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SUPERHYDROPHOBIC AND SUPERHYDROPHILIC COPPER COATINGS ELECTRODEPOSITED ON COPPER SUBSTRATE

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The aim of the paper was to determine electrochemical deposition conditions for superhydrophobic and superhydrophilic copper coatings on copper substrates. Through variable conditions of the two-stage electrodeposition process (cathode overpotential, process duration), copper layers with different wettability, i.e. high 150° and low contact angle 8°, were created. In particular, low wettability was achieved in the electrodeposition process involving low overpotential and long process time in the first stage, and high overpotential and short process time in the second stage. However, high wettability was obtained for stage I, including low overpotential and long time, and stage II, for low overpotential and long time. The morphology of the hierarchical layers was analyzed using a scanning electron microscope. The experiment suggests that the electrodeposited copper surface can exhibit stable wettability in real applications.

Keywords: copper, coatings, electrodeposition, wettability, surface morphology

INTRODUCTION

Lotus leaves, rose petals, butterfly wings, penguin feathers – these are just a few examples of natural superhydrophobic surfaces found in nature that effectively repel water [1]. These surfaces exhibit a visible contact angle of over 150° when a droplet is stationary on them. Furthermore, a moving droplet does not adhere to these surfaces. These layers have long inspired engineers to explore laboratory and industrial methods for producing everyday products using various materials, including metals, to provide exceptional functional properties such as self-cleaning, anti-icing, or corrosion resistance [2]. Moreover, with the emergence of modern smart fabrics that protect against moisture, reinforced with metal fibers exhibiting antimicrobial properties, we can observe that contemporary research trends focus on materials and processes often based on well-established physical and chemical mechanisms. Hence, in contemporary materials engineering at the micro- and nanoscale, there is a dynamic development of methodologies aimed at deliberate surface texture modification. Given the use of products wetted by liquids, i.e., hydrophilic, as well as products non-wetted by liquid media, i.e., hydrophobic, this branch of surface engineering holds significant importance in both fundamental scientific research and applied studies [3].

It is already known that for a surface to have wettable or non-wettable properties, it must have an appropriate surface topography. This topic is the subject of many scientific works, the authors of which presented the results of research on superhydrophobic surfaces produced by the following methods: sol-gel processing, self-assembly technique, electrospinning, hydrothermal synthesis, laser etching, plasma etching, physical and chemical vapor deposition, anodic oxidation and spray method [4].

The superhydrophobic copper coating stands out among conductive coatings, garnering significant attention for its excellent thermal conductivity, electrical performance, as well as its commendable thermal, antimicrobial, and mechanical durability. While various techniques in the literature focus on creating superhydrophobic copper surfaces by altering surface topography, some methods also involve modifying the chemistry of the copper surface [5]. However, such chemical alterations may lead to unintended changes in crucial surface properties. Moreover, in certain techniques, the outermost layer of the copper surface is converted into a superhydrophobic film, whereas for many applications, the preferred approach involves coating a substrate with an additional layer of superhydrophobic copper film [6].

One of the methods of producing coatings with different wettability on the surface of a copper substrate is the electrodeposition method [7]. Due to its speed and cost-effectiveness, electrodeposition has become increasingly popular for producing hierarchical coatings on surfaces of varying sizes and shapes without the need for templates. This has led to a growing interest and broader application of template-free deposition techniques.

To summarize the introduction to the publication, in the further experimental section of the paper, we presented an experiment with an electrodeposition method that allows for controlling the wettability of copper surfaces ranging from superhydrophobic to superhydrophilic. This is achievable by depositing a hierarchical copper layer on the substrate. Based on the conducted experiment, it can be inferred that this method can be applied to metals other than copper, thus creating opportunities for new applica-

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tions for both wettable and non-wettable surfaces with anti-corrosive or antimicrobial properties in materials engineering, chemical engineering (e.g., microfluidic systems).

