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PERFORMANCE OF SELECTIVE PLATED COPPER COATINGS ON STAINLESS STEEL 316L AND NICKEL ALLOY Ni201: MICROSTRUCTURE, MICROHARDNESS, WEAR RESISTANCE, AND CORROSION RESISTANCE

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Abstract

This study investigates the properties and performance of selective plated copper coatings on stainless steel 316L and nickel alloy Ni201 substrates, using acidic and alkaline electrolyte solutions. The analysis encompasses surface microstructure, elemental distribution, microhardness, surface roughness, wear resistance, and corrosion resistance of the coatings. The results demonstrate that the selective plated copper coatings exhibit a uniform and continuous deposition, free from visible irregularities or structural imperfections. Notably, the alkaline copper coatings exhibit significantly higher microhardness values compared to the acidic coatings, irrespective of the substrate materials. Surface roughness measurements reveal an increase in roughness after wear testing for all coatings, with the alkaline coatings showing lower initial roughness values and superior wear resistance compared to the acidic coatings. Concerning corrosion resistance, the alkaline copper coatings display a higher susceptibility to corrosion compared to the acidic coatings. Generally, the findings underscore the effectiveness of the selective plating process in producing high-quality, uniform, and defect-free copper coatings on stainless steel and nickel alloy substrates.

Key words: copper coating, selective plating, antibacterial surfaces, mechanical properties, wear resistance

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Introduction. Nosocomial infections, also known as hospital-acquired infections (HAIs) pose a significant risk to patients, as they are often caused by antibiotic-resistant bacteria and can result in serious complications. The primary sources, responsible for the supply and transmission of pathogens are people, including healthcare personnel, patients, and visitors, and surfaces in patient care areas and on medical devices. People can serve as reservoirs for pathogens, and improper hand hygiene and other infection control practices can further increase the risk of transmission. For example, when healthcare providers come into contact with germs present on medical equipment or frequently-touched surfaces in hospital settings, their hands can become contaminated. By touching a susceptible person afterwards, they can inadvertently spread the germs, potentially causing an infection [1–4]. Each year a growing number of scientific studies and health organizations reports emerge to indicate continuously increasing number of HAIs. Therefore, effective strategies to mitigate the risk of HAIs should prioritize interventions aimed at reducing the transmission of pathogens [5,6].

The viability of germs can vary depending on the type of surface they persist on, with some surfaces enabling pathogens to remain viable for prolonged periods. This characteristic makes these surfaces potential sources of contamination and transmission, thus increasing the risk of infection. Some materials such as copper have natural antimicrobial properties that make an effective agent against a range of pathogens, including bacteria and viruses. This property has led to the use of copper coatings on various surfaces, particularly in healthcare settings, as a means of reducing the risk of HAIs. Copper coatings have been proven to effectively reduce the viability and transmission of pathogens on surfaces, and studies have demonstrated that copper-coated surfaces can reduce the incidence of HAIs in hospital settings. As a result, copper coatings are becoming increasingly popular as a complementary measure to traditional infection prevention and control strategies in healthcare settings [7–10].

Several methods can be used to coat surfaces with copper, each with its own advantages and limitations. The selection of the appropriate method depends on several factors, including the type of surface being coated, the desired thickness and uniformity of the coating, and the environment. Regardless of the employed method, it is essential to ensure that the copper coating is uniform and adheres tightly to the surface to achieve optimal antimicrobial efficiency. Additionally, wear resistance and corrosion resistance are two critical factors for the reliable performance of the coating over time [11,12].

An interesting approach to deposit copper coatings is through selective plating. This process involves the deposition of thin layers of copper onto conductive surfaces using electric current. Selective plating is a highly specialized electroplating process that