

PHASE ANALYSIS, MICROHARDNESS AND WEAR
RESISTANCE OF SELECTIVE PLATED COPPER-BASED
COATINGS CONTAINING SILVER PARTICLES

Radostina Yankova[✉], Deyan Veselinov, Hristo Skulev, Veneta Koeva

Received on January 16, 2024

Presented by Ch. Roumenin, Member of BAS, on February 27, 2024

Abstract

This study investigated the composition and properties of copper-based selective electrochemical coatings containing silver particles deposited on 316L stainless steel substrates. The method of formation of the coatings, using acid and alkaline electrolyte solutions, is described. A comparative analysis of the obtained coatings with selective copper coatings without added particles was carried out. An X-ray structural analysis was performed to determine the phase composition. Mechanical properties such as microhardness, surface roughness and wear resistance were investigated. The results show that the coatings are continuous, without visible defects, and the particles are deposited in depth as well. In both types of copper coatings with added silver particles, a dominant Cu phase and the presence of Ag were registered. It was established that the type of oxides formed in the deposition process is an important factor determining the microhardness and wear resistance of the coatings. The conclusions drawn confirm the effectiveness of the selective electrochemical deposition method for obtaining copper-based coatings containing silver particles and determine their characteristic mechanical properties.

Key words: copper coating, selective plating, silver particles, mechanical properties, wear resistance

This work was supported by the Bulgarian National Science Fund within the financial support of basic research projects – 2022, Project “Investigation of the biocidal activity of selective plated copper-based coatings containing silver particles”, No. KP-06-H 67/14.

<https://doi.org/10.7546/CRABS.2024.04.11>

Introduction. Since ancient times, metals such as silver (Ag), copper (Cu) and brass have been used to produce commonly used objects. These materials have been deliberately selected, due to their antibacterial and antiseptic properties, applied to various materials that are frequently touched by human traffic in an urbanized environment. Copper has been used as a disinfectant for thousands of years – long before humans acquired knowledge of germs and viruses. In the past, copper was used to purify drinking water and wounds. During the time of the Roman Empire, copper piping was used to improve public hygiene. To clean ship hulls for faster travel, great merchants such as the early Phoenicians fixed copper strips to ship hulls to discourage biofouling. Also, over the centuries, different cultures from different continents put copper coins in water vessels to prevent diseases like dysentery. Until the nineteenth century, all these civilizations used copper without knowing about the existence of the microorganisms [1, 2].

Silver (Ag) is another material known for its antibacterial properties [3]. The material containing silver ions is an effective antimicrobial agent against MRSA bacteria at high (above 90%) air humidity and high temperature (above 35 °C). However, this effect of silver disappears in conditions of low humidity and normal room temperature, unlike copper, which retains its full effectiveness [4].

In the presence of a surface composed of copper with added silver particles, the antibacterial effect of the surface increases, and the established defense mechanisms of pathogens can be overcome [5]. Furthermore, it is known that the attachment stage is often characterized by polarity of the attached cells. Therefore, the presence of a certain surface microstructure provides greater effectiveness against microorganisms of different polarity. Surface roughness is also known to stimulate the release of antibacterial agents from the copper coating, which block the occurrence of bacterial infections. The microroughness regulates the active area between the pathogens and the surface.

In order to evaluate the effectiveness of copper-based coatings containing silver particles in the production of frequently touched objects, it is necessary to clarify the degree of wear – as a function of the surface hardness as well as the phase composition of the coatings [6]. The article presents a method by which selective copper-based coatings containing silver particles are formed. The main characteristics of the coatings were studied – structure, phase composition, microhardness and roughness. To determine the behaviour of copper-based selective coatings containing silver particles under sliding friction conditions, pin-on-flat wear studies were performed [7–9]. The interrelationship between the phase composition, the mechanical characteristics and the wear resistance of the coatings was determined.

Experimental. The method used to form the coatings is selective electrochemical deposition [10–12]. Through selective deposition, continuous, uniform and long-lasting coatings are created on almost any conductive surface. This technology allows the application of coatings on elements with complex geometry.

