

DOI: 10.24425/amm.2019.126212

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## INFLUENCE OF MAGNETIC FIELD ON ELECTROLESS METALLIZATION OF 3D PRINTS BY COPPER AND NICKEL

3D printing is a technology with possibilities related to the production of elements of any geometry, directly from a digital project. Elements made of plastic are metalized to give new properties such as conductivity or corrosion resistance. In this work, experimental work related to the electroless deposition of metallic coatings on plastics was carried out. For this purpose, the copper and nickel coatings were catalytically deposited on elements printed using hard-lightened resin. The effect of the metallization time on the properties of copper and nickel coatings was determined. In addition, the process of deposition metals in the magnetic field was analyzed with different direction of magnetic field to the surface of the samples. The coatings were analyzed by XRF, XRD method and morphology of surface was observed by scanning electron microscopy (SEM).

*Keywords:* 3D print, metallization, magnetic field, roughness

### 1. Introduction

Electroless deposition is a well-known method for the preparation of metallic and alloy coatings both on conductive [1,2] and non-conductive [3,4] substrates. In compare to PVD or CVD method, chemical deposition is cheaper due to the fact, no expensive equipment nor high temperature is needed. Thanks to this technique, it is possible to obtain coatings which are characterized by no cracks, homogeneous thickness on the entire surface of metallized elements. The electroless deposition on a non-conductive substrates is a process based on catalysis. The surface is prepared in several steps process, the final one is the catalyst deposition. Depending on the metal deposited, silver, gold, palladium, platinum are used. Metallic coatings deposited on plastics find wider and wider applications, including electronics [5,6], energy sector [7,8], Micro Electro Mechanical Systems (MEMS) synthesis [9,10].

One of the technologies for the production of plastic components is 3D printing. Three-dimensional printing is currently one of the most popular techniques of printing due to the possibility of direct production from a digital project, scalability and the possibility to produce elements of any geometry. This technique is used in for example medicine [11,12], the food sector [13], energy [14-16], as well as in other technological processes [17].

As a result of the 3D printing method with plastic and electroless metallization combining, it is possible to obtain elements with properties both of plastics such low density or flexibility and metals, which is conductivity or corrosion resistance.

Kaewvilai et al. [18] obtained copper coatings on non-conductive glass substrate. The process was carried out by two ways – conventional two-step activation and single-step activation. In single-step activation it was obtained nano-metallic silver as a catalyst for Cu thin films deposition. Sharma et al. [5] obtained Cu electroless films to produce printed circuit boards. It was analyzed influence of parameters such substrate type and electrolyte temperature. In this work it was used the commercial electrolyte containing copper and nickel ions, nickel was deposited as hydroxide. In work [19] the polymer films were metallized by copper in alkaline solutions. It is analyzed the influence of pH on mechanism of deposition and characterization of obtained coatings. Luo at al. [20] proposed electroless copper deposition in palladium-free surface activation process on polycarbonate plastic.

Electroless deposition of metals has many applications. Despite the process is well-known, it is needed to optimize every steps due to use new type of materials as substrate, necessity of obtaining special type or the best parameters of coatings.

During recent years, the influence of magnetic field on electrochemical processes is analyzed. The most impact is magnetohydrodynamic (MHD) effect coming from Lorentz force. This is a macroscopic effect which is connected with additional stirring of electrolyte as in result – increased mass transport. Also, magnetic field gradients act on ions by magnetic field gradient force. In many works it was observed that magnetic field influences on morphology and other properties of obtained coatings [21-23].

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In this work the external magnetic field was applied during the metallization process and the orientation of this field to sample surface was analyzed. The goal of this work was analysis of influence of magnetic field on electroless deposition on non-conductive substrates, which were 3D prints obtained from light-hardened resin. There were deposited two metals with different magnetic properties: ferromagnetic nickel and diamagnetic copper.

## 2. Experimental section

In experimental work there were used chemical reagents from Avantor S.A. company with analytical purity. The coatings were deposited on plastic surface. The substrate were 3D prints prepared by SLA 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 remaining of the liquid resin from the surface, washed in distilled water and dried.

