

CORROSION RESISTANCE AND WETTABILITY OF
SELECTIVE PLATED COPPER-BASED COATINGS
CONTAINING SILVER PARTICLES

Radostina Yankova, Ivan Rusev, Ina Koleva, Deyan Veselinov

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Abstract

This study investigates the corrosion resistance and wettability of selective plated copper-based coatings incorporating silver particles. The coatings were deposited onto 316L stainless steel substrates, and the effects of silver particle size and electrolyte composition on the surface topography and corrosion behaviour were examined. Changes in the wettability of the coatings were evaluated by measuring the water contact angle on the coated surfaces. The results revealed that coatings obtained from an alkaline electrolyte containing silver particles exhibited a lower corrosion rate, whereas those produced from an acidic electrolyte demonstrated a higher contact angle.

Key words: selective plating, copper-based coatings, silver particles, corrosion resistance, wettability

Introduction. The practical applications of copper-based coatings containing silver particles are broad and technologically significant. Such coatings are widely used in marine environments, where resistance to chloride-induced corrosion is critical, as well as in biomedical devices, due to the combined antibacterial properties of copper and silver. Additionally, these coatings are used in electronic components, where improved surface conductivity and corrosion resistance are

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required, and in heat exchangers and pipelines, where prolonged exposure to aggressive environments necessitates durable protective layers. The incorporation of silver nanoparticles further enhances antimicrobial performance, making these coatings particularly attractive for hygienic and medical surfaces.

Combining copper and silver particles in the formation of selective electrochemical coatings can lead to a synergistic effect that improves corrosion resistance [1]. Copper provides a passivation layer, while silver particles have a protective barrier effect, preventing the penetration of aggressive liquids such as chlorides into the base material [2]. Copper can also improve the stability of silver particles, reducing their tendency to oxidize. An important factor in the corrosion resistance of selective copper coatings is the pH of the electrolytic copper solution.

Under alkaline conditions (high pH), copper and silver ions in the solution can be reduced and deposited on the surface of the metal, forming a passive oxide layer on the copper. This oxide layer (usually Cu_2O or CuO) provides corrosion protection by preventing the metal from aggressive external factors (such as oxygen, water and acids) [3]. Under alkaline conditions, passivation of copper is significantly more effective.

In acidic conditions, a less stable oxide layer can form on copper, which is more susceptible to chemical attack. Silver nanoparticles added in acidic environments can also be subject to a higher tendency to oxidize and aggregate if not properly stabilized, which can reduce their effectiveness. Coatings obtained by electrochemical deposition in alkaline solutions are generally less porous and more uniform. This is a result of better stabilization of the deposited layer and a lower tendency for silver nanoparticles to aggregate. In acidic solutions, the electrochemical deposition process can result in more porous coatings that allow water and oxygen to easily reach the base metal. This increases the potential for corrosion of the coating, especially if unstable layers of copper or silver salts are formed [4].

The size of the silver particles in the coatings can have a significant impact on the corrosion resistance of these coatings. This is due to the differences in surface properties, activity and stability of silver nanoparticles depending on their size. Nanoparticles have higher surface energy and better surface distribution, which provides uniform and effective protection when they are evenly distributed on the surface [5]. Aggregation of particles can lead to increased porosity in the coating, which facilitates the penetration of water and corrosive agents and weakens its protective properties. A major factor in the course of corrosion processes is the retention of moisture on the surface.

The degree of wetting is a critical indicator of surface properties, such as adhesion, corrosion resistance, surface energy, biocompatibility, etc. [6]. Corrosion is often accelerated in the presence of electrolytes (e.g. salts, acids) dissolved in water. Limited contact is observed on hydrophobic surfaces, which reduce the possibility of entry and retention of such solutions [7]. Silver nanoparticles added

to a copper coating can significantly alter the hydrophobicity of the surface and often increase it [8].

The aim of this study is to investigate the influence of particle size and electrolyte solution character on the corrosion resistance and wetting degree of selective plated copper-based coatings containing silver particles.

Materials and methods. In this study, two types of selective copper-based coatings (CuAcid and CuAlk) containing silver (Ag) particles with sizes of 20 nm and 3 μm were investigated. The coatings were deposited using a controlled electrochemical selective plating process. The applied current density and voltage were optimized through preliminary experiments to ensure uniform coating thickness and good adhesion. The deposition time was adjusted to obtain coatings with a thickness of approximately 20 μm , as verified by cross-sectional analysis.

