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# ELECTROLESS PLATING PROCESS OPTIMIZATION FOR SUCCESSFUL COPPER COATINGS DEPOSITION ON SURGICAL TOOLS

Copper coatings are valued for their protective, decorative, and antibacterial properties, driving their market growth. Traditional electroless copper baths use cupric sulphate ($CuSO_4$) and carcinogenic formaldehyde (HCOOH), which harms the environment and humans. This study proposes sodium hypophosphite ($NaH_2PO_4 \cdot H_2O$) as an eco-friendly reducer for nickel-substrate copper deposition. Three plating process variables were optimized for successful copper plating: sodium hypophosphite concentration (0.55 M-0.75 M), bath pH (9.5-12.5) and temperature (65-90°C). Next, the deposited coatings underwent the microstructural and chemical analyses using scanning electron microscopy and X-ray diffractometry followed by roughness determination by atomic force microscopy. Based on them, the optimum conditions for effective electroless copper plating were identified, ensuring an environmentally safer alternative for classic formaldehyde- based electroless baths.

*Keywords:* Coatings; Copper; Electroless deposition; Sodium hypophosphite

## 1. Introduction

Sales of copper-coated films reached USD 3.4 billion globally in 2024 [1] especially regarding the copper coated films between 25-100 microns, being highly required due to their flexibility and durability with possible diverse applications in industries like: electronics (circuit boards and displays), food (packaging), photovoltaics (solar panels), automotive and aerospace sectors (lightweight properties), and the healthcare sector (medical devices). There is another possible need for the copper coatings – human health and safety, arose due to their antipathogenic properties [2,3]. At the same time, the need for eco-friendly and economically favorable technological solutions has become one of the foremost production issues. A well-known method for producing metallic layers, particularly used for electroless nickel plating as described in [4] is electroless deposition using a sodium hypophosphite reducer. As copper undergo an autocatalytic deposition, the electroless plating process is one of the possible technologies to obtain a uniform copper coating [5]. In the industrial scale the source of copper ions is usually cupric sulfate, while the primary reducer of copper salts is formaldehyde, being however a carcinogen agent [6-8]. Although the hazard effect of formaldehyde can be reduced by lowering the plating temperature (reducing solution fumes), this can't be treated as perfect solution regarding the ecology restrictions matters. To overcome the problem, application of sodium hypophosphite as the reducer for copper salts can be imposed. However, this approach is burden with the co-deposition of phosphorus in the coatings and requires the presence of a nickel sulfate [7-12]. It is also important to note the relation between Ni ions amount during electroless process with the coating quality and the deposition rate [10]. The typical electroless copper plating comprising of the alkaline solutions takes place in the temperature range of 50-70°C, however decomposition of the sodium hypophosphite reducer to hydrogen requires external energy i.e. increase of the temperature (60-95°C).

Therefore, this study was focused on the systematic examination of plating technology practice comprising the effects of the: 1) concentration of sodium hypophosphite (reductant), 2) process temperature and 3) pH of the electroless bath solution on the chemical composition and morphology of the electroless plated copper coatings to propose the optimal production conditions for coating of surgical tools in real-industrial conditions.

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## 2.Material and methods

Nickel 201 material has been applied as the substrate to be covered by copper, which underwent shot peening with glass beads of an average size of 40-70 μm (SABLUX machine) to mat the finish as it is performed for final surgical tools processing. Next, the pretreatment of substrates using ultrasounds in the sequence: deionized water for 2 minutes, ethyl/isopropyl alcohol for 2 minutes, deionized water for 2 minutes took place. Substrates were activated by washing them with deionized water and digestion in a 10% $H_2SO_4$ for 2 minutes.