Before the metallization, the samples were prepared in a multi-stage process. After each step the samples were washed in distilled water and dried. The first step was degreasing in 5% wt. NaOH solution at 70°C for 10 minutes. Subsequently, the samples were etched in a solution made up of CrO<sub>3</sub> (50 g), 95% H<sub>2</sub>SO<sub>4</sub> (250 ml) and H<sub>2</sub>O (150 ml) for one minute at 70°C. To remove chromium ions from the surface of the plastic, the samples were placed in a 5% wt. HCl solution with an addition of 5% wt. K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> for 2 minutes at 25°C. The last step was sensitization in the 1% wt. SnCl<sub>2</sub> solution with the addition of 1.75% HCl for 2 minutes. Tin ions were adsorbed on the neutralized surface.

In the case of metallization by nickel coatings, the samples were activated in a solution of 0.2 g/dm<sup>3</sup> PdCl<sub>2</sub> with the addition of ammonia (0.25%) for 2 minutes, and then the samples were placed in a metallizing bath with the following composition: 30 g/dm<sup>3</sup> NiCl<sub>2</sub>·6H<sub>2</sub>O, 20 g/dm<sup>3</sup> NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O, 50 g/dm<sup>3</sup> Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, 15 g/dm<sup>3</sup> NH<sub>4</sub>Cl. The pH of the solution was 9. Nickel coatings were obtained in 5 to 60 minutes, the bath temperature was 60 °C.

Samples coated by copper were activated in a solution of 2 g/dm<sup>3</sup> AgNO<sub>3</sub> and 0.25% ammonia for 2 minutes. The metallization took place in a solution: 10 g/dm<sup>3</sup> CuSO<sub>4</sub>·H<sub>2</sub>O, 50 g/dm<sup>3</sup> potassium sodium tartrate with the addition of 10 cm<sup>3</sup>/dm<sup>3</sup> phenolphthalein. Metallization time ranged from 15 to 120 minutes, the process took place at room temperature.

The influence of the magnetic field on the obtained coatings was analyzed. For this purpose, an electromagnet (LakeShore – Model 642) was used, it was generated a homogeneous magnetic field with an intensity of 0.5 T. The samples were placed perpendicularly and parallel to the magnetic field lines.

The composition of coatings was determined by XRF spectrofluorimetry (Rigaku Primini). Phase analysis was performed using the XRD method (Rigaku MiniFlex II). Elemental analysis was performed using the SEM technique (JCM-6000 Plus Versatile Benchtop SEM).

## 3. Results and discussion

In the first part the results of the nickel coatings electroless deposition are presented. As the coatings contain phosphorus from the reductant, the elemental composition was determined in terms of nickel and phosphorus content, and the mapping of selected samples was made. In the second part the results from the electroless deposition of copper were presented. In both cases, the results of the metal mass increase during the deposition time and the magnetic field direction used during metallization were presented. Thanks to the presented XRD curve, it was possible to determine phase composition of the obtained coatings, and also to determine the size of crystallites basing on the Scherrer's equation.

### Nickel coatings deposition

The mass concentration of phosphorus and nickel was analyzed by XRF spektrofluorimetry. Fig. 1a shows the content of phosphorus in coatings depending on the time of metallization