EXPERIMENTAL PROCEDURE

Material selection

In the present study, commercially available Cu-ETP copper sheets were employed. Table 1 provide a material including their chemical composition and EN designation. Samples measuring 30 mm x 30 mm were cut from sheets that were 0,5 mm thick. These samples were subsequently mechanically polished to eliminate the corrosion inhibitor present on commercial copper sheets. Following this, the materials underwent cleaning in an ultrasonic bath filled with acetone, followed by rinsing in distilled water.

Electrodeposition method

During electrodeposition a copper sample was used as the cathode in the electrolysis circuit. The anode was a platinum wire. The electrolyte used was 1 M $CuSO_4$ + 0.5 M H_2SO_4. Measurements were conducted at a temperature of 25 °C with variable cathodic overpotential ranging from 0 - 2 V (using an Autolab potentiostat / galvanostat) and a time range of 1 - 120 s. During electrolysis, the cathode potential relative to a silver chloride reference electrode was recorded at one-second intervals. The theoretical mass of the copper samples and current efficiency were calculated.

Table 1 **Chemical composition of the tested copper sheet according to EN 12163 standard / wt. % [8]**

Material identification		Component	Cu	Bi	O	P	Pb	Other component together (without Ag, O)
EN symbol	EN number							
Cu-ETP	CW004A	min	99,90	-	-	-	-	-
		max	-	0,0005	0,040	-	0,005	0,03

Methods of surface properties research (wettability and microstructural analysis)

The surface morphology of the samples was examined using scanning electron microscopy. The wettability of the materials was assessed by placing a 2 µl droplet of demineralized water at 20 °C and 50 % relative humidity on a horizontal microscope stage equipped with a protractor eyepiece and an environmental chamber (drop shape analyzer Krüss DSA25). Ten measurements of the contact angle were taken for each sample, and the results were then averaged.

The microstructures were observed on conventional metallographic sections in light and scanning electron microscopes (SE detector, magnification: x 50 – x 5 000). The evolution of the structure were monitored using Scanning Electron Microscope (SEM).

RESULTS AND DISCUSSION

The experimental part of the work included three stages of research. The first one was to create copper layers in the process of electrodeposition on the surface of copper sheets. The second one was the measurement of the contact angle using the sitting drop method for the materials obtained in the first stage. The third part of the research concerned the analysis of the microstructure using a scanning electron microscope for the surface layer of materials after the electrodeposition process.

Electrodeposition method

In the process of electrodeposition of layers, using various parameters, copper layers were created on the surface of the copper sheet with various parameters of the electrolysis process presented in Table 2. The variables were the cathodic overpotential and the duration of the process. For sample no. 1 (mass before process m_1 = 2,7081 g; mass after process m_2 = 2,7136 g) the electrodeposition process included one stage. However, the layers for sample no. 2 (mass before process m_1 = 2,5875 g; mass after process m_2 = 2,5961 g) were obtained in a two-stage process.

Table 2 **Summary of measurement data and parameters of the electrodeposition process of copper layers on the surface of a copper substrate**

Stage no.	Electrodeposition parameters	Sample 1	Sample 2
Stage 0	Potential of the working electrode E_K / V	0,11	0,11
Stage 1	Cathodic overpotential η_K / V	-1,0	-1,0
	Process duration t / s	120	120
	Potential of the working electrode E_K / V	-0,89	-0,89
Stage 2	Cathodic overpotential η_K / V	0,0	-2,0
	Process duration t / s	1	30
	Potential of the working electrode E_K / V	0,11	-1,89

In all measurements, stage 0, i.e. electrode stabilization for an overvoltage of 0 V (E_k = OPC), lasted for 10 s. The OCP value during the measurements was 0,11 V (relative to Ag/AgCl). Data regarding the electrical charges of the process were recorded. The potential of the working electrode for the given overpotential and the current efficiency were calculated. Table 3 shows the results of tests on the electrodeposition of copper layers on the copper surface for samples along with the calculated theoretical mass and current efficiency.

Figure 1 shows the curves of changes in current intensity during electrodeposition for samples number 1 (a) and 2 (b).