The electroless deposition of copper coatings from hypophosphate solutions has been carried out for 30 min with continuous stirring (200 rpm) using copper sulphate pentahydrate $CuSO_4 \cdot 5H_2O$ (0.03 M) as the Cu ion source and sodium hypophosphite $NaH_2PO_4 \cdot H_2O$ as the reductant. Compounds such as sodium citrate $Na_3C_6H_5O_7 \cdot 5H_2O$ (0.05 M) and boric acid $H_3BO_3$ (0.19 M) were introduced into solution as a stabilizing and complexing agent, respectively. Nickel sulphate heptahydrate $NiSO_4 \cdot 7H_2O$ (0.004 M) were also used to improve process efficiency. Deionized water (18.2 MΩ·cm$^{-1}$, Millipore) was used for solution preparation and washing of electrolytic precipitates. Process variables included the $NaH_2PO_4 \cdot H_2O$ concentration (0.55-0.75), temperature (65-90°C ±5) and pH value (9.5-12.5).

The surface morphology observation of the coatings was conducted with the Scanning Electron Microscope FEI E-SEM XL30 equipped with EDAX energy dispersive X-ray spectrometer (EDS) to examine chemical composition of each sample. The phase composition and average crystallite size was analyzed using the X-ray diffraction (D8 Discover, Bruker) with a cobalt anode (a wavelength of 1.79 Å). A Bruker Innova Atomic Force Microscope (AFM) operating in tapping mode was used to analyze the topography and roughness of the examined coatings surfaces.

## 3. Results and discussion

### 3.1. Effect of the reductant concentration

In the present study, the influence of the sodium hypophosphite concentration on the structure, morphology and chemical composition of the coatings, as well as on the process efficiency, was verified. Some literature reports indicate that it is significant parameter that influences the dynamics of the deposition process. Anki et al. [12] examined the effect of reducer concentration in the range of 0.18-0.55 M on the deposition rate. According to their study, sodium hypophosphite as a reducer influences both anodic and cathodic processes, showing a visible increase in process efficiency with increasing reducer concentration. Yuan et al. [13] also observed this trend. These observations align with studies on Ni-P coatings [14], where the authors noted that the deposition rate initially increased and then reached a certain maximum with specific reducer concentration, after which process efficiency began to decline. The reduction potential increases with reducer concentration, but when the concentration of $NaH_2PO_2$ exceeds a certain maximum, bath stability decreases due to possible decomposition processes, leading to a slowdown in the deposition process [13]. All deposited coatings in this study were brown in color and characterized by a nodular microstructure (Fig. 1a-c) typical for electroless cooper as can