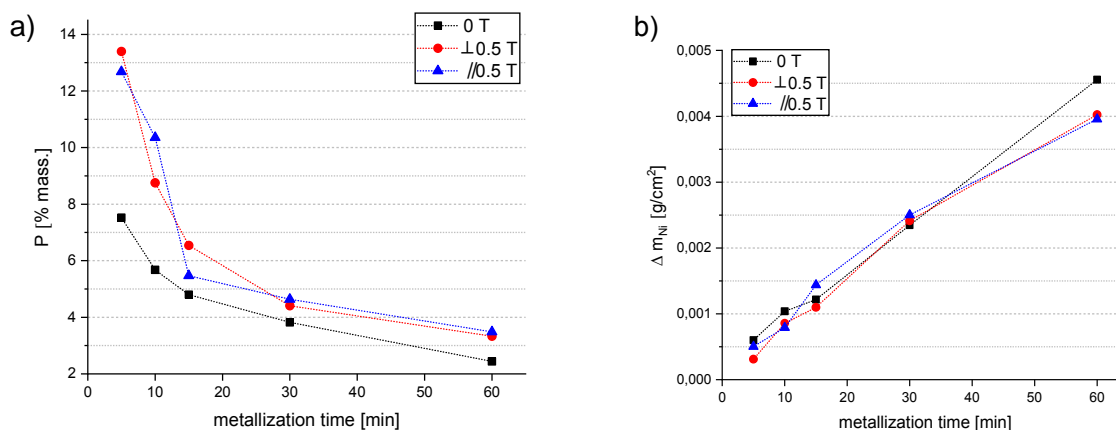


Fig. 1 a) Phosphorus content in nickel coatings depending on the time of metallization and magnetic field, b) Nickel mass increase depending on the time of metallization and the magnetic field

and the magnetic field. Analyzing the obtained data, it can be concluded that in the initial phase of metallization, more phosphorus is deposited in the coatings, along with the deposition time, the content of this element decreases exponentially. In the initial stage of the process, coatings are characterized by higher concentration of phosphorous. Along with the increasing time, the amount of phosphorus is decreasing to the value of approximately 3% by mass. Applied magnetic field, both perpendicular and parallel, influences on the elemental composition of the obtained coatings – the concentration of phosphorus is higher in compare to the case when the coatings were deposited without the use of an external magnetic field.

Fig. 1b presents the nickel growth rate depending on the deposition time and the magnetic field. In all cases, a linear relationship was found,  $R^2$  coefficient ranges from 0.97 to 0.99. Moreover, no significant influence of the magnetic field on nickel deposition in the coatings was determined.

Fig. 2 presents the phase composition of the obtained coatings determined by XRD X-ray diffraction. In each case, with the increase of deposition time of the peak at the angle of  $2\theta$ , approximately 20 degrees decreases. It is a peak originating from the substrate, its disappearance is observed due to the increasing thickness of the metallic coating. Based on the obtained diffractograms, the crystallite size was calculated using the Scherrer's equation. The highest peak at the angle of  $2\theta$ , equal to 44.51 degrees, was used for calculations. Coatings deposited in an external magnetic field directed parallel to the surface of the

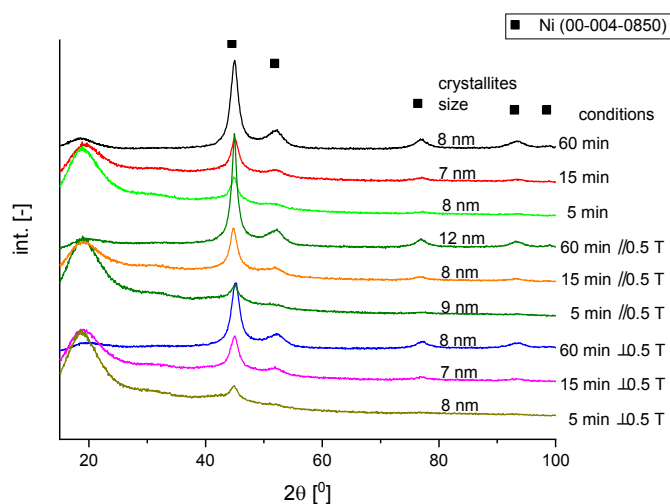


Fig. 2. X-ray diffraction patterns of Ni coatings depending on the conditions of metallization

sample, are characterized by a larger average value of crystallites in relation to the others. In the case of a perpendicular magnetic field, no major differences are observed.

