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INVESTIGATION OF TWO-STEP METALLIZATION PROCESS OF PLASTIC 3D PRINTS FABRICATED BY SLA METHOD

This paper presents the results of experiments on metallization of plastic elements produced using 3D printing technology from the light-hardened resins. The obtained coatings were bimetallic (Cu/Ni). The first step of metallization was the electroless deposition of copper. The second one was electrodeposition of nickel on the previously prepared copper substrate. The parameters of 3D prints preparation and metallization processes were deeply investigated.

The etching of plastics substrates and duration of electroless metallization of 3D prints by copper were analyzed. In the next step the influence of nickel electrodeposition time was investigated. The coating were analyzed by XRD method and morphology of surface was analyzed by scanning electron microscopy (SEM). The thickness of coatings was calculated based on mass differences and measured by using optical microscopy method. The optimal parameters for both processes were specified.

Keywords: Electroless Deposition, Electrodeposition, Thin Films, Metallization, 3D Printing

1. Introduction

The 3D printing technology is more and more popular due to its number of application and possibilities to produce elements directly from digital project, high accuracy and complicated shape at low amount of waste. Often in this technology plastics are used, but depending on the purpose, the prints can be improved by additional properties through applying metallic coatings. It gives the combination of properties of plastic and metal. The metallized plastic elements are characterized by easy formability, low weight, durability, lower cost and corrosion resistance, electrical and thermal conductivity.

Metallization of plastics is well-known process [1] which has many applications, for example in the automotive, aerospace industry or electronics [2], medicine [3], household industry or interior design. Generally, the metallic coatings are obtained using few techniques like physical vapor deposition (PVD) [4], chemical vapor deposition (CVD) or electroless metallization [5-8]. The processes based on electrochemical reactions have several advantages, namely it is relatively cheap processes, there is not required specialized equipment. Also, there is a possibility to obtain different types of coatings, both metallic and alloys. However, these processes demand the optimization of processes parameters depending on the established properties of deposits.

Currently, research related to metallization is developing for the final use in the production of capacitors [9][10] or microdevices systems controlled by a magnetic field [11].

The aim of this work is the optimization of metallization process. The experimental part consists of electroless deposition of copper and nickel electrodeposition on light-hardened resin. The work is a preliminary stage of synthesis of micro elements with possibility of controlled transport by magnetic field.

2. Experimental section

The experimental part has been divided into few steps: 3D printing of samples, preparation of plastic elements, electroless deposition of copper and electrodeposition of nickel.

The elements were made with the use of the 3D printing method in SLA (stereolithography) technology on Formlabs Form 2 printer from light-hardened resin (Clear – GPCL02) indicating chemical resistance. The printed elements were cleaned in isopropyl alcohol to remove the liquid resin from the surface. The surface analysis was made by the confocal scanning microscopy (Fig. 1). There are visible layers of hardened resin, with the thickness equal to 50 μm

The preliminary preparation of surface for electroless metallization is few steps process carried out at different conditions. The bath composition, concentration of components and parameters of processes are gathered in Table 1. After every step the samples were washed in distilled water and dried. All chemicals were supplied by Avantor company and were of analytical purity.

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TABLE 1

Parameters for electroless copper deposition on the resin surface (Clear – GPCL02)

No.	Name of process	Parameters			
		Bath composition	Amount / Concentration	Time [min]	Temperature [°C]
1	Degreasing	NaOH, [wt. %]	5	5	50
2	Etching	Cr_2O_3, [g]	50	5-10	60
		95% H_2SO_4, [cm^3]	1500		
		H_2O, [cm^3]	250		
3	Neutralization	HCl, [wt. %]	5	3	25
		$K_2S_2O_5$, [wt. %]	5		
4	Sensitization	$SnCl_2$, [g/dm^3]	10	3	25
		35% HCl, [cm^3/dm^3]	50		
5	Activation	$AgNO_3$, [g/dm^3]	2	3	25
		25% NH_4OH, [cm^3/dm^3]	10		
6	Metallization	$CuSO_4 \cdot H_2O$, [g/dm^3]	10	30-180	25
		$C_4H_4O_6NaK$, [g/dm^3]	50		
		37% HCHO, [cm^3/dm^3]	10		