Compared to electroplating, selective plating uses less energy, requires a much smaller amount of plating electrolyte, and can be performed on-site when needed.

Acidic and alkaline copper electrolyte solutions enriched with silver particles (size 1–5 μm) are used in this method. The coatings were applied to 316L stainless steel test specimens.

To achieve optimal results in electrochemical selective application, preliminary preparation of the base is carried out. This preparation includes operations such as electro-cleaning, electrochemical etching and surface activation, using a solution suitable for the base material. Before depositing the copper coating on the 316L stainless steel substrate, a 1 μm thick nickel underlayer is deposited to aid diffusion processes in the deposition. The duration of each operation to achieve a certain thickness is determined by calculated parameters of the operating mode (ampere-hours), according to the area to be applied.

Four types of selective coatings with a thickness of 10 μm and an area of 875 mm^2 were formed using two types of copper solutions with pH 0.5 (CuAC) and 8.5 (CuALK). The deposited CuAC and CuALK selective coatings without added Ag particles were used as reference samples. The copper-based selective coatings containing silver particles (CuAC+Ag) and (CuALK+Ag) were formed by adding mechanically powdered Ag particles with a size of 1–5 μm in the deposition process, which were fixed on the surface with the corresponding copper dissolved. A current source (impulse power supply unit) with the ability to control current and voltage, as well as change polarity, is used in the operations of preparation and application of the coatings.

Results and discussion. Structure and phase composition. Structural analysis was performed using a metallographic optical microscope. The cross-sectional surface structure of copper coatings with added silver particles was investigated. The copper coating was found to be dense, with no pores or other defects present. When observing the cross-section, it is found that the coating has the required thickness set by the parameters of the working mode during the deposition. The structure of the coatings is preserved regardless of the addition of silver particles. As a result of the electrochemical processes in the selective deposition method, some of the particles formed clusters that were deposited in depth (see Fig. 1). No defects were found at the interface between the coating and the base material, which indicates a good adhesion bond, regardless of the type of base solution (acidic or alkaline). The presence of an oxidized layer formed as a result of the interaction with the environment during the deposition process was found on the surface of the coating. This fact is also confirmed by the X-ray phase analysis of the selective copper-based coatings containing silver particles.

The XRD analysis procedure involved qualitative (phase identification) phase analysis using a TDM-10 Tongda diffractometer with $\text{CoK}\alpha$ radiation ($\lambda = 1.79026 \text{ \AA}$) at room temperature. XRD patterns were obtained in 2-Theta coupled mode in the range 20–100°, and were identified and matched to the peaks by X'pert HighScore Plus XRD analysis software.