Prior to deposition, the substrates underwent a multistep preparation procedure, including mechanical polishing, electropolishing, chemical etching, and surface activation, to remove surface oxides and contaminants. These steps are essential for achieving strong adhesion and a uniform coating morphology.

The coatings were deposited onto 316L stainless steel samples with dimensions of $30 \times 20 \times 3$ mm, cut using a low-speed cutting machine with continuous coolant supply. Deposition was carried out using two types of electrolyte solutions. The first solution was acidic (pH 0.5) and had the following composition: CuSO_4 – 20%; H_2SO_4 – 10%; H_2O – 70%. The second solution was alkaline (pH 8.5) and contained: $\text{CH}_4\text{O}_3\text{S} \cdot 1/2\text{Cu}$ – 30%; $\text{C}_2\text{H}_8\text{N}_2$ – 20%; H_2O – 50%. The substrate preparation procedures were performed using appropriate electrolyte solutions, as described in [9, 10].

Silver particles were incorporated into the copper electrolyte prior to deposition. Micrometer-sized particles (3 μm) were obtained by ultrasonic dispersion followed by vacuum filtration. For coatings containing 20 nm silver particles, a colloidal solution of dispersed Ag nanoparticles was used and added to the copper electrolyte. Silver nanoparticles exhibit characteristic light absorption at approximately 400 nm, which gives the colloidal solution its amber colour. The intensity of this colour provides a qualitative indication of nanoparticle concentration and size. The colloidal solution containing 20 nm Ag nanoparticles had a characteristic yellow-gold colour at a concentration of 20 ppm [11].

A DC power supply (PSU) with adjustable current and voltage, along with a graphite electrode equipped with a sheath, was used for the deposition process. The technological parameters were pre-calculated to achieve a coating thickness of approximately 20 μm .

The electrochemical corrosion of the selective coatings was evaluated by measuring electrochemical parameters – corrosion potential, corrosion current density, polarization resistance. For this purpose, a potentiostat/galvanostat Cor-test CS350 was used. The corrosion resistance of the coatings was evaluated by determining the corrosion rate in a 3.5 wt.% sodium chloride (NaCl) solution at

room temperature. The exposed working area of the samples was 1 cm^2 . Electrochemical measurements were performed using a conventional three-electrode configuration, consisting of a platinum counter electrode, an Ag/AgCl reference electrode, and the coated sample as the working electrode.

After stabilization of the open circuit potential (OCP), potentiodynamic polarization tests were conducted to assess the corrosion behaviour of the coatings. The measurements were carried out at a scan rate of 0.5 mV/s to ensure quasi-steady-state conditions and reliable determination of electrochemical parameters.

The wettability of the coatings was evaluated by measuring the contact angle of a $5 \mu\text{l}$ droplet of deionized water using a Droplet Lab dropometer.

Results and discussion. Corrosion resistance. The corrosion behaviour of the selectively plated Cu-based coatings containing Ag particles was evaluated through open-circuit potential (OCP) and measurements and potentiodynamic polarization tests.

The corrosion parameters were extracted from the polarization curves shown in Fig. 2, while the principal electrochemical quantities – anodic (b_a) and cathodic (b_c) Tafel slopes, corrosion potential (E_0), corrosion current density (i_0), and corrosion rate are summarized in Table 1. These parameters provide quantitative insight into both anodic dissolution and cathodic reduction processes occurring at the electrode surface. The Tafel slopes describe the polarization kinetics, while E_0 reflects the thermodynamic tendency of the coating to corrode. The corrosion current density (i_0) serves as a direct indicator of the electrochemical degradation rate, and the corresponding corrosion rate quantifies the overall protective efficiency of each coating system.