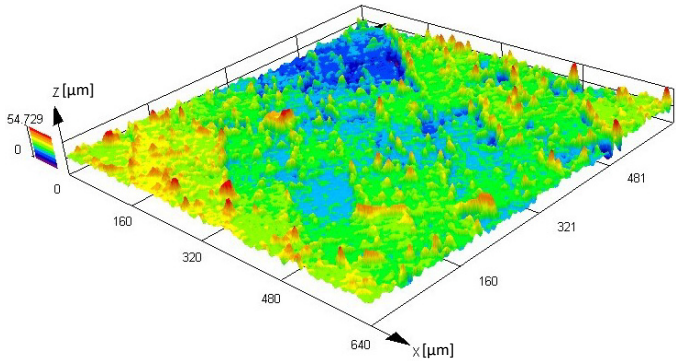

Fig. 1. 3D view of plastic elements surface

The bath for etching process consists of chromium (VI) compound which indicates oxidizing properties and sulfuric acid as reagent increasing these properties of Cr_2O_3. During the neutralization process the reduction of Cr (VI) to Cr (III) ions form takes place. This step is needed due to fact even the slight amount of Cr (VI) ions transported to next baths oxidizes the reducing substances. The aim of sensitization is an adsorption of Sn (II) ions on the plastic surface. During activation silver as precious metal is reduced by tin ions and deposited on plastic surface. Minor amount of precious metal is a catalyst in reaction of chemical deposition of copper.

The electrodeposition of nickel was carried out in room temperature (25°C). The electrolyte composition is presented in Table 2. The electrodeposition processes were realized in three electrodes cell. The working electrode was plastics covered by copper, the counter electrode was platinum sheet (Pt) and the reference electrode was standard calomel electrode (SCE).

The thickness of obtained coatings has been determined by two method. The theoretical one was calculated based on mass change of samples before and after processes. The experimental thickness was determined by optical microscopy method. The cross-section of samples was observed and the thickness was measured from the pictures at least three times and averaged.

TABLE 2

Composition of electrolyte used in electrodeposition of nickel

Bath composition	[g/dm^3]
$NiSO_4 \cdot H_2O$	190
$NiCl_2 \cdot 6H_2O$	30
NH_4Cl	25
H_3BO_3	30

The measurements were conducted at constant temperature of 298 K. Elemental analysis was performed using the SEM technique (Hitachi Su-70). Phase analysis was performed using the XRD method (Rigaku MiniFlex II). All electrochemical measurements were performed with the use of potentiostat/galvanostat AutoLab PGSTAT30.

3. Results and discussion

The theoretical thickness of coatings was calculated from the change of samples mass before and after processes:

$$d = \frac{(m_2 - m_1) \cdot 10000}{D \cdot S} \tag{1}$$

Where: d – thickness [µm], m_1, m_2 is a mass of sample before and after metallization respectively [g], D – density of metal [g/cm^3], S – area of the surface [cm^2].

Influence of etching time

The first analyzed parameter was the etching time. This process took place at higher temperature in the solution described in Table 1. There were analyzed samples without etching and after 2, 5 and 10 min of etching process. The others processes – neutralization, sensitization, activation and metallization – were carried out at constant parameters, specified in Table 1. The copper electroless deposition was carried out for 90 min.

On the sample without etching no metal deposit was observed on the plastic surface. After 2 min etching the coating was

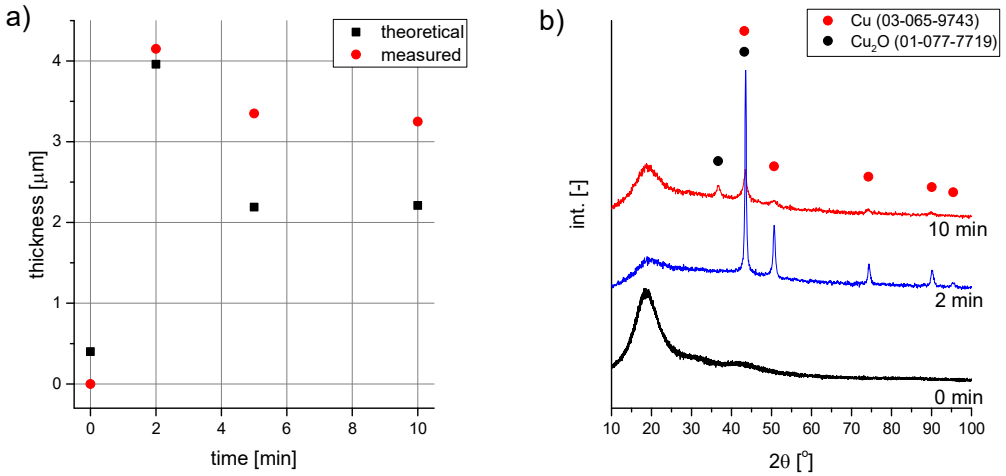

Fig. 2. Thickness and XRD analysis of copper coatings obtained after electroless deposition at different etching time: a) theoretical and measured thickness, b) X-ray diffraction patterns

steady and tight. The longer time of etching results inhomogeneous and unstable coatings. The color of deposit was dark brown.