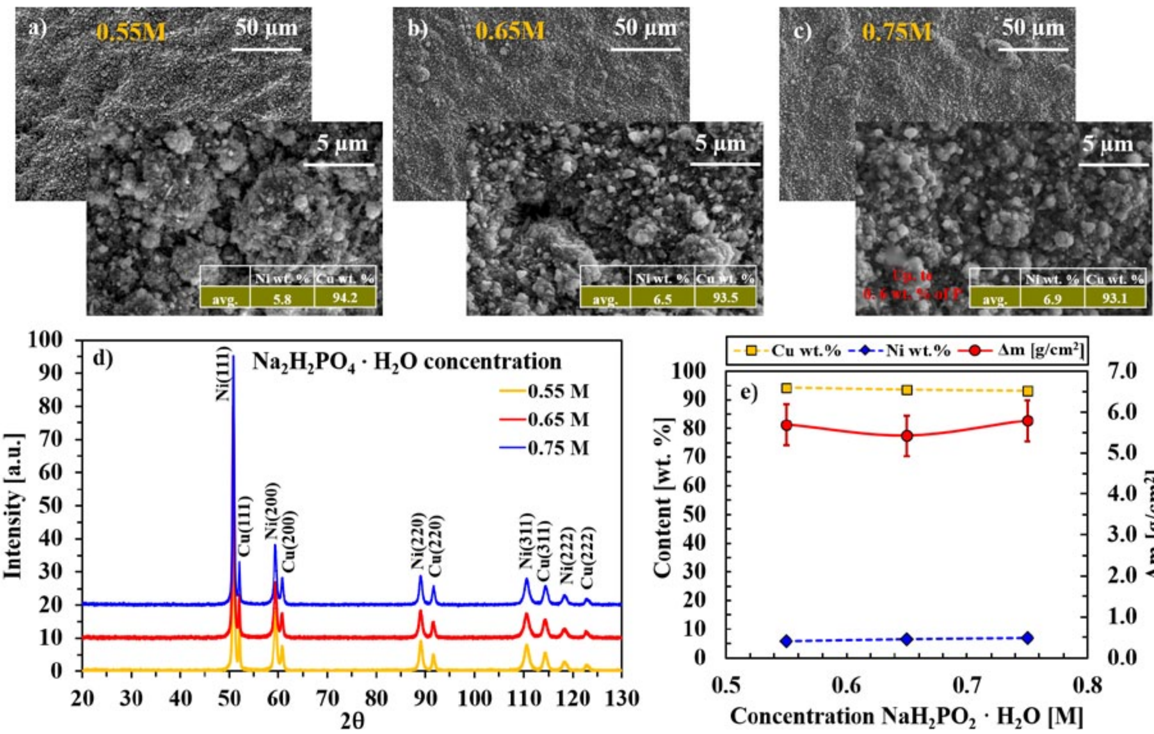


Fig. 1. Copper series coatings data obtained by plating at 70 ± 5°C for 30 min and pH = 9.5 with varying $Na_2H_2PO_4 \cdot H_2O$ concentrations (0.55 M, 0.65 M, and 0.75 M): SEM surface topography images (a-c), X-ray diffraction patterns (d), and graph showing chemical composition and mass changes of copper (e)

be seen in [8]. An increase in $NaH_2PO_4 \cdot H_2O$ concentration in our experiment in the range of 0.55-0.75 M did not affect the microstructure and chemical composition. Therefore, present study does not confirm the relationship described by Anki et al. [12]. The maximum concentration of $NaH_2PO_2$ (0.55 M) used in [12] is the lowest concentration examined in the current investigation. It may be assumed, that the reducer concentration in the plating solution influences the coating microstructure up to some concentration level (in an appropriate ratio to the other bath components) and further increase does not make any change.

Additionally, in the X-ray diffractograms series of copper coatings produced with different concentration of $NaH_2PO_2$ both Cu (coating) and Ni (substrate) reflexes were detected (Fig. 1d). They were of the same intensity regardless of the plating conditions. As the electroless copper deposition is initiated on the random catalyst centers on the substrate, the grain structure is determined by the substrate surface microstructure. The coatings were characterized by strong (111) reflex intensity with the accompanying (200), (220), (331) and (222) reflexes. These observations are consistent with the data presented in the literature for electroless cooper [15,16]. The absence of diffraction peaks from elements other than Cu and Ni in the XRD pattern indicates that the plating consists just of a Cu film. For all examined cases the crystallite size has been determined to be of $20 \pm 2$ nm. As for the coatings obtained using the highest reductant concentration, a trace amount of phosphorus in the coating was observed, therefore the lowest reductant concentration was economically justified in subsequent plating experiments.

### 3.2. Effect of the pH electroless plating solution

One of the most important operating factors is the bath pH value, as this parameter strongly effects on reduction potential [17], surface morphology and coatings' quality [18-19]. Therefore, in our study the effect of the pH electroless plating solution in the range of 9.5-12.5 on the chemical composition and morphology of the copper coatings was verified. All deposited coatings were brown in color and characterized by a nodular microstructure (Fig. 2). With increasing pH, the morphology of

