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The influence of current density and electrodeposition time on the quality of nickel coating

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Abstract

Nickel is one of the most important metals deposited by electrodeposition. The obtained coatings serve as a barrier between the metal and the aggressive medium, which slows down or prevents the occurrence of corrosion. Bright nickel coatings are electrolytically deposited on a brass substrate using a bright nickel plating electrolyte containing $NiCl_2$ $6H_2O$, $NiSO_4 \cdot 6H_2O$ and H_3BO as a base. The pH of the electrolytes was in the range of 4-4.6, and the temperature was 48-55°C. The influence of current density and deposition time on the quality of the metal coating and its corrosion stability was examined. It was experimentally determined that the best light nickel coating is achieved at a current density of 2 to 3 A/dm^3 and a duration of 10 min.

Keywords: Brass, nickel coating, current density, time, electrodeposition

1. Introduction

Applying a coating of a chemically stable material on the surface of a less stable material is the most widespread method of corrosion protection [1]. Thanks to the ability to protect technically important metals from corrosion, good mechanical properties and beautiful appearance, nickel coatings are the most important of all metal coatings [2]. The obtained coatings serve as a barrier between the metal and the aggressive medium, which slows down or prevents the occurrence of corrosion [3]. The coating depends on the type of coating, its thickness, degree of compactness and its adhesion. The base metal, which is covered with another metal for the purpose of protection, affects the choice of the type of metal for the coating as well as the method of applying that coating. Galvanization is the most widespread procedure of applying metal coatings to metal and non-metal objects by electrolysis of ionic solutions, i.e. electrolyte [4]. It is based on the cathodic reduction of metal ions from the electrolyte using electric current [5]. Objects are immersed in an electrolyte containing metal ions whose coating is applied and connected to the negative pole of a low-voltage direct current source (4-10 V), i.e. as a cathode. The anode is usually metal that is applied as a coating, and is connected to the positive pole of the direct current source. In this case, the anode is dissolved or oxidized during the process and thus compensates for the ions consumed by cathodic deposition from the electrolytes. Brass is subject to an electrochemical process of selective corrosion by which zinc dissolves in contact with the electrolyte (dezincification process), leaving behind a porous layer of copper [6]. Bright nickel coatings are characterized by high gloss and good surface alignment with subsequent chrome plating. The basic material on which it is applied is steel, copper, brass, aluminum or stainless steel [7]. Electrochemical metal deposition includes ion transport, ion adsorption, multistage charge transfer, nucleation and other deposit growth phenomena [8, 9]. During the deposition of nickel, the discharge of metal ions and protons takes place simultaneously, so the utilization coefficient of the deposition current depends on the composition of the electrolyte and the density of the deposition current. According to the assumed mechanisms of iron group metal deposition, the reduction is a two-step electrochemical reaction and can be represented by the following equations [10-15]:

$$Ni^{2+} + e^- \rightarrow Ni^+_{ads} \tag{1}$$

$$Ni^+_{ads} + e^- \rightarrow Ni \tag{2}$$

The process takes place by passing a constant current through two electrodes that are immersed in the electrolyte, in which the nickel salts are dissolved. The action of the current causes the anode to melt, which results in the cathode being covered with nickel. Watts' solution is most often used for the electrochemical nickel plating process, given that other solutions (e.g. sulfate) are also increasingly used. Watt's solution gives glossy or semi-glossy coatings [16]. The rate of nickel deposition on the base material depends on several parameters, one of the most significant of which is the current density distribution. In the literature, one can find a large number of studies describing the application of constant and periodically variable regimes of electrochemical deposition [17-25]. If we talk about the influence of the current density on the quality of the coating, we can say with certainty that the higher the current density, the higher the rate of crystal cores formation, resulting in a finer-grained metal deposit [26]. Therefore, with the increase in current density, the overvoltage on the cathode also increases. Also, if there is an increase in the current density above a threshold, critical value, there will be an increase in the pH-value of the electrolyte [27]

The objectives of the work are to examine the influence of current density and deposition time on the thickness of the coating and to compare the visual appearance of the Ni coating based on the investigated parameters using the Hull test cell.

2. Experimental part
2.1 Material and Methods
A brass tile was chosen as the base material for testing the application of the nickel coating, and in accordance with the tested parameters. The brass plate was first cleaned and prepared for plating. As an electrolyte for bright nickel plating, a commercial electrolyte was selected, the main ingredients of which are presented in table 1:

Table 1: Electrolytic solution composition and plating parameters

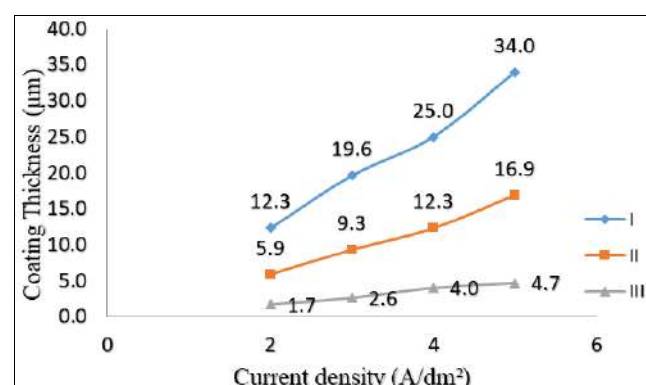| Chemical Name	Composition
Nickel Sulfate ($NiSO_4 \cdot 6H_2O$)	10 g/L
Chloride ($NiCl_2 \cdot 6H_2O$)	10 g/L
Boric Acid (H_3BO_3)	10 g/L
Operating Conditions Bath	
Temperature	48-52 °C
Type of Agitation	Air
Anode	Nickel
Cathode	Brass
pH	4
Current Density	2-5 A/dm^2
Plating Time	10 minutes

The standard coulometric method, also known as the anodic solution or electrochemical removal method according to ISO 2177, was used to measure the coating thickness. The analysis was performed for each sample at three different marked locations. Hull's cell was used to determine visual quality and the presence of pitting. Hull cell test was performed on brass plates, mixing was done using compressed air, at a temperature of 50-55 °C. Test duration: 10 min. The test was performed for 8 different nickel-coated brass tiles, 4 for tiles whose current density interval during plating ranged from 2-5 A/dm^2 at a constant time of 10 min, and 4 for tiles whose time interval ranged from 5-20 min, at a constant current density of 2 A/dm^2.

3. Results and Discussion
Table 2 shows the difference in the weight of samples before and after bright nickel plating carried out at different current densities, and diagram 1 shows the influence of current density on nickel coating deposition. From the obtained results (table 2), variations in the weight of the coatings can be observed, where it is clearly seen that the thickness of the nickel coating increases linearly with the increase in current density.

Table 2: The weight of the tested sample before and after the nickel plating process

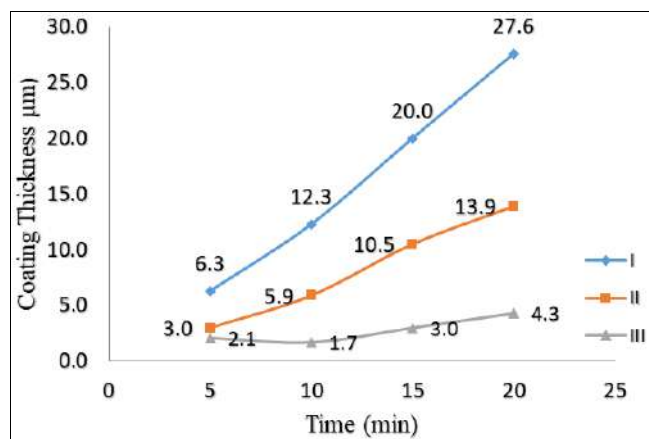| Current density (A/dm²)	The weight of the sample (g)		
	before	after	coating
2	15.78	16.15413	0.37413
3	15.76	16.37990	0.6199
4	15.75	16.54199	0.79199
5	15.78	16.78364	1.00364

Fig 1: Diagram of the dependence of the current density on the thickness of the nickel coating

The results showed that applying a current density of 4 A/dm^2 causes slight twisting and damage on the left side, and using a current density of 5 A/dm² also causes damage on the tile on the far right side. Also, after 3 min., and then after 8 min., there was a change in amperage and voltage. The formation of coarse secondary nodules (current density of 4-5 A/dm^2) is the result of the autocatalytic activity of the initially formed coating, while the basic layer is the result of nucleation. Therefore, as the current density increases, defect regions such as crystal boundary volume and double boundary volume increase thereby increasing the amount of microstrain. From the obtained results, it can be concluded that the optimal current density for the examined sample ranges from 2 to 3 A/dm^2. The actual thickness at any point on the surface of the molded object depends on the current density at that point. The current density at the protrusions is higher due to the shorter anode-cathode distance and the lower resistance to current that implies. Conversely, recessed areas, further away from the anode, will have a lower current density due to increased flow resistance. This means that raised areas will have thicker coatings than recessed areas. Therefore, the limiting diffusion current density on a flat plate electrode along which the electrolyte flows in a laminar manner decreases along the electrode, i.e. there is a distribution of current density along the electrode. The obtained results of the thickness of the investigated coatings obtained in the electroplating process are presented in table 3, and show that the distribution of the current density is not the same in all points at the same deposition conditions.
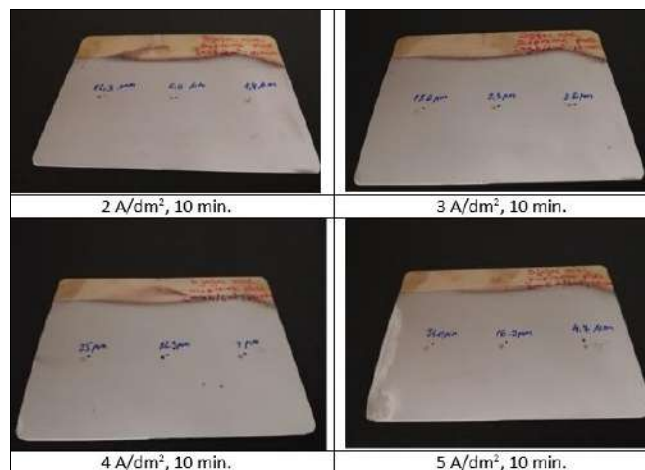
Table 3: Variation of coating thickness distribution depending on current density