The calculated and measured thickness of the obtained coatings are presented in Fig. 2a. In samples obtained after short period of time, it is quite good correlation between theoretical and experimental values. The largest thickness was obtained in experiments with etching time equal to 2 minutes. For metallization after longer etching of samples there is observed decrease of amount of deposits. The difference between measured and calculated values probably come from non-homogeneous crystal growth on the plastic surface, resulting in dendritic form of the morphology.

Fig. 2b shows the XRD curves of obtained coatings as a dependence of etching time. Analyzing the diffraction pattern obtained for the sample etched during 2 minutes sharp peaks coming from metallic copper are visible. In the sample etched during 10 minutes peaks at angle 36.63 and 43.21 coming from copper oxide (Cu_2O) are detected. The presence of Cu_2O probably contributes the cracking of the coatings and causing the dark color of deposit.

In no etching case no deposit and no peaks at XRD pattern was observed. Higher intensity of XRD patterns was observed close to 2θ (equal to 20°) angle. It comes from the plastic substrate. Lower intensity observed at this area provides good covering of plastics.

SEM pictures shown in Fig. 3 present the morphology of copper coating obtained after etching time equal to 2 and

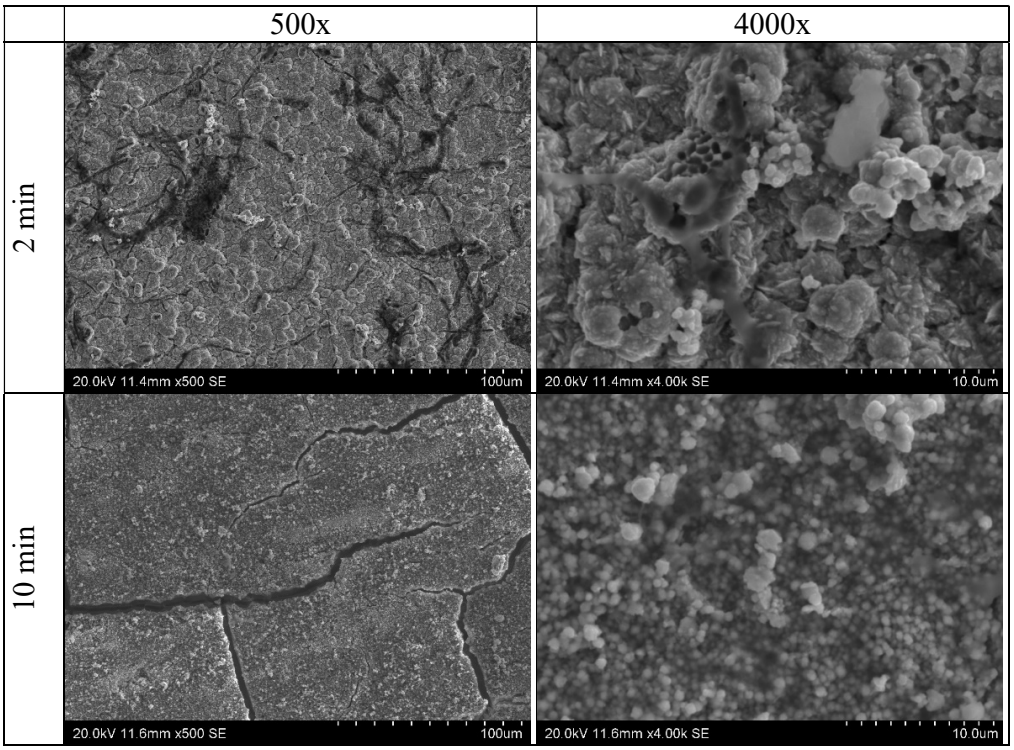

Fig. 3. SEM picture of the copper coatings obtained after 2 and 10 min etching of the sample

10 minutes. The coating obtained in process with 2 minutes of etching is rough and with no cracks. The surface of coating etched during 10 minutes is more smooth and homogeneous but some cracks are observed.

All measurements confirmed that the best time of etching is 2 minutes. This parameter was chosen for subsequent experiments.