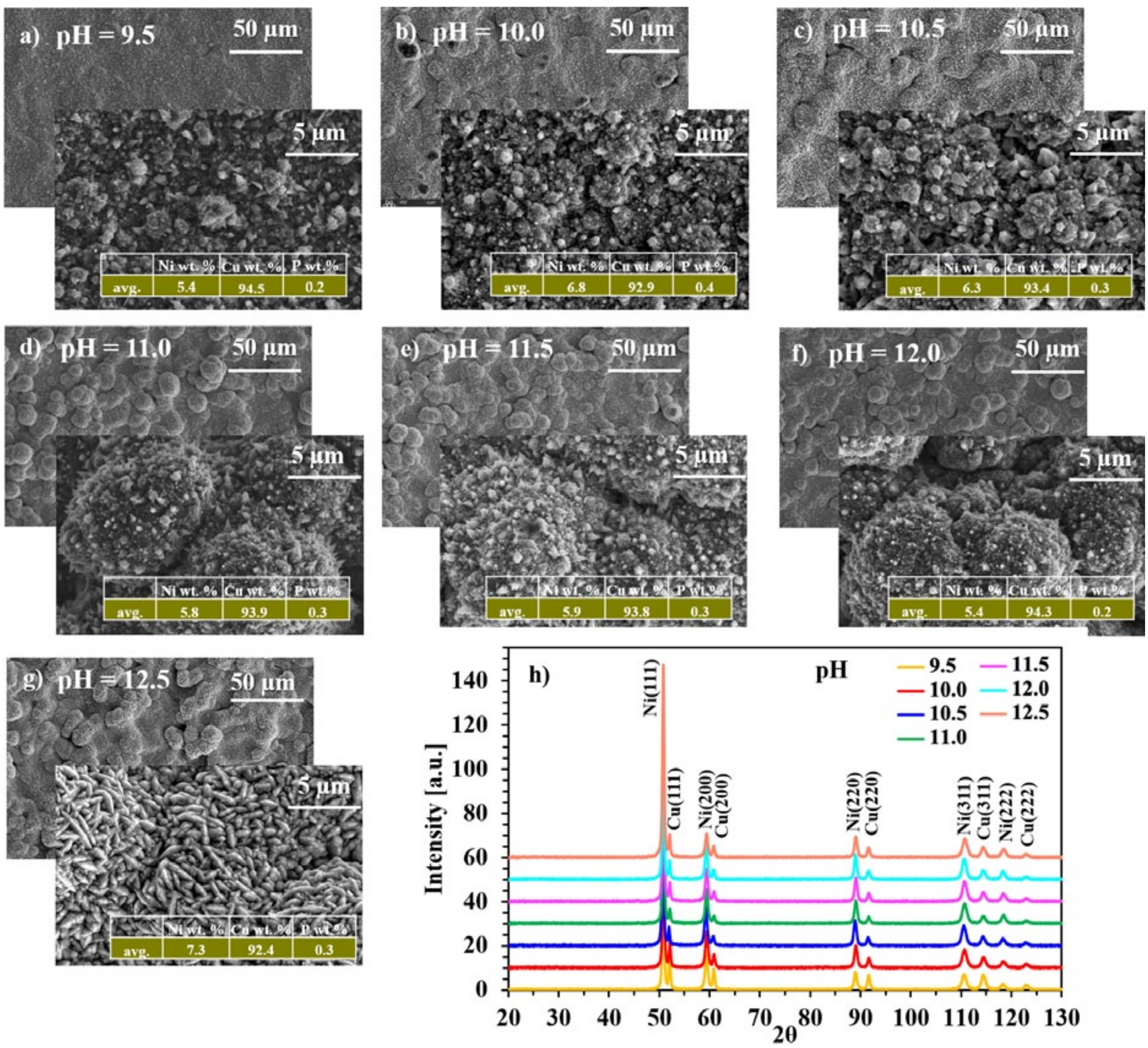


Fig. 2. Copper coatings deposited using a concentration of 0.55M $NaH_2PO_4 \cdot H_2O$ for 30 minutes at $70 \pm 5$°C using different pH of solution: (a) 9.5, (b) 10.0 (c) 10.5, (d) 11.0 (e) 11.5, (f) 12.0, (g) 12.5

the coatings changed from fine-nodular to coarse-nodular, and at pH of 12.5 a characteristic microstructure with elongated crystals was observed. Similar observation was derived by Kulyk et al. [18], that showed smooth and small grains deposits obtained from low-pH electrolytes and rougher surfaces with larger grains size from high-pH baths. Changes in pH between 9.5 and 12.5 only slightly effect the chemical composition of Cu coatings. However, at the pH above 11.5, rapid bath decomposition occurs during the deposition. Regardless of the pH value, the copper (111) reflex dominated at the XRD pattern (Fig. 2h) and the average crystal size was of 20 ± 2 nm.