Table 3 **Summary of electrodeposition results along with the calculated theoretical mass and current efficiency**

Parameters	Sample 1	Sample 2
Electric charge Q_1 / C	17,03	17,71
Electric charge Q_2 / C	-	2,57
Electric charge Q_3 / C	-	-
Electric charge total Q / C	17,03	26,32
Theoretical mass m_t / g	0,006	0,009
Current efficiency η / %	98,11	99,25

At the beginning of the process, a cathodic overpotential of -1,0 V was assigned to the copper sample no. 1, and in the second phase it was 0 V. The potential of the electrode working in the 1st and 2nd stage was -0,89 V or Ag/AgCl and 0,11 V resp. Ag/AgCl. The second stage lasted 1 s and was not recorded in the data downloaded from the program. This fact is also visible in Figure 1a). Copper sample no. 2 was subjected to a two-stage chemical process in which cathodic overpotentials of -1,0 V and -2,0 V were applied, with a working electrode potential of -0,89 V or Ag/AgCl and -1,89 V resp. Ag/AgCl in the first and second stage of the process, respectively.

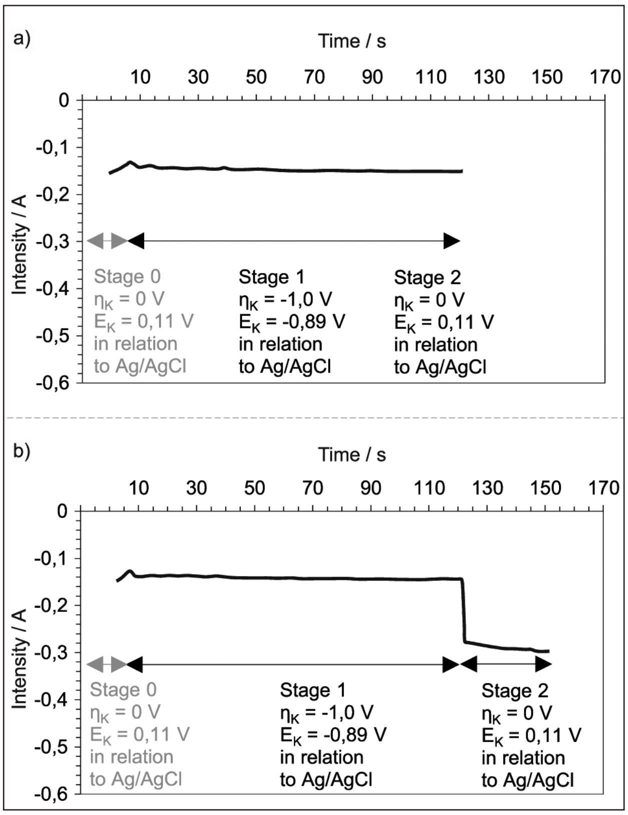

Figure 1 Results of current intensity changes during the electrochemical deposition of copper layers with different wettability on the surface of a copper sample. Two-stage process (stage 0: η_K = 0,0 V, t = 10 s) involves stage 1: η_K = -1,0 V, t = 120 s, a) sample 1: stage 2: η_K = -2,0 V, t = 1 s, b) sample 2: stage 2: η_K = -2,0 V, t = 30 s

Wettability

The wetting angle of the copper substrate as the starting material for the tests was approximately 95 °, which indicates hydrophobic properties. In turn, the analysis of the surface microstructure at various magnifications did not reveal any irregularities, but only the presence of small longitudinal scratches that are remnants of the industrial production process. Both photos from a scanning electron microscope (SEM) and the shape of a drop of demineralized water recorded on the surface of the copper substrate are shown in Figure 2.

The copper layer formed on sample no. 1 exhibited an average contact angle of Θ = 150° on both the right and left sides of the droplet, indicating superhydrophobic properties, i.e., low wettability by demineralized water, as illustrated in Figure 3a). Conversely, the contact angle value for copper layer no. 2 demonstrates superhydrophilic properties, with a recorded value of Θ = 8° (Fig. 3b).