Influence of copper electroless deposition time

The next analyzed aspect of metallization was duration of electroless deposition of copper. This process was carried out in a solution containing copper sulfate, additives of sodium and potassium tartrate and formalin (Table 1). The copper coatings were deposited within 30 to 180 minutes.

Based on the results of thickness coating as a dependence of metallization time (Fig. 4a), it is observed an increase of the thickness with time. The samples metallized during 30 and 60 minutes are characterized by some cracks. The best quality of coating has been obtained after electroless metallization within 120 minutes and the thickness was close to 4.5 μm. The copper deposited in a longer time (180 min) creates not well adherent coating probably due to the instability of electrolyte. Namely, the presence of precipitates was observed. The coating obtained after 90 minutes of electrodeposition is characterized by electrical conductivity comparable to the bulk copper.

XRD diffraction patterns of copper coatings are shown in Fig. 4b. In the diffraction patterns obtained for sample metallized in 30 minutes peaks from copper oxide Cu_2O are observed.

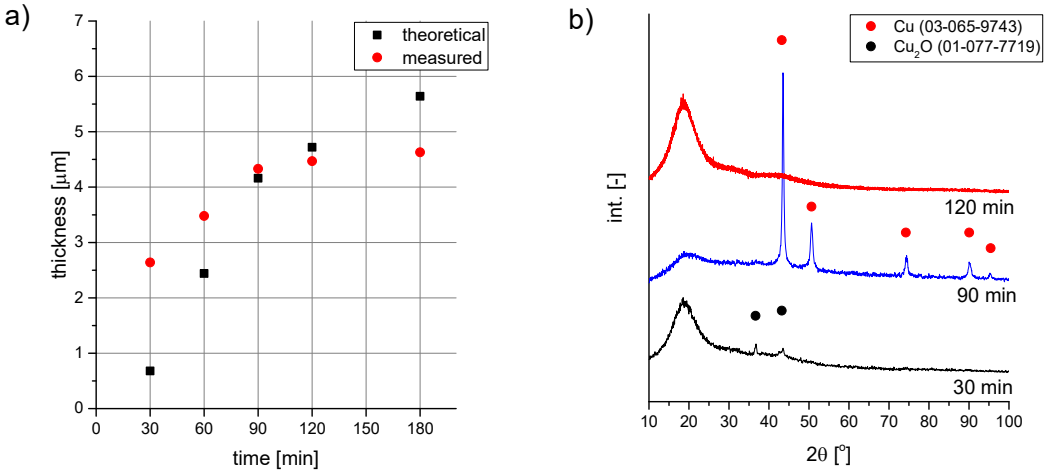

Fig. 4. Thickness and XRD analysis of copper coatings obtained after electroless deposition as a function of metallization time: a) theoretical and measured thickness, b) X-ray diffraction patterns