SEM photos of the microstructures of the obtained coatings depending on the time of deposition and the applied magnetic field are shown in the Fig. 3. As the metallization time increased, the surface of each sample became smoother. Coatings deposited at time equal to 5 min were characterized by a very extensive surface. The influence of the magnetic field is noticeable for

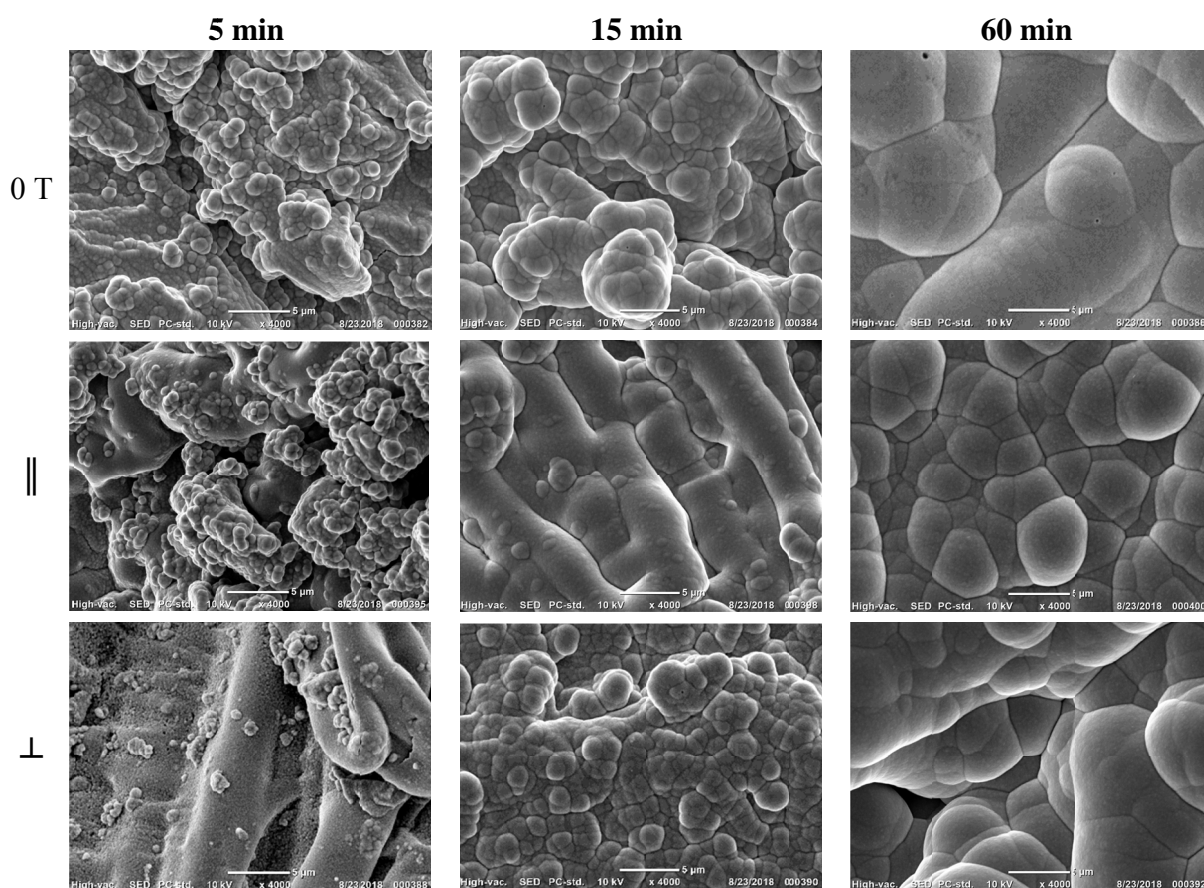


Fig. 3. SEM picture of the nickel coatings obtained after 5, 15 and 60 min of metallization