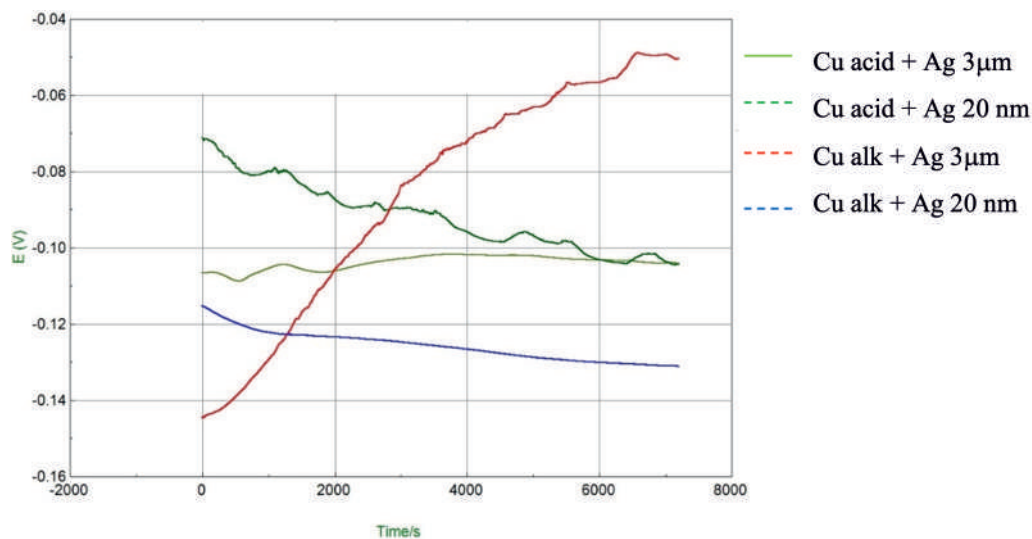


Fig. 1. OCP curves of selective plated copper-based coatings containing silver particles

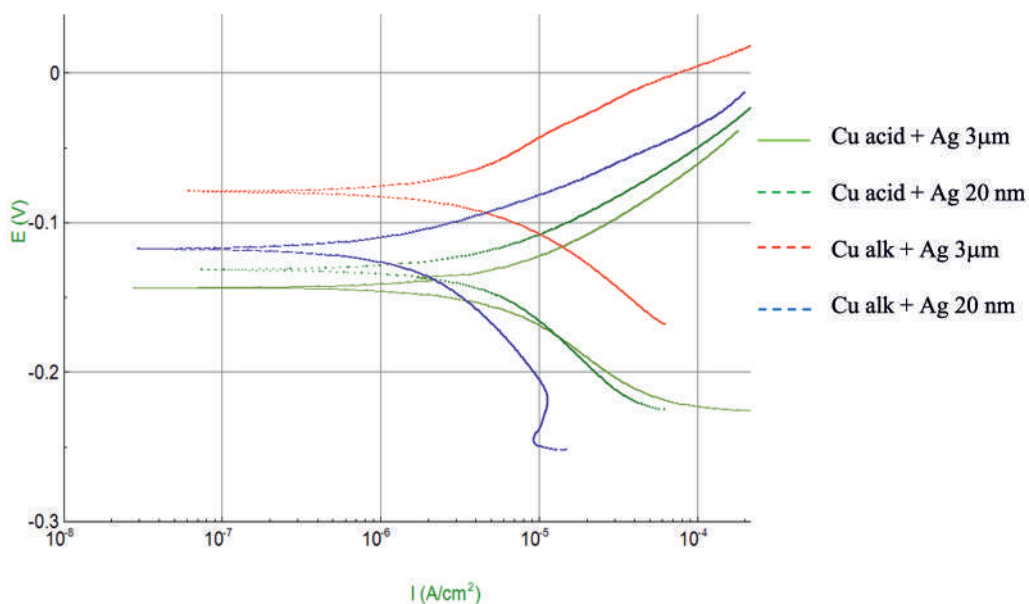


Fig. 2. Tafel curves on selective plated copper-based coatings containing silver particles

T a b l e 1

Electrochemical parameters b_a , b_c , i_{corr} , E_{corr} , corrosion rate and residual on selective plated copper-based coatings containing silver particles

Parameters	CuAcid + Ag3µm coating	CuAcid + Ag20nm coating	CuAlk + Ag3µm coating	CuAlk + Ag20nm coating
b_a (mV)	83.304	76.244	58.485	52.423
b_c (mV)	105.23	138.09	65.653	179.03
i_{corr} (A/cm ²)	8.7595E-06	7.6608E-06	3.2936E-06	2.455E-06
E_0 (V)	-0.1438	-0.13167	-0.079419	-0.11763
Corrosion rate (mm/y)	0.10276	0.089871	0.038638	0.028493
Residual	5.1186E-07	2.1779E-07	1.4704E-06	1.3945E-08

The temporal evolution of the open-circuit potential for all coatings is presented in Fig. 1. Distinct trends were observed between the coatings obtained from acidic and alkaline electrolytes and between those containing micrometer-sized (3 µm) and nanometer-sized (20 nm) Ag particles.