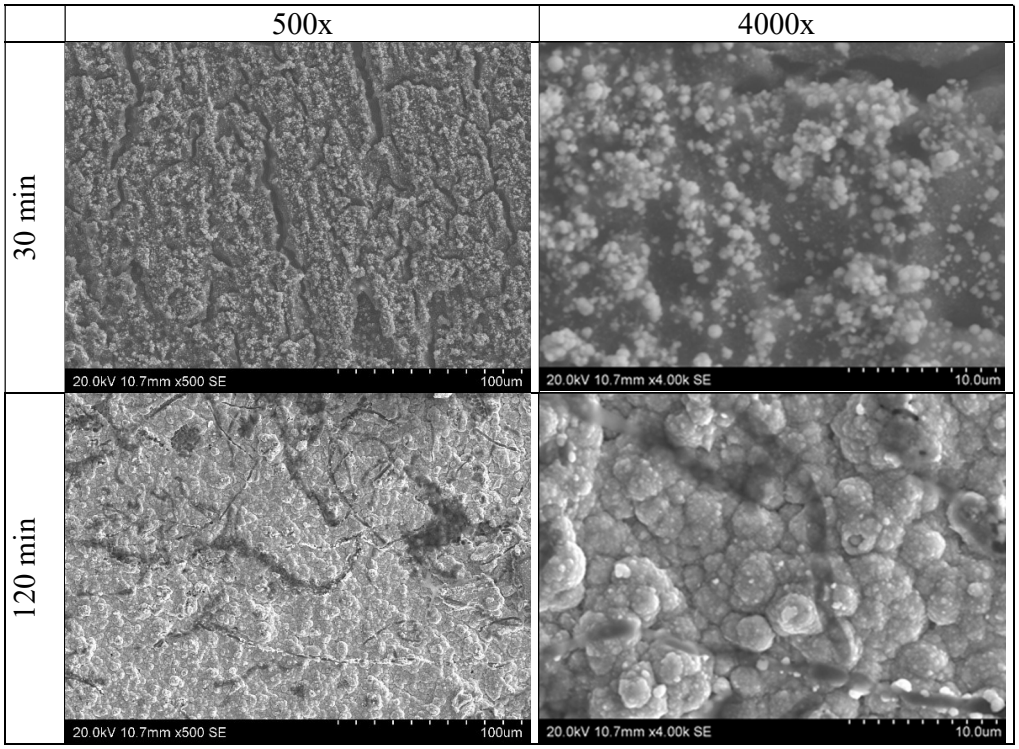

Fig. 5. SEM picture of the obtained coatings in 30 min and 120 min metallization time

Extending of the metallization time to 90 min results in metallic copper appearance. After 120 minutes of metallization the coating has the amorphous character.

The copper coating platted for 30 minutes (Fig. 5) consists of many small copper particles. There are also dark spots on the surface which are connected with the presence of Cu_2O. The copper coating platted for 120 minutes contains copper grains with larger, irregular shapes. However, its surface is uniform. On the basis of SEM pictures, small size copper particles were observed.

In all cases the increase of the thickness of the copper coating with time of chemical plating was observed. Coatings obtained after 90 and 120 minutes of the copper plating process are characterized by good tightness and thickness. The copper coating plated for 30 minutes does not have a noticeable layer of deposited copper.

Influence of nickel electrodeposition time

The next stage of experimental part was electrodeposition of nickel on the copper surface. Copper plating was carried out according to optimized parameters in the first part of the study: etching time – 2 minutes, plating time – 120 minutes. The samples before nickel electrodeposition have been etched using 5% H_2SO_4 solution for 15-30 seconds. The composition of used electrolyte is given in Table 2. At first, the influence of electrodeposition time on the quality of coatings was analyzed. Nickel plating was carried out using current density equal to 1 A/dm^2.

Based on the results shown in Fig. 6a, it was observed that nickel plating for 5 minutes does not allow to obtain a coating with appropriate quality and thickness. The best coating was obtained after nickel deposition during 20 and 30 minutes. These coatings are characterized by bright and intense metallic color.

Phase analysis presented in Fig. 6b shows the amorphous nature of the nickel coatings. No nickel oxide was found in the cathode deposit. Also, there is no peaks coming from the copper substrate, which is explained by the good coverage and sufficient thickness of the nickel coating.

Analyzing the SEM photographs (Fig. 7), irregular shape of nickel particles can be observed. For the nickel deposition time equal to 30 minutes, larger particles than on the coating obtained after nickel deposition for 10 minutes are present. Small cracks were observed on the nickel coating probably due to internal stresses present between nickel deposited and plastic/copper substrate.

4. Conclusions

The aim of this work was to optimize the metallization process of plastics, consisting of electroless deposition of copper and electrochemical nickel deposition. In the experimental work, the samples were prepared using the 3D printing method from the light-hardened resins and then metalized. Experimental work was divided into two stages. One of them was concerned the electroless copper-plating process of plastics. The next one was electrodeposition of nickel on the obtained copper coatings.

The influence of etching time and catalytic copper plating was analyzed. An omission of etching stage did not allow to obtain copper coating. The optimal time of the etching is 2 minutes. Extending this time results in a bad quality of deposits. The XRD phase analysis confirms these conclusions, peaks from metallic copper were observed.

The next parameters of electroless metallization was the time of catalytic copper plating of prepared plastics substrates. From the obtained results, it was noticed that after a time of 120 minutes a copper coating with a thickness of ~4.5 μm was obtained with electrical conductivity sufficient for electrodeposition process. Increase of metallization time leads to the not well adherent coatings due to instability of bath.

