc at the described setup. For instance, metals that can be plated with zinc are Cu, Ag, Pt, Au, etc. and metals that can't be plated with zinc: Mg, Be, Al, Fe, Cd, Ni, etc. That statement can be tested experimentally by using the described procedure for Al and Ni. We have used aluminum foil as a source of aluminum and some nickel-copper coins (50 and 20 pence from 1997) for Ni.

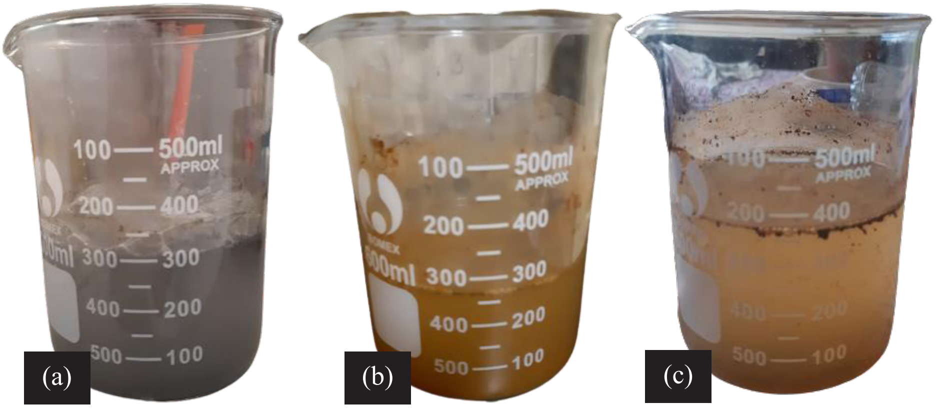

Figure 7. (a) The zinc solution before adding anything and after heating up; (b) The zinc solution after the immersion of the nickel coins; (c) The zinc solution after the immersion of aluminum foil

After spending 20 minutes in the reaction mixture there were not observed any significant changes to both the coins and foil except some zinc lumps which were cleaned immeddiately in cold water. Note that there is difference between forming lumps and layer. The layer is formed due to the described electrochemical reactions and the lumps were formed because of the substrate being stucked with the powder.

On Fugure 7 it can be seen that there is change in the color of the original solution. That is because the aluminum (stands before zinc in the RSOM) replaced zinc and produced $AlCl_3 AlCl_3$ which is white. However, aluminum foil consists also of some amount of iron which in the solution produced iron (III) chloride (changes the color of the sample to yellow, fig. 7c) [11]. On the other hand, nickel dichloride (supposed to be yellow) with combination of zinc powder produces brownish color (seen on fig. 7b) [12]. This means that nickel and aluminum have partially dissolved which confirms our hypothesis.

7.Conclusion

When the copper coin is immersed together with zinc in a solution of zinc chloride electroless plating reaction occurs and a thin layer of zinc appears onto the coin surface. The phenomenon was explained. Different types of plating reactions were mentioned and a detailed mechanism for electroless plating was presented. Third-degree equation for the average thickness of the deposited zinc was derived and Newton's numerical algorithm was used for the solution. Thicknesses of the layers were estimated to be in the order of 1 μm. Criteria for metals that can perform in such reactions was shown and proved – only metals after hydrogen in RSOM can be plated with zinc using the described setup.

8. Acknowledgements

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