At the initial immersion stage, all coatings exhibited relatively negative potentials, indicative of surface activation upon exposure to the electrolyte. The CuAlk+Ag3µm coating displayed the most negative initial potential (≈ -0.145 V) followed by a continuous positive shift during immersion, stabilizing near -0.055 V. This pronounced ennoblement suggests the progressive formation of a protective

passive film, likely assisted by the presence of silver particles. The more noble Ag phase promotes passivation and suppresses anodic dissolution of copper, resulting in improved corrosion stability.

The CuAlk + Ag20nm coating showed a comparatively stable but slightly decreasing potential, suggesting a uniform and electrochemically steady surface. The smaller Ag nanoparticles likely contributed to a homogeneous microstructure that minimizes local galvanic effects.

In contrast, both acidic coatings (CuAcid + Ag3 μ m and CuAcid + Ag20nm) exhibited limited potential variation, remaining in the range -0.10 V to -0.12 V. This behaviour indicates lower passivation capability and a higher degree of ongoing electrochemical activity, probably due to microstructural defects such as cracks or micropores formed during deposition from the acidic bath.

The CuAlk + Ag3 μ m coating reached the most positive and stable OCP, confirming that the alkaline electrolyte promotes the development of a more adherent and protective oxide or mixed Cu-Ag film, whereas coatings formed in acidic media remain more susceptible to corrosion.

The potentiodynamic polarization data further substantiate the trends observed in the OCP tests. As shown in Table 1, the coatings deposited from the alkaline electrolyte exhibit substantially lower corrosion current densities than those produced from the acidic electrolyte, demonstrating superior corrosion resistance. The CuAlk+Ag20nm coating achieved the lowest i_0 (2.46×10^{-6} A/cm $^{-2}$) and the smallest corrosion rate (0.028 mm/y), followed by CuAlk + Ag3 μ m (3.29×10^{-6} A cm $^{-2}$; 0.039 mm/y). Conversely, the acidic coatings exhibited i_0 values nearly three times higher – 8.76×10^{-6} A/cm 2 for CuAcid + Ag3 μ m and 7.66×10^{-6} A/cm 2 for CuAcid + Ag20nm corresponding to corrosion rates above 0.09 mm/y.

The corrosion potentials (E_0) of the alkaline coatings (-0.079 V and -0.118 V) are notably more positive than those of the acidic coatings (-0.144 V and -0.132 V), reflecting their greater thermodynamic stability. The positive E_0 shift suggests that alkaline-deposited coatings are less prone to anodic dissolution and exhibit enhanced passivity.

Particle size also plays a crucial role. In both electrolyte systems, the incorporation of 20 nm Ag nanoparticles lowered i_0 and reduced the corrosion rate, indicating refinement of the microstructure and improved electrochemical uniformity. Finely dispersed nanosilver likely promotes a more continuous Cu-Ag interface, reducing the density of active corrosion sites.

The Tafel slope analysis provides additional mechanistic insight. The anodic slopes ($b_a = 52$ – 58 mV) of the alkaline coatings are lower than those of the acidic ones (76 – 83 mV), indicating a slower anodic dissolution rate and a more effective barrier film. The CuAlk + Ag20nm sample, with its exceptionally high cathodic slope ($b_c = 179$ mV), demonstrates a markedly hindered cathodic reaction, most likely oxygen reduction, confirming the superior passivation effect of this coating.

Taken together, the electrochemical data clearly show that coatings deposited from alkaline electrolytes, especially those containing 20 nm Ag nanoparticles, exhibit the most favourable corrosion characteristics: low corrosion current, positive corrosion potential, and high polarization resistance. These effects are attributed to the synergistic influence of the alkaline deposition conditions and nanoscale Ag addition, which promote the formation of a compact, adherent, and corrosion-resistant coating.

The obtained results are consistent with recent studies reported in the literature. For example, EKERENAM et al. [3] report that copper-based coatings deposited under controlled alkaline conditions exhibit improved corrosion resistance due to enhanced passivation behaviour. Similarly, STERGIODI et al. [12] demonstrate that the incorporation of silver into metallic matrices leads to a reduction in corrosion current density, attributed to the formation of more stable electrochemical interfaces.