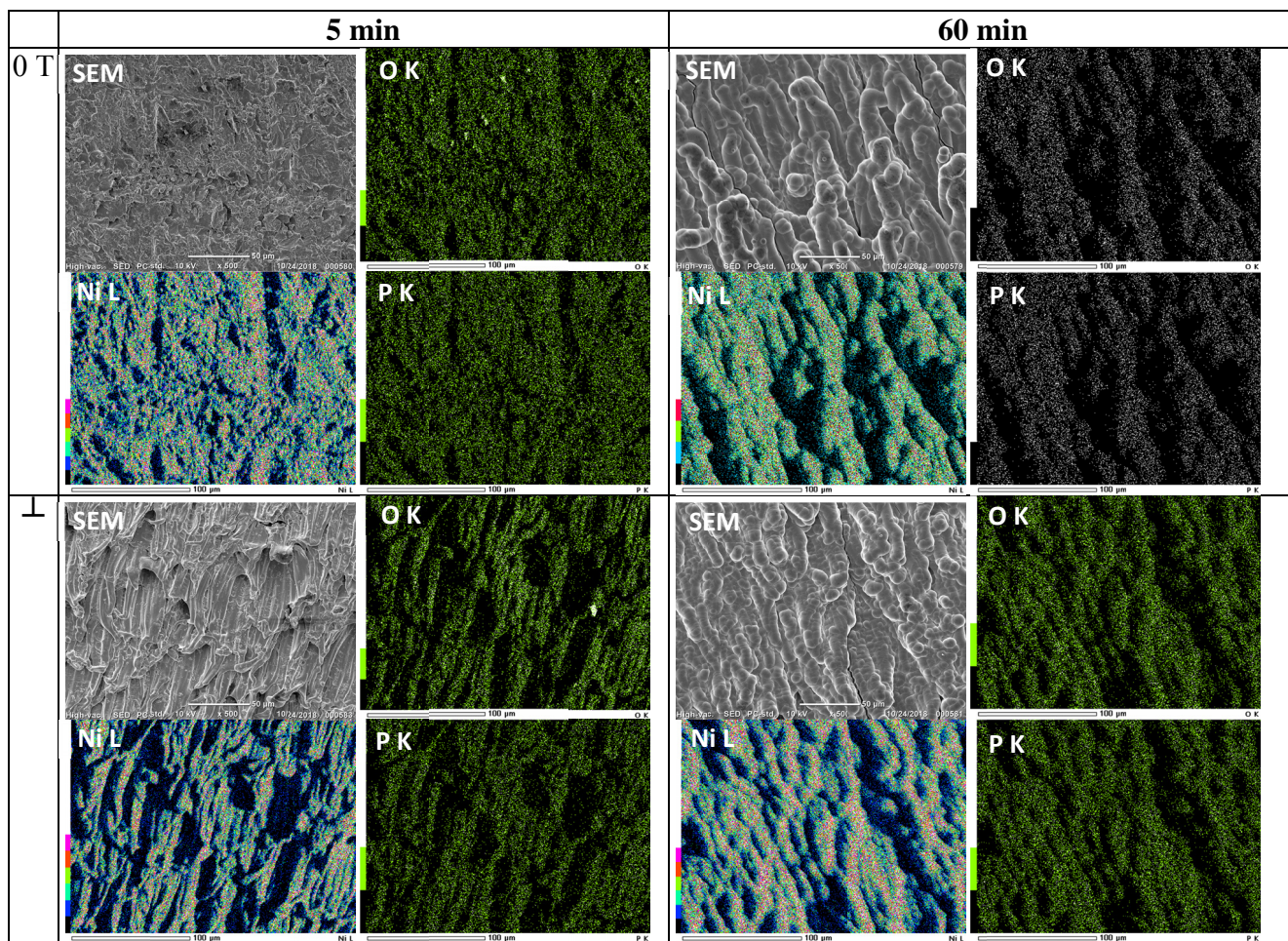


Fig. 4. SEM pictures and mapping of Ni samples obtained during 5 and 60 minutes, without and with external perpendicular magnetic field

deposition time equal to 60 min – smaller grains were obtained than for samples deposited without magnetic field. The noticeable linearity of the deposit is the result of the restoration of the substrate shape, coming from the resin layers obtained during the printing of the elements.

Additionally, mapping of selected samples at a magnification of 500× was made. SEM images show the overall, linear nature of the coating for each sample. It can be concluded that in each of the analyzed cases the elemental distribution is even. For a sample deposited for 5 minutes without a magnetic field, the coating is more smooth than when using a perpendicular field. The extended metallization time allows to obtain a higher intensity of Ni, and also in case of deposition without field and with the field a more rough surface is observed – the lines of deposited metal are more convex.