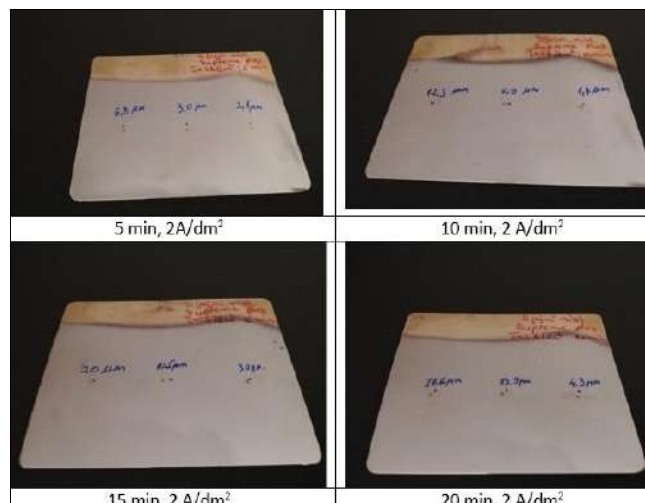| Current density (A/dm²)	Time t (min)	Coating thickness (µm)			Average thickness (µm)
		Point I	Point II	Point III	
2	10	12.3	5.9	1.7	6.63
3	10	19.6	9.3	2.6	10.5
4	10	25.0	12.3	4.0	13.76
5	10	34.0	16.9	4.7	18.53

Figure 2 shows a diagram of the dependence of the deposition time interval and the thickness of the nickel coating. The obtained results presented in Figure 2 show that the thickness of the nickel coating increases linearly with time, which indicates a constant rate during deposition, but non-linearly at all points. This can be attributed to the fact that the cathodic current efficiency remains constant for increasing application time from 5 to 20 min. An almost constant current efficiency was observed, which indicates constant electrochemical reactions taking place at the anode and cathode. This shows that the application time will have a direct effect on the thickness of the coating. There is an increase of about 100% in the coating thickness value for the 10 minute application time compared to the coating thickness for the 5 minute application time.

Fig 2: Diagram of dependence of coating thickness and deposition time

The obtained results of the Hull cell test are shown in Figure 4, where it is possible to visually see the influence of the current density on the quality of the coated coating on each of the tiles obtained. The visual appearance is very important for the quality of the shiny nickel coating, which is one of the main reasons why this method of surface protection is chosen for certain positions. Due to the very shape of the cell, the tile on which the protection is applied has different current densities along the entire surface, which gives us important information for the nickel plating process itself. Using this tool, it is possible to predict the results of the nickel plating process in production and show the influence of the current density on the power of applying the electrolyte and the quality of the coating. In the photos shown, we can see that the power of application (covering) increases with increasing current density (Figure 3). However, at current densities of 4 and 5 A/dm², peeling and damage to the tile (burning) occurs. From the obtained results of the Hull cell test, it can be concluded that the optimal current density for applying a nickel coating to brass ranges between 2 and 3 A/dm².

Fig 3: Display of Hull plates at different current densities

Based on the obtained results (Figure 4), we can see that the application power does not change significantly with time, at a constant current density of 2 A/dm².

Fig 4: Display of Hull tiles at different time intervals

4. Conclusions

1. The improved properties of brass are obtained by coating it with metals that are basically more resistant to corrosion and have a decorative role. Nickel is one of the most important metals that is electrodeposited on brass.
2. The thickness of the nickel coating increases linearly with increasing current density. The results showed that using a current density of 4 A/dm² causes slight twisting and damage on the left side (strong current), and using a current density of 5 A/dm² also causes damage on the coating on the far right side. From these data, it was determined that the optimal current density is in the range of 2-3 A/dm²
3. The current density distribution is not the same at all points under the same deposition conditions. The actual thickness at any point on the surface of the molded object depends on the current density at that point.
4. The results show that the Ni coating thickness increases linearly with time, indicating a constant rate during deposition, but non-linearly at all points. Therefore, the time period during which the substrate is immersed in the electrolyte is the main factor in determining the thickness of the resulting coating.

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