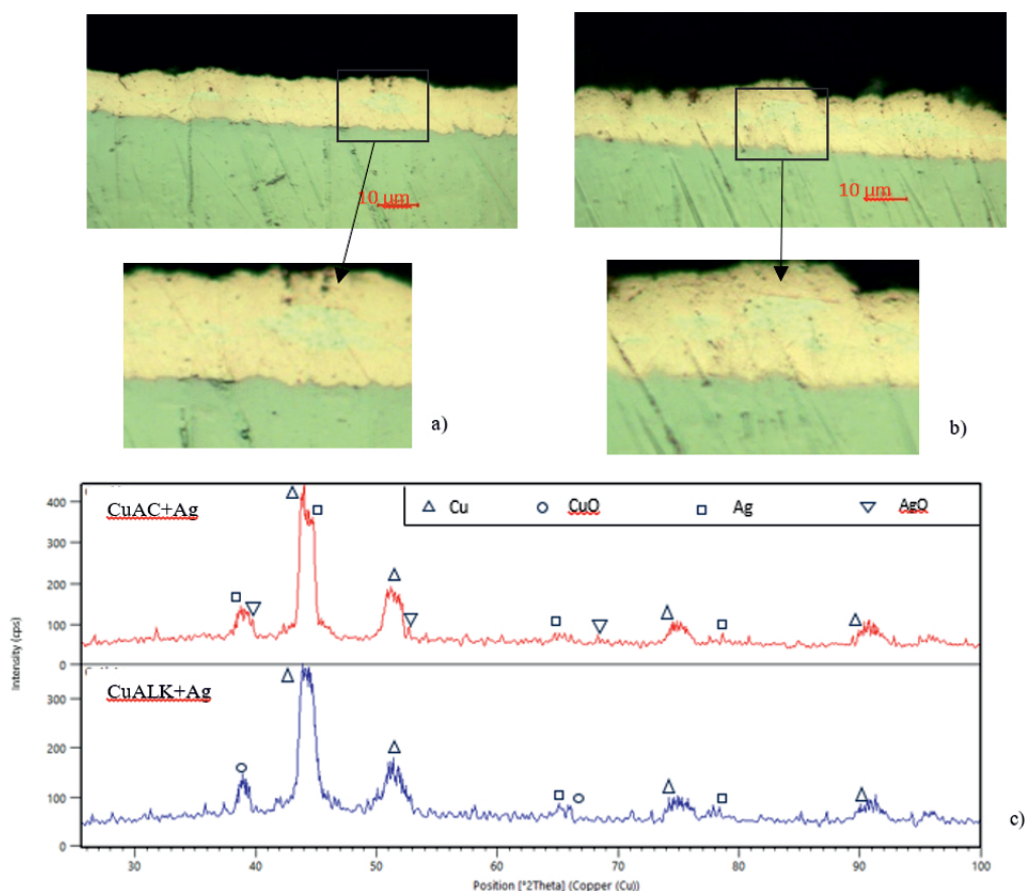


Fig. 1. Structure and phase composition of selective plated copper-based coatings containing silver particles; a) structure of acid solution, b) structure of alkaline solution, c) phase composition

In both types of coatings, CuAC+Ag and CuAL+Ag, a dominant Cu phase and the presence of Ag are registered. As a result of the interaction between the components of the copper solutions and the silver particles, various chemical compounds were formed. In the CuAC+Ag selective coating obtained from a copper solution with pH 0.5 and silver particles, AgO was recorded, in contrast to the CuAL+Ag selective coating, where the presence of CuO was observed.

Microhardness. The microhardness in the cross section of the copper coatings was measured using the Knoop method with a load of 0.01 kgf [13]. It was found that the addition of silver particles in the electrolytic solution led to a decrease in the microhardness of the copper coatings.

The values of the microhardness of the coatings with added silver particles from the two types of copper solutions of acidic and alkaline nature are of the same order, and in the coating obtained from the copper solution with pH 0.5, the microhardness in the cross section is higher by 7 units (see Fig. 2).

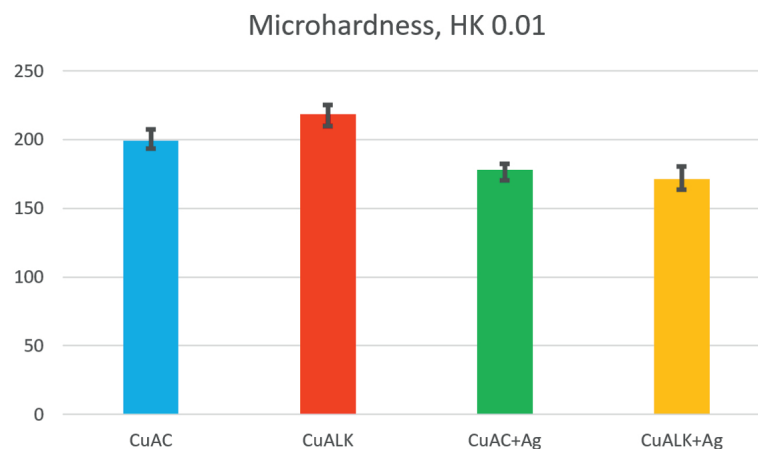


Fig. 2. Microhardness of selective plated copper coatings – acidic solution (CuAC), alkaline solution (CuALK), acidic solution and silver particles (CuAC+Ag), alkaline solution and silver particles (CuALK+Ag)

Surface roughness and wear resistance. In the samples coated with copper-based coatings with added Ag powder particles, a different surface topography with clearly defined inclusions was observed (Fig. 3). The particles are fixed on the surface, and their distribution is relatively uniform. Larger particle sizes are observed in the alkaline copper solution coating due to the agglomerations that form during deposition. This results in significantly higher surface roughness as illustrated in Fig. 3.