Compared to these studies, the present work shows comparable or even lower corrosion current densities, particularly for the CuAlk + Ag20nm coating. This suggests that the combination of alkaline electrolyte conditions and nanoscale silver particles provides a more uniform and compact coating structure than many conventional deposition methods. Furthermore, the observed influence of nanoparticle size aligns with findings in nanostructured coatings, where finer particles improve barrier properties and reduce defect density.

Wettability. The wettability of the selectively plated Cu-based coatings containing silver particles was assessed using water contact angle measurements (Fig. 3). The measured values ranged from 69.7° to 82.6°, indicating moderate hydrophilicity to near-hydrophobic behaviour. According to the literature, surfaces with contact angles below 90° are considered hydrophilic, while values above 90° indicate hydrophobicity [13].

The results demonstrate that both the chemical composition and microstructure of the coatings play a crucial role in determining their wetting behaviour. It is well established that wettability is governed by a combination of surface chemistry and surface morphology, including roughness and heterogeneity. In particular, the incorporation of nanoparticles can significantly modify surface structure, leading to changes in contact angle.

This observation is consistent with previous studies on silver-coated copper systems, where the formation of micro- and nanostructured surfaces resulted in enhanced hydrophobicity and improved corrosion resistance. For example, [12] reported that silver-coated copper surfaces with hierarchical morphology can achieve superhydrophobic behaviour (contact angles up to 152°), effectively acting as a barrier against corrosive media. Although the coatings in the present study do not reach superhydrophobic regimes, the increase in contact angle with decreasing particle size suggests a similar trend toward improved surface structuring.

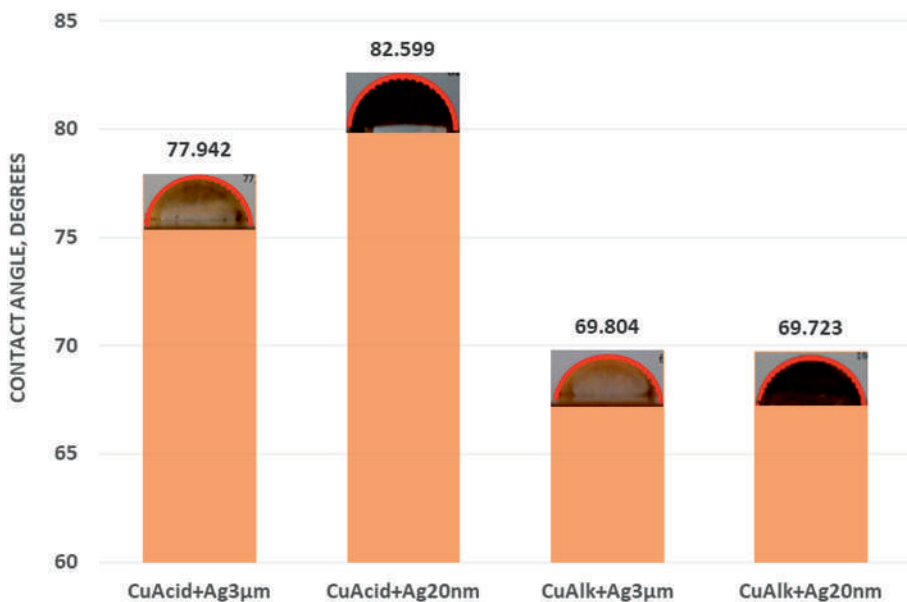


Fig. 3. Contact angle of the selective plated copper-based coatings containing silver particles

For the acidic electrolyte, the addition of smaller Ag nanoparticles (20 nm) increased the contact angle from 77.9° to 82.6°, indicating reduced surface wettability due to finer microstructural features. In contrast, coatings obtained from the alkaline electrolyte showed minimal dependence on particle size, with contact angles remaining in the range of 70–72°, suggesting that electrolyte composition dominates the surface formation process.

Despite the slightly higher contact angles observed for the CuAcid + Ag20nm coating, it did not exhibit superior corrosion resistance. This confirms that wettability alone is not the determining factor for corrosion protection. While increased hydrophobicity can reduce electrolyte contact, effective corrosion resistance primarily depends on coating compactness, uniformity, and electrochemical stability. The results highlight that an optimal combination of surface morphology and chemical stability is required to achieve enhanced protective performance.

Conclusion. Electrochemical evaluation demonstrated that the incorporation of silver particles into copper coatings significantly influences their corrosion performance, with the effect strongly dependent on both the particle size and the electrolyte environment. The CuAlk + Ag20nm coating exhibited the lowest corrosion rate (0.028 mm/y) and corrosion current density (2.46×10^{-6} A/cm²), confirming its superior corrosion resistance. These results indicate that the combination of nanoscale Ag particles and an alkaline electrolyte promotes the formation of a compact, adherent, and stable protective layer that effectively suppresses both anodic and cathodic reactions.

Conversely, the CuAcid + Ag3 μ m coating displayed the highest corrosion activity (0.103 mm/y) and the most negative corrosion potential (-0.144 V), underscoring the detrimental influence of the acidic medium and larger Ag particles on coating integrity.

Although coatings with smaller Ag particles exhibited slightly higher hydrophobicity, the results show that wettability alone does not determine corrosion resistance. The overall protective behaviour is primarily governed by the microstructural uniformity and chemical stability of the coating formed under specific electrolyte conditions.

REFERENCES

- [1] VASILIEV G., A.-L. KUBO, H. VIJA et al. (2023) Synergistic antibacterial effect of copper and silver nanoparticles and their mechanism of action, *Sci. Rep.*, **13**, 9202.
- [2] VIDEIRA V. DE C. G., B. N. HARADA, V. G. VITAL et al. (2024) Structural and antibacterial evaluation of copper, silver, and bimetallic silver/copper nanoalloys synthesized in chitosan biopolymer, *Next Mater.*, **3**, 100071.
- [3] EKERENAM O. O., A. I. IKEUBA, C. N. NJOKU et al. (2025) Advancements in corrosion studies and protective measures for copper and copper-based alloys in varied environmental conditions, *Results Eng.*, **26**, 105257.
- [4] MIKHAILOVA E. O. (2020) Silver nanoparticles: mechanism of action and probable bio-application, *J. Funct. Biomater.*, **11**(4), 84.
- [5] ZAHOOR M., N. NAZIR, M. IFTIKHAR et al. (2021) A review on silver nanoparticles: classification, various methods of synthesis, and their potential roles in biomedical applications and water treatment, *Water*, **13**(16), 2216.
- [6] KWOK D. Y., A. W. NEUMANN (1999) Contact angle measurement and contact angle interpretation, *Adv. Colloid Interface Sci.*, **81**(3), 167–249.
- [7] DONG H., X. WANG, H. HE et al. (2025) Study on superhydrophobicity and corrosion resistance of the micro-nano structure prepared by femtosecond laser, *Corros. Eng. Sci. Technol.*, **60**, 250–265.
- [8] SONG J. E., T. PHENRAT, S. MARINAKOS et al. (2011) Hydrophobic interactions increase attachment of gum arabic- and PVP-coated Ag nanoparticles to hydrophobic surfaces, *Environ. Sci. Technol.*, **45**(14), 5988–5995.
- [9] YANKOVA R., D. VESELINOV, H. SKULEV et al. (2024) Phase analysis, microhardness and wear resistance of selective plated copper-based coatings containing silver particles, *C. R. Acad. Bulg. Sci.*, **77**(4), 560–568.
- [10] VESELINOV D., R. YANKOVA, H. SKULEV et al. (2024) Fabrication and characterization of advanced selective plated copper coatings incorporating nanosized particles of ZnO and TiO₂, *C. R. Acad. Bulg. Sci.*, **77**(10), 1498–1508.
- [11] MLALILA N., H. SWAI, A. HILONGA et al. (2016) Antimicrobial dependence of silver nanoparticles on surface plasmon resonance bands against *Escherichia coli*, *Nanotechnol. Sci. Appl.*, **10**, 1–9.
- [12] STERGIODI F., A. BAXEVANI, A. MAVROPOULOS et al. (2021) Deposition of superhydrophobic silver film on copper substrate and evaluation of its corrosion properties, *Coatings*, **11**(11), 1299.

- [13] CAO Y., A. SALVINI, M. CAMAITI (2020) Current status and future prospects of applying bioinspired superhydrophobic materials for conservation of stone artworks, *Coatings*, **10**(4), 353.

Institute of Metal Science, Equipment and Technologies with Hydro- and Aerodynamics Centre "Acad. A. Balevski", Bulgarian Academy of Sciences, 67 Shipchenski Prohod Blvd, 1574 Sofia, Bulgaria
e-mails: radyankova@ims.bas.bg, rusev@ims.bas.bg, inakoleva@ims.bas.bg, dveselinov@ims.bas.bg