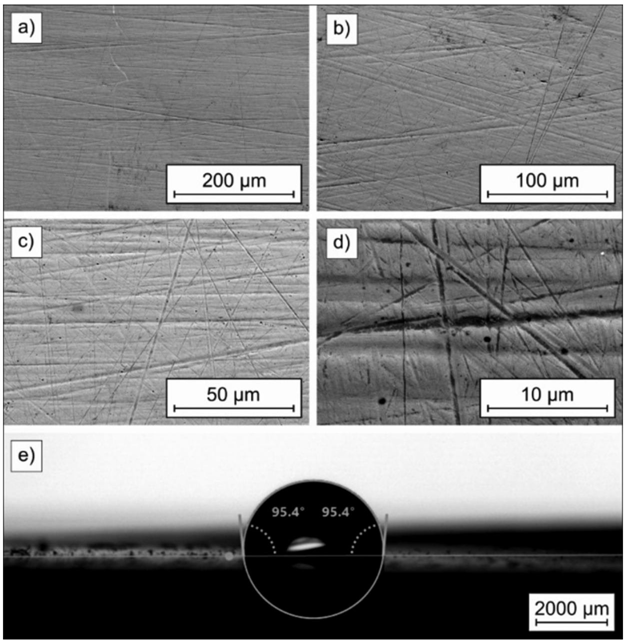

Figure 2 Surface morphology of copper sheet as base substrate in different magnification (SEM): a) x 250, b) x 500, c) x 1 000, d) x 5 000 and e) image of water droplet on this copper substrate with static contact angle

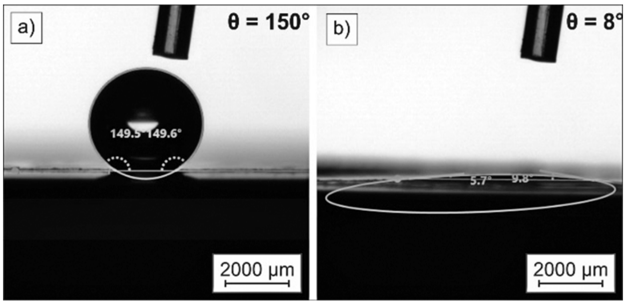

Figure 3 Shapes of water droplet on the modified: a) superhydrophobic for sample no. 1 and b) superhydrophilic for sample no. 2 copper coatings electrodeposited on copper substrate according with parameters in Table 2 and Table 3

Microstructural analysis

The layers obtained in the electrodeposition process on the copper surface after the wetting process were subjected to microstructure analysis using a scanning electron microscope (SEM). The observations were carried out at a magnification of x 50 - x 2 000, and the results are presented in Figure 4 (sample no. 1) and Figure 5 (sample no. 2).

The morphology of the obtained copper layers shows that they have a certain roughness. In particular, the smaller the contact angle (the layer is wettable, hydrophilic, sample no. 2), the larger the spacing between the cauliflower-shaped structures forming the layer. This should be identified with large and numerous spaces into which a drop of water penetrates and the material exhibits hydrophilic properties (the contact angle Θ decreases). Layers with high contact angles Θ are also covered with copper cauliflower-shaped structures, but of smaller sizes than for hydrophilic materials, and based on microstructure observations, it is concluded that they form a compact and tight coating that does not create potential places for drops to penetrate (the contact angle Θ is high , sample no. 1).