For nickel electrodeposition process, the focus was on determining the appropriate duration time at constant current density equal to 1 A/dm^2. All coatings obtained at different time (from 5 to 30 min) are characterized by the good tightness and well adhesion to the copper substrate. Extending the nickel-plating time contributes to the obtaining coatings with increasing metallic

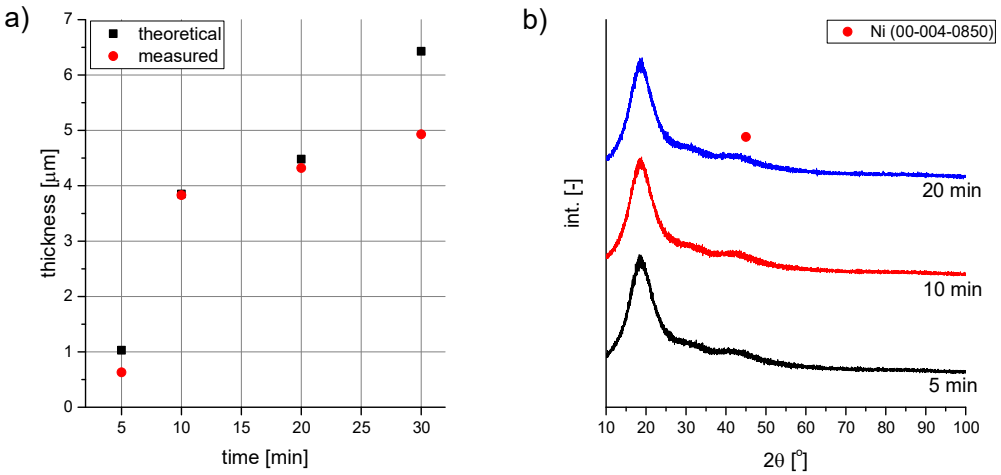

Fig. 6. Thickness and XRD analysis of nickel coatings obtained after its electrodeposition as a function of time: a) theoretical and measured thickness, b) X-ray diffraction patterns

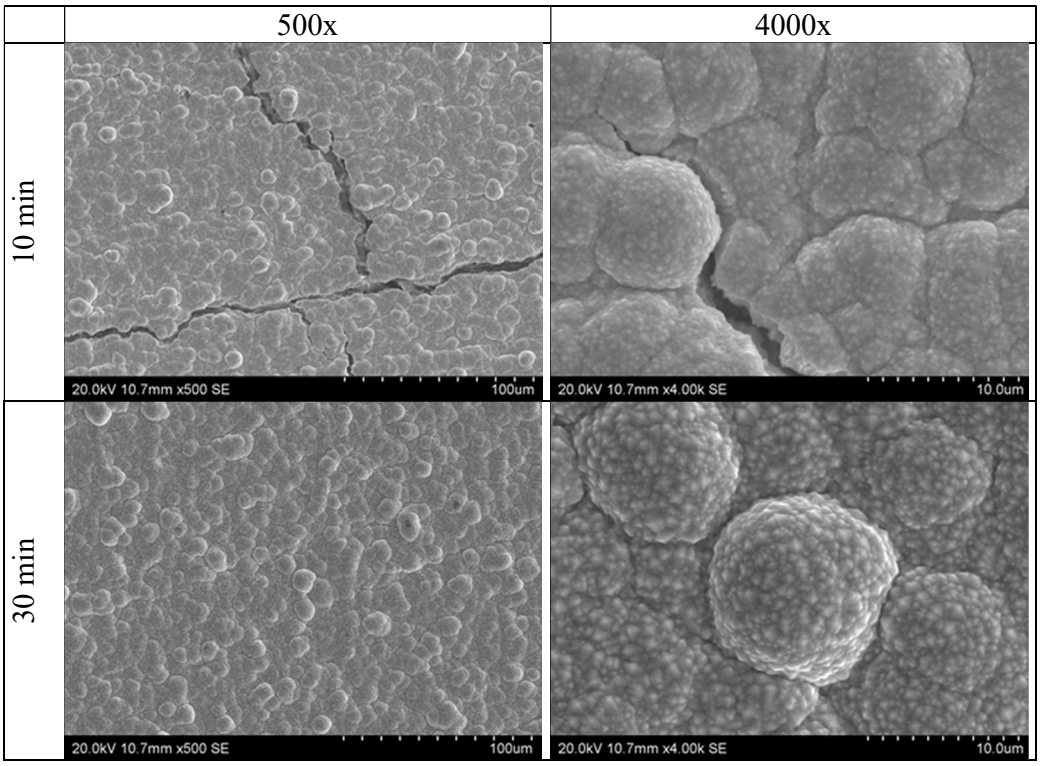

Fig. 7. SEM picture of the obtained coatings after 10 and 30 min of nickel electrodeposition

gloss. It was found that for this metallization stage, the optimal nickel electrodeposition time is 20-30 minutes. The nickel coatings obtained in such conditions are amorpous, no characteristic peaks were observed on the XRD diffraction pattern.

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