### 3.3. Effect of the process temperature

The bath temperature during the deposition process is one of the most crucial parameters which dramatically can affect the deposition rate. The effect of the deposition temperature on the chemical composition and morphology of the coatings was examined in the range of 65-90 ± 5°C. With increasing temperature, the color of the coatings changed from brown to typical orange-copper one, and all coatings were characterized by a nodular microstructure (Fig. 3a-e). Above 85°C the bath disintegrated during the deposition process. Significant differences were observed in the morphology of the coatings, which changed with increasing deposition temperature. Small oval-shaped microstructure elements grew and changed into a conical shape with increasing temperature. The XRD patterns (Fig. 3f) revealed the difference in the intensities of Cu (200), (220), (331) and (222) reflexes showing their tendency to decrease with the increasing process temperature. With the process temperature, a significant increase in the process efficiency was also observed (Fig. 3g), while the chemical composition of the Cu coatings remained constant, which agrees with the SEM and XRD results. The strong increase of the deposition efficiency was noted when operating temperature increased from 70-80°C. In the temperature range of 80-85°C, an efficiency of the process is almost constant. Second jump of deposition efficiency is between 85-90°C, but above 85°C the deposition process is unstable. Similar observation was presented by Yuan et al. [13].

In the context of coatings for surgical tools, a crucial factor is the coating's morphology, especially parameters such as topography (surface development) expressed as the surface roughness, which determines the antipathogenic properties of

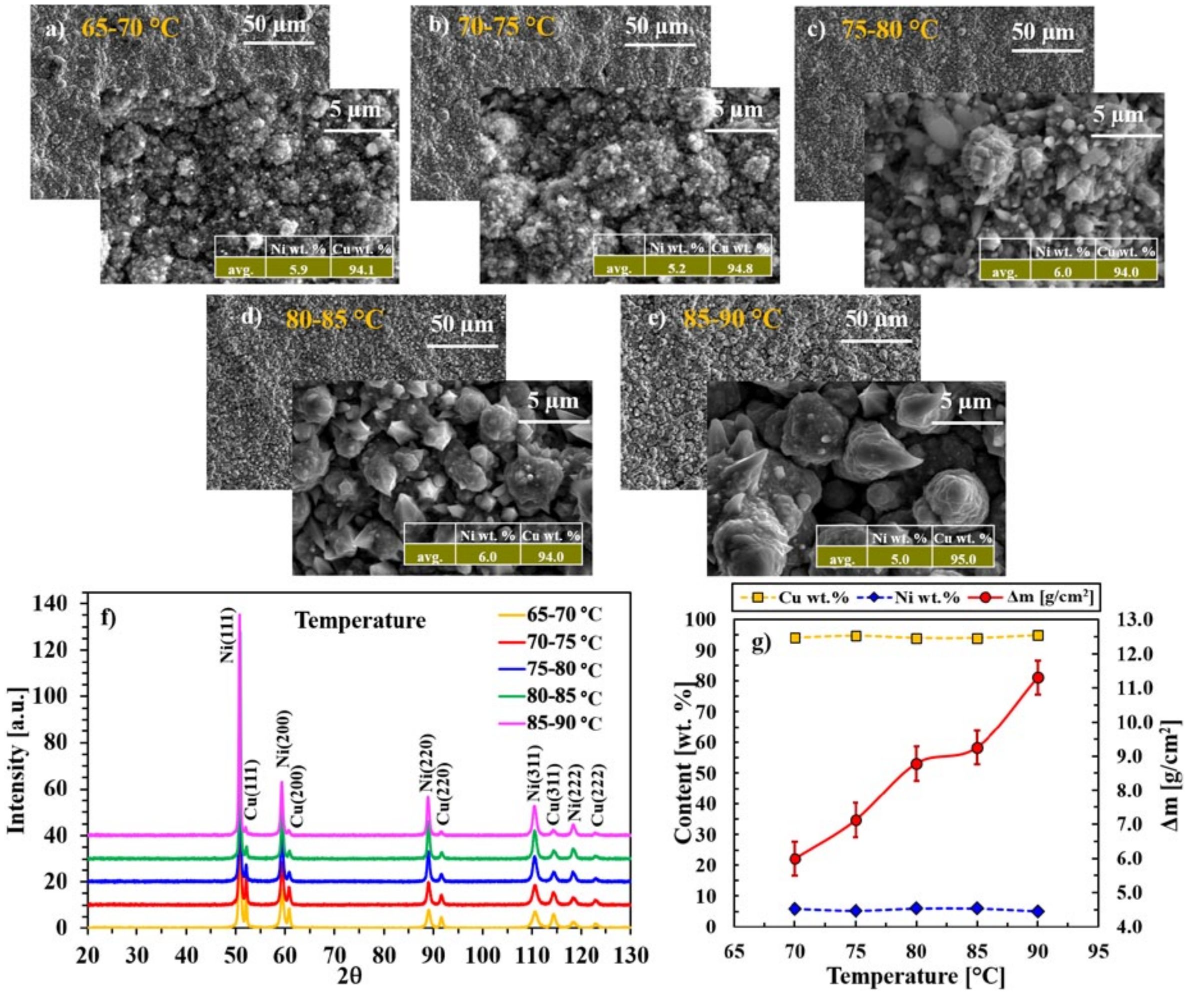


Fig. 3. Copper series coatings data from plating using a concentration of 0.55 M $NaH_2PO_4 \cdot H_2O$ and pH = 9.5 for 30 minutes with varying temperature (65-70°C, 70-75°C, 75-80°C, 80-85°C, and 85-90°C): SEM surface topography images (a-e), X-ray diffraction patterns (f), and graph showing chemical composition and mass changes of copper (g)

copper, particularly in relation to the accumulation of pathogens on the surface. The measured initial average value of Ni substrate surface roughness (Sa) was of 574 nm. According to AFM measurements, all deposited Cu coatings exhibited higher roughness. Three-dimensional AFM images presented in Fig. 4 revealed the highly developed topography of the investigated copper coatings, characterized by the needle-like structures. All AFM images present randomly distributed topographical elements with similar shapes, representing indentations surrounded by peaks of varying heights. The surface topography

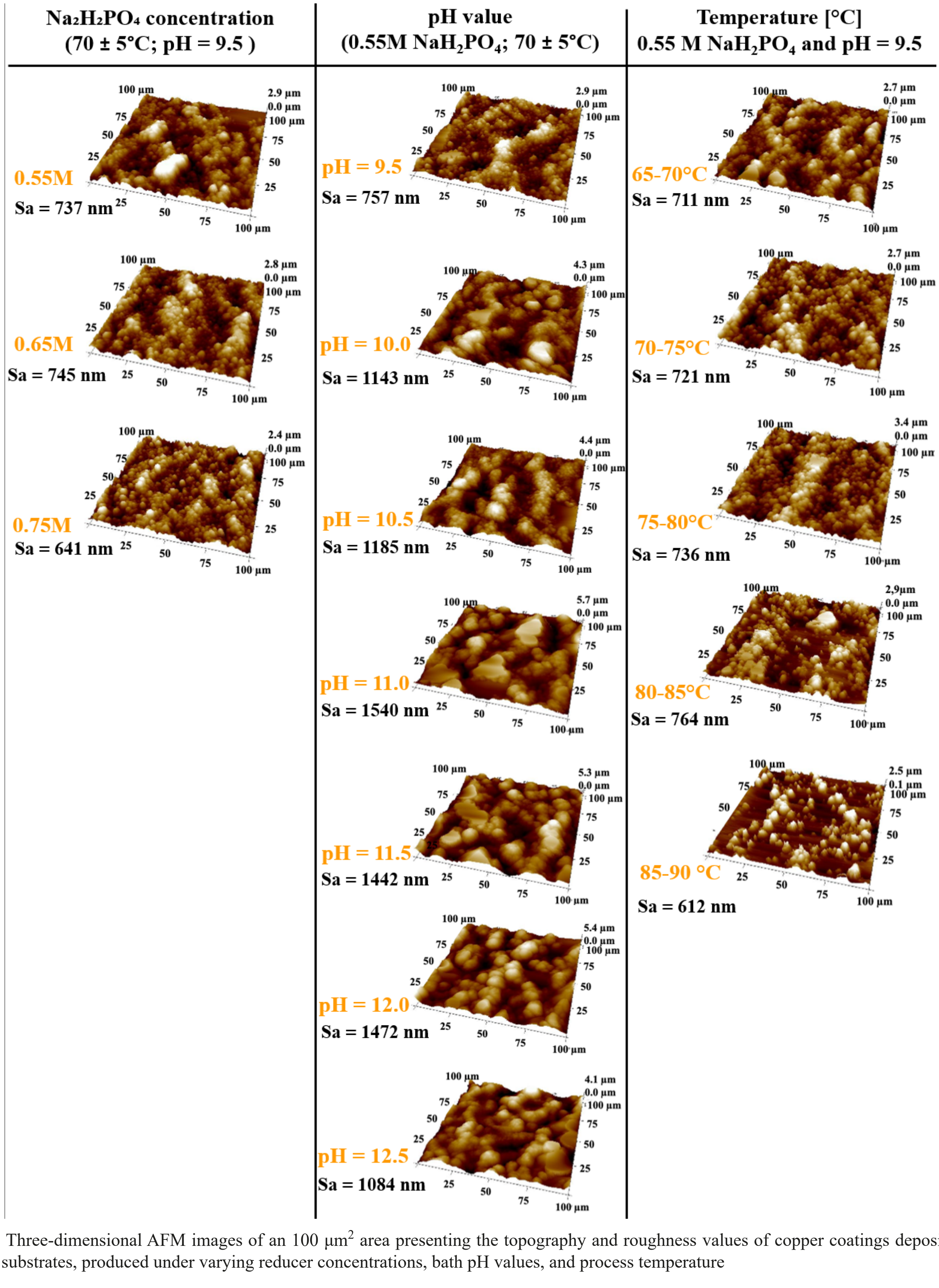


Fig. 4. Three-dimensional AFM images of an 100 μm$^2$ area presenting the topography and roughness values of copper coatings deposited on nickel substrates, produced under varying reducer concentrations, bath pH values, and process temperature

of Cu coatings produced within the variety of $Na_2H_2PO_4$ concentration (reducer) and for the temperature series is similar, while the most visible topographical differences were observed in the case of coatings deposited from the solutions of different pH values. According to the images presented in Fig. 4, the pH value of the electrolyte influenced the coating growth manner, limiting the formation of needle-like structures. As in the case of surface topography, the roughness value is comparable within the reducer concentration and temperature series, while for the pH series, certain trends were observed. The roughness value increased gradually from Sa = 757 nm (pH = 9.5) up to a peak value of 1540 nm (pH = 11.0), and finally decreased to Sa = 1084 nm (pH = 12.5). Such roughness fluctuations may result from changes in the process dynamics with increasing pH and, additionally, from bath decomposition, which occurs during the deposition process above pH 11.5.

The optimal coatings, selected based on economic and environmental considerations and microstructural characteristic, were produced at 70 ± 5°C for 30 minutes in a solution containing 0.55 M $NaH_2PO_4 \cdot H_2O$ at pH 9.5. The effect of reducer concentration is negligible, and the selected temperature minimizes solution evaporation during the process. The resulting coatings were uniform and compact, with fine morphology and preferred nanocrystalline structure and low roughness, which may potentially contribute to their antimicrobial properties. The optimal recommended bath composition and plating parameters determined in this work differ from those reported by Yuan et al. [13]. They recommended a higher concentration of hypophosphite as a reducing agent while simultaneously using a higher concentration of $CuSO_4$ as a copper source compared to this study. In this experiment, higher bath pH values were used. The authors of [13] indicated that the optimal pH is 6.0 when using a temperature of 80°C, while in the current investigation, a pH of 9.5 was the lowest value that enabled the deposition process to proceed independently of the selected temperature. Other research on electroless copper coatings produced using sodium hypophosphite has reported pH values in the range of 8.0-10.0 and temperatures of 60-70°C [9-10,19], which are similar to the parameters selected in this study. Importantly, in the referenced works, substrates based on iron [9-10] and ABS (Acrylonitrile-Butadiene-Styrene) [13,19] were used. In this study, the main aim was to determine the stable parameters of the electroless copper deposition process for producing coatings as a cover for nickel tweezers used in medicine, with the potential for implementation them in an industrial environment. Fig. 5 shows a photograph of a nickel tweezer coated with copper, produced under the optimal conditions established in this study.

## 4. Conclusions

This study was dedicated to electroless plating process of copper coatings. Changes in the concentration of $NaH_2PO_4 \cdot H_2O$ in the range of 0.55 M to 0.75 M did not significantly affect the microstructure, chemical composition and roughness of the coatings or the efficiency of the process. Changes in pH in the range of 9.5 to 12.5 slightly effected the chemical composition of the Cu coatings. As the pH increased, the morphology of the coatings' changed from finely to coarsely nodule, while at pH 12.5 a characteristic microstructure with elongated crystallites was observed. As the pH value of the solution increased, the coatings roughness increased, reaching a maximum at pH 11.0. Beyond this value, the coatings roughness decrease. At a pH above 11.5, rapid decomposition of the bath occurred. As the temperature of the deposition process increased, the efficiency of the process increased significantly, and the morphology of the Cu coating changed, while the chemical composition and roughness of the coatings remained unchanged. At temperature above 85°C, the bath disintegrated during the deposition process. Based on the above, the optimum plating conditions recommended for the successful copper coatings plating can be proposed as follows: 70 ± 5°C; 0.55M $NaH_2PO_4 \cdot H_2O$ and pH = 9.5.

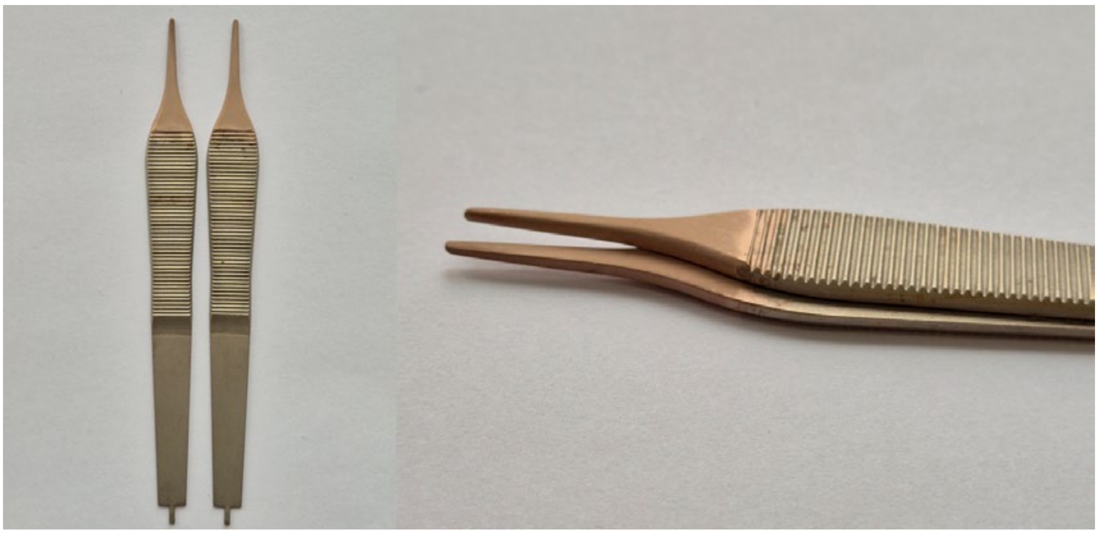

Fig. 5. Copper-coated nickel tweezers. The coatings were produced under optimum conditions: 70 ± 5°C for 30 minutes in a solution containing 0.55 M $NaH_2PO_4 \cdot H_2O$ at pH 9.5

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