### Copper coatings deposition

In the case of copper electroless deposition, the influence of the magnetic field on the rate of metal mass increase on the sample surface is observed (Fig. 5). In general, it can be concluded that the use of an external magnetic field – independently of the orientation to the surface of the sample – results in the deposi-

tion of a smaller amount of metal. The graph of the copper mass increase in deposition time has a different character depending on the deposition conditions. In the case of metallization without using a magnetic field, the copper growth in time is exponential. The use of an external magnetic field increases the initiation time of the metallization process – after 30 minutes the mass of

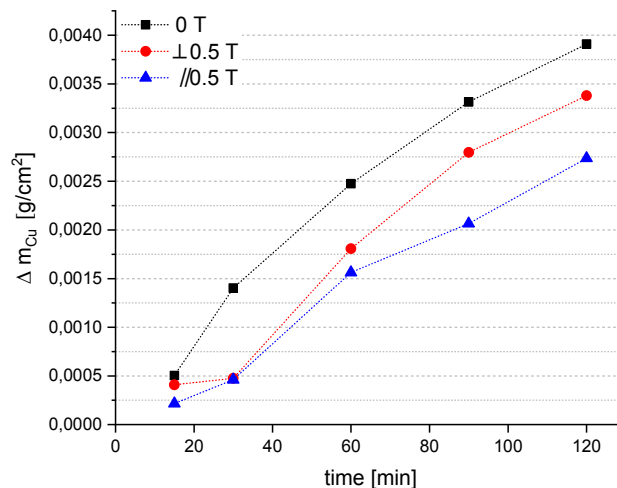


Fig. 5 Copper mass increase depending on the time of metallization and the magnetic field

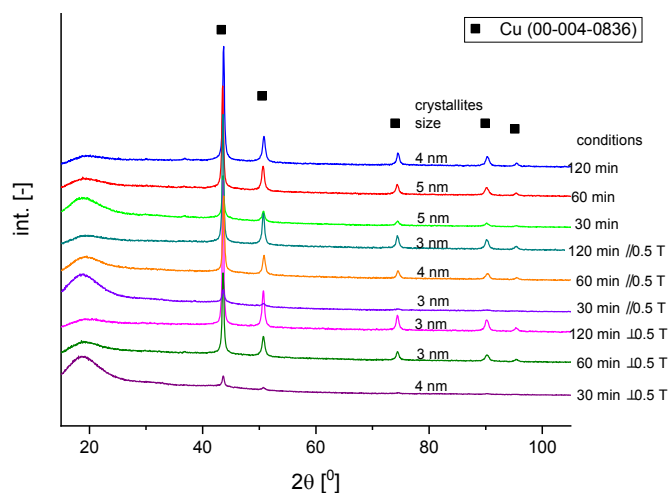


Fig. 6 X-ray diffraction patterns of Cu coatings depending on the conditions of metallization

deposited copper increases significantly. The deposition process is also slower, especially when using a parallel magnetic field.

The X-ray patterns of the obtained samples are presented in Fig. 6. The sizes of the peaks coming from copper grow during deposition in each case – however, they are more intense for the process carried out without a magnetic field. Its presence does not affect the size of crystallites, they are similar.

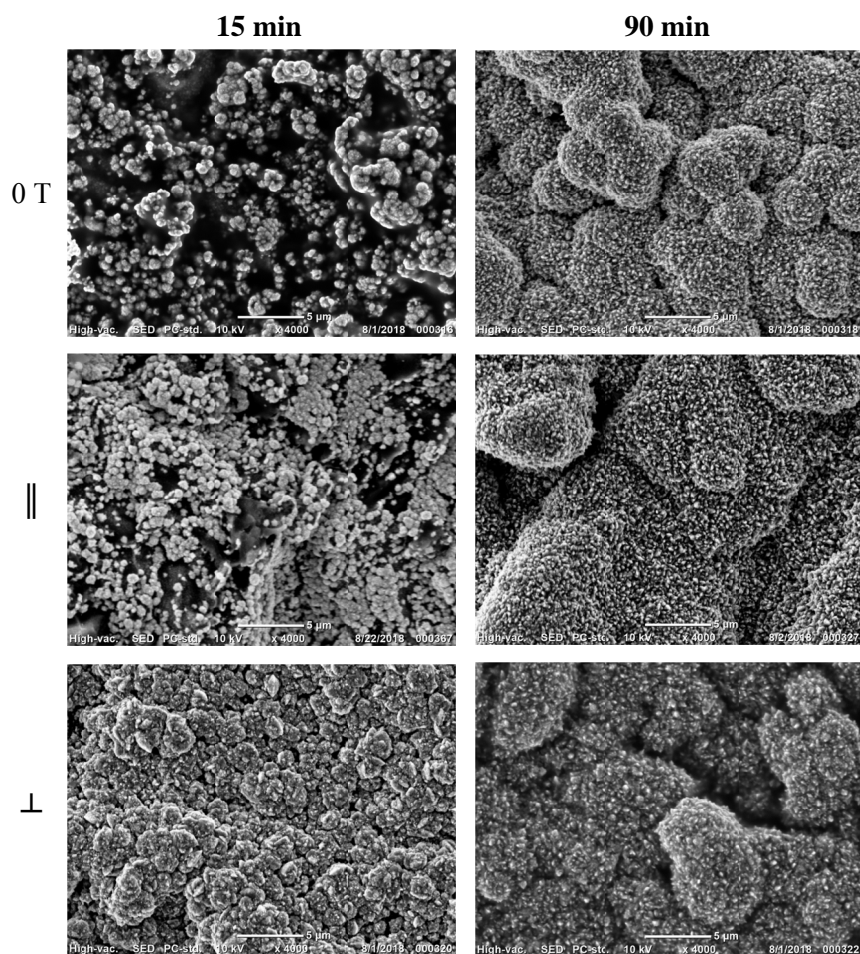


Fig. 7 SEM picture of the copper coatings obtained after 15 and 90 min of metallization

In Fig. 7 the microstructures of the deposited coatings are presented. In case for 15 minutes deposition time, coatings have a more dendritic character than for samples deposited at time equal to 90 min. With a shorter deposition time, the effect of the magnetic field on the morphology was observed. Namely, without the presence of a magnetic field, dendrites perpendicular to the surface of the substrate are obtained. In the case of a perpendicular and parallel magnetic field, these dendrites are in different directions. For samples deposited at time equal to 90 min, there was no effect of the magnetic field on the surface morphology.

#### 4. Conclusions

The aim of this work was the electroless deposition of nickel and copper coatings on non-conductive substrate, which were 3D prints obtained from light-curing resin. The research involved analysis of the influence of time and direction of the external magnetic field on the properties of metallic coatings. A magnetic field with an intensity of 0.5 T.

The content of phosphorus in nickel coatings depends on the time of metallization and the influence of the external magnetic field used during metallization is observed. The highest content of phosphorus was found in coatings deposited in a short time, along with the extended time this value drops to 3%. The magnetic field, both perpendicular and parallel, contributes to the coating with a higher content of phosphorus. The nickel mass increase coefficient does not change significantly depending on the external conditions of the deposition process, moreover, in each case a linear increase in nickel mass was observed over time. Based on the Scherrer's equation, it was found that the largest crystallites are found in coatings obtained in the presence of a parallel magnetic field. On the basis of SEM photos, the deposit was observed to be linear, coming from the resin layers obtained during the printing of the elements. With the increase of metallization time, the surface of each sample became smoother. Samples deposited in time equal to 60 min in the presence of a magnetic field were characterized by a smaller grain size than for deposits deposited without a field.

In the case of catalytic copper deposition, the effect of the magnetic field on the increase of the mass of the metal over time was observed. For the metallization process carried out without the presence of a magnetic field, this function is exponential. The presence of a magnetic field extends the initialization time of the deposition process, during the process carried out under such conditions, a smaller

amount of copper is deposited, which is confirmed by the intensities of the peaks on the XRD curves. The obtained X-ray patterns showed no effect of the magnetic field on the size of crystallites. Coatings deposited in shorter times have more dendritic character. The effect of the magnetic field is noticeable for shorter metallization time. In the case of its absence, dendrites perpendicular to the surface of the substrate were obtained – the field application causes dendrites in different directions.

#### Acknowledgment

The financial support from Faculty of Non-Ferrous Metals under grant number 15.11.180.968/2018 is gratefully acknowledged.

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