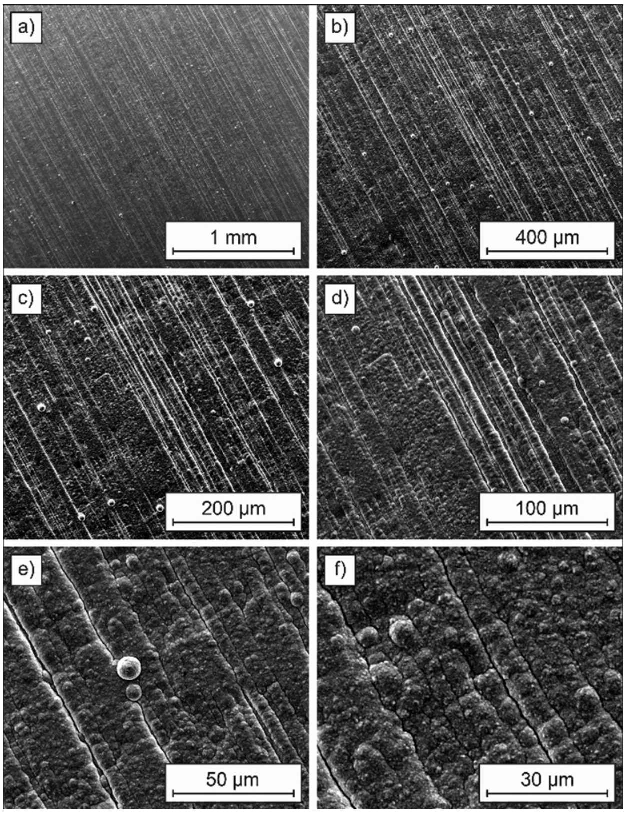

Figure 4 Surface morphology of coatings on copper substrate (Θ = 150 °) no. 1. Magnification: a) x 50, b) x 150, c) x 300, d) x 500, e) x 1 000, f) x 2 000 (SEM)

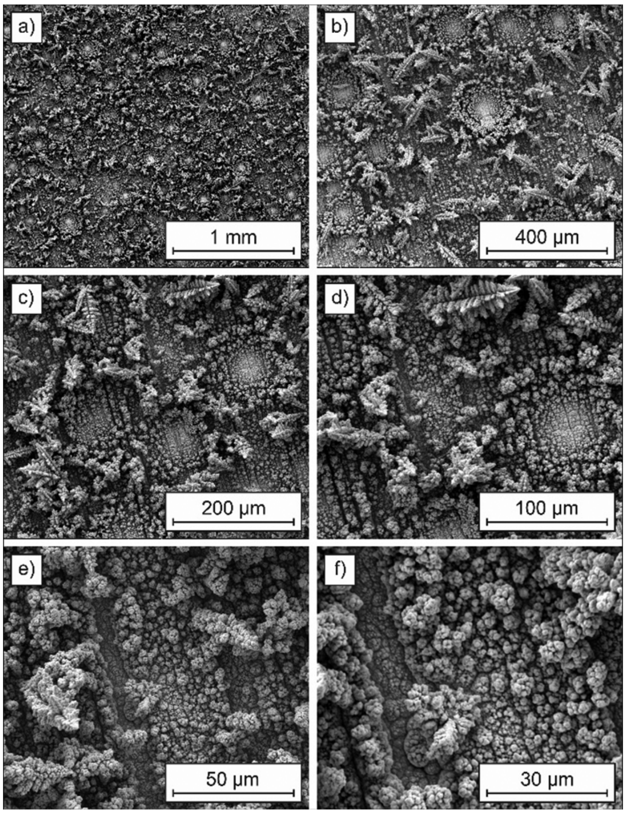

Figure 5 Surface morphology of coatings electrodeposited on copper substrate (Θ = 8 °) no. 2. Magnification: a) x 50, b) x 150, c) x 300, d) x 500, e) x 1 000, f) x 2 000 (SEM)

CONCLUSIONS

The results presented in this work show that a superhydrophobic coating can be produced on the copper surface by electrodeposition. For this purpose, a single-stage process was used for the electrolyte of 1 M $CuSO_4$ + 0.5 M H_2SO_4, the cathodic overpotential was 1,0 V and the process duration was 120 s. Under these conditions, the surface was covered with tightly attached structures. It has also been shown that superhydrophilic copper layers with a contact angle < 10 ° can be produced in the two-stage electrodeposition process. Good wettability was attributed to the cauliflower-shaped structures form on the deposit surface with high roughness.

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[8] EN 12163 Copper and its alloys-Rod for general purposes.

Note: The translator responsible for English language: Małgorzata Zasadzińska, AGH University of Krakow, Krakow, Poland