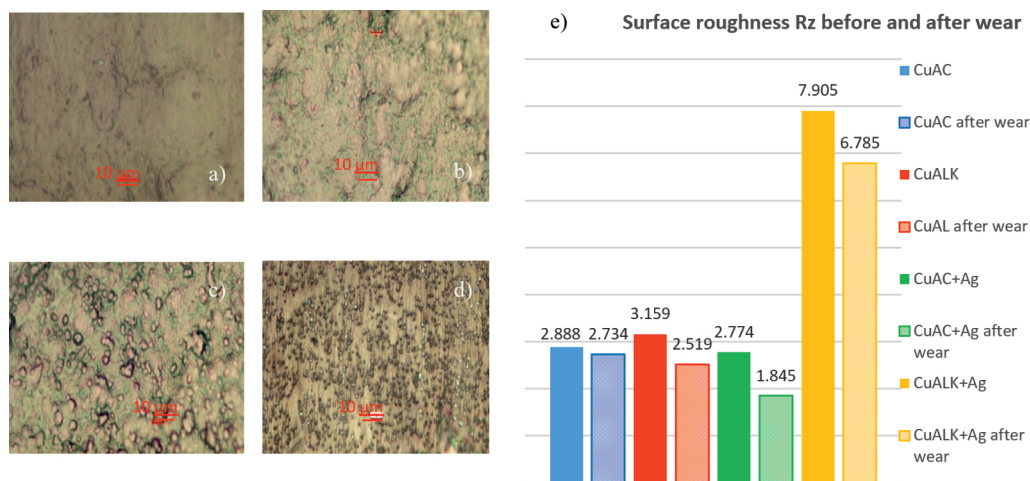


Fig. 3. Surface topography and roughness of selective plated copper coatings; a) surface topography of selective plated copper coatings CuALK, b) surface topography of selective plated copper coatings CuAC, c) surface topography of selective plated copper coatings CuALK+Ag, d) surface topography of selective plated copper coatings CuAC+Ag, e) surface roughness of selective plated copper coatings

When forming the copper coatings without added Ag particles, the surface roughness changes within narrow limits (R_z 2.888 μm when using an acidic solution, and R_z 3.159 μm when using an alkaline solution).

Research was conducted to determine the wear resistance of selective coatings using the pin-on-flat method. During the test, the ability of the coating to withstand sliding wear under specific loading conditions was evaluated using a Glomro BXT-MAR306 wear test bench.

In the wear test, a cylindrical counterbody made of rubber with hardness Shore 70A, with a diameter of 7 mm and a contact area of 38.5 mm², was used, which was loaded with 0.5 kg and moved along a trajectory of 60 mm. Five series of 2000 cycles were performed with a total wear distance $S = 600$ m. The degree of wear is determined by the weight method using an analytical balance with an accuracy of 0.0001 g. All specimens are cleaned, dried and weighed at the beginning and end of each test series. The change in the mass of the samples allows the wear dynamics to be obtained. Mass wear (Δm) was defined as the difference between the sample mass at the beginning and at the end of each test series. Values were calculated for wear intensity (I), which represents the ratio between mass wear and wear path travelled, as well as for wear resistance (E), a dimensionless quantity defined as the reciprocal of wear intensity [14, 15] (see Fig. 4).

The selective copper coating obtained from an alkaline solution without added Ag particles exhibited the highest degree of wear resistance in all test series. The introduction of silver particles to the alkaline copper coating leads to a noticeable increase in the wear rate. This significant growth can be attributed to the formation of agglomerations on the surface during deposition, which leads to a change in density and the formation of larger particles, unstable in the wear process.

Coatings with selective copper layers obtained from a solution of an acidic nature do not show a significant difference in wear resistance with the addition of silver particles.

In the comparative analysis of the coatings with added silver particles, it was observed that a lesser degree of wear was observed in the CuAC+Ag coating, where the phase analysis reported the presence of AgO. The presence of CuO in the CuALK+Ag coating contributes to lowering the wear resistance and reducing the hardness of the coating.

As a result of the study of the relationship between the mechanical characteristics of the coatings and the degree of wear, it was found that under the specific test conditions, the increase in hardness leads to an increase in the wear resistance of the coatings. The degree of wear changes within narrow limits at low values of the surface roughness R_z (2.774; 2.888 μm). A significant increase in the degree of wear is observed at high values of the surface roughness $R_z - 7.905$ μm .

Conclusion. The selective electrochemical deposition method is effective for obtaining copper-based coatings containing silver particles. At the interface be-

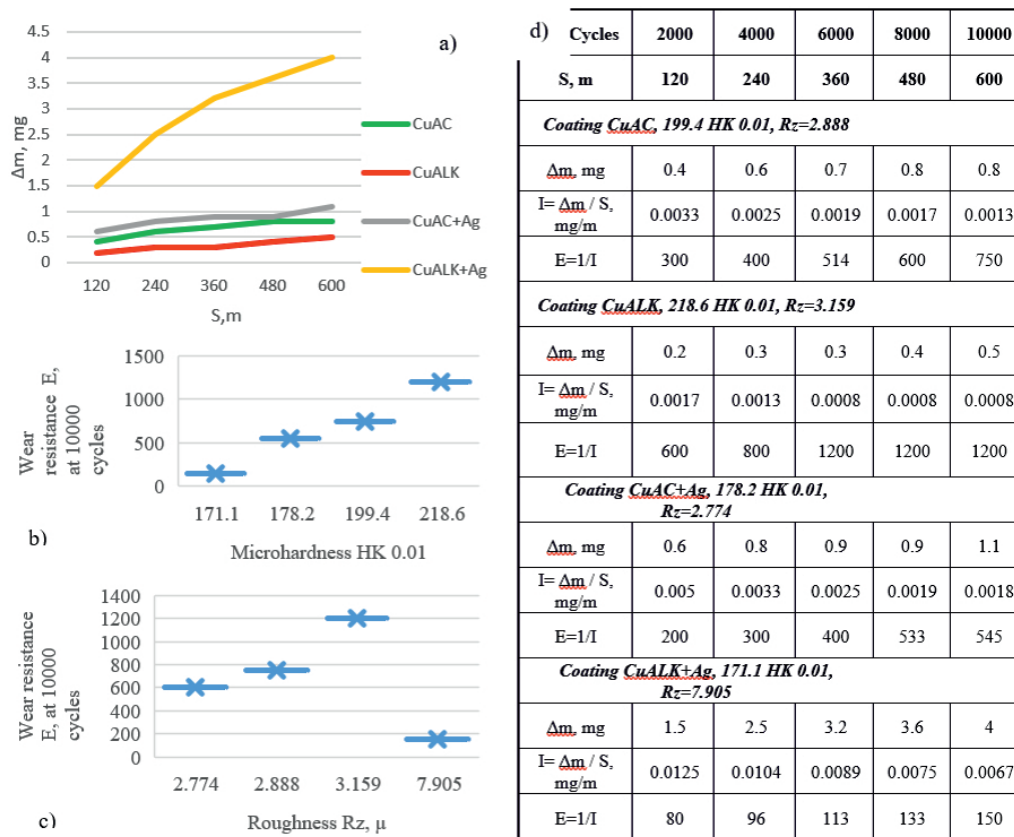


Fig. 4. Wear resistance of selective plated copper coatings; a) mass wear Δm depending on the wear path S , b) wear resistance E at 10 000 cycles depending on the microhardness, c) wear resistance E at 10 000 cycles depending on the roughness, d) mass wear, wear intensity and wear resistance for five series of 2000 cycles

tween the coating and the base material there is a good adhesion bond and no structural imperfections are observed. The thickness of the coatings corresponds to the set parameters of the operating mode. Phase identification revealed a dominant Cu phase and the presence of Ag, regardless of the nature of the electrolyte solution. The difference in the phase composition when using acidic and alkaline copper solution is expressed in the type of oxides formed in the deposition process. The added Ag particles in the copper coatings lower the microhardness, the change being more significant when using an alkaline copper solution. Microhardness values and surface roughness are essential for the wear resistance of copper-based selective coatings containing silver particles. Under the specific test conditions, wear resistance increases with increasing hardness and decreases significantly with high surface roughness.

REFERENCES

- [1] ESPÍRITO SANTO C., N. GERMAN, J. ELGUINDI et al. (2014) Biocidal Mechanisms of Metallic Copper Surfaces. In: Use of Biocidal Surfaces for Reduction of Healthcare Acquired Infections (ed. G. Borkow), Springer Int. Publ., Cham, 103–113, https://doi.org/10.1007/978-3-319-08057-4_6.
- [2] MAHLTIG B. (2018) Metal Pigments as Antimicrobial Agent and Coating Additives, Handbook of Antimicrobial Coatings, Elsevier, 283–299.
- [3] OĆWIEJA M., Z. ADAMCZYK, M. MORGA et al. (2015) Silver particle monolayers – Formation, stability, applications, Adv. Colloid Interface Sci., **222**, 530–563.
- [4] MICHELS H. T., J. O. NOYCE, C. W. KEEVIL (2009) Effects of temperature and humidity on the efficacy of methicillin-resistant *Staphylococcus aureus* challenged antimicrobial materials containing silver and copper, Lett. Appl. Microbiol., **49**(2), 191–195.
- [5] 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, <https://doi.org/10.1038/s41598-023-36460-2>.
- [6] RIGOU V. I., G. MARGINEAN, D. FRUNZEVERDE, C. V. CAMPIAN (2012) Silver based composite coatings with improved sliding wear behaviour, Wear, **290–291**, 61–65.
- [7] JASON Y. J. J., H. G. HOW, Y. H. TEOH et al. (2020) A study on the tribological performance of nanolubricants, Processes, **8**, 1372, <https://doi.org/10.3390/pr8111372>.
- [8] MUKRAS S. M. S. (2020) Computer simulation/prediction of wear in mechanical components, Adv. Tribology, **1–2**, 1–15.
- [9] MARUI E., H. ENDO (2001) Effect of reciprocating and unidirectional sliding motion on the friction and wear of copper on steel, Wear, **249**(7), 582–591.
- [10] VESELINOV D., H. SKULEV, R. YANKOVA et al. (2023) Enhancing antibacterial performance: Structure, phase composition, and microroughness of selective plated copper coatings on medical-grade stainless steel 1.4021 and nickel alloy Ni200, Appl. Sci., **13**(17), 9840.
- [11] VESELINOV D., H. SKULEV, R. YANKOVA, V. KOEVA (2023) Performance of selective plated copper coatings on stainless steel 316L and nickel alloy Ni201: Microstructure, microhardness, wear resistance, and corrosion resistance, C. R. Acad. Bulg. Sci., **76**(10), 1581–1590.
- [12] COTELL C. M., J. A. SPRAGUE, F. A. SMIDT (eds) (1994) Selective (Brush) Plating. In: ASM Handbook Vol. 5 Surface Engineering, ASM International, 277–281.
- [13] EN ISO 4516 Metallic and other inorganic coatings – microhardness tests (ISO 4516:2002).
- [14] RAGHAVENDRA N., V. S. RAMAMURTHY (2017) Development and tribological characterization of dual particle and triple particle reinforced Al-7075/Al₂O₃ metal matrix composite, Int. J. Recent Adv. Mech. Eng., **6**(2), 11–22.
- [15] SPASOVA D. (2019) Investigation of the abrasion resistance of stainless-steel composites with Al₂O₃ reinforcement phase produced by using the capillary forming method, IOP Conf. Ser.: Mater. Sci. Eng., **564**(1), 012035, 7 pp.

*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, dveselinov@ims.bas.bg, skulev@ims.bas.bg,
koeva@ims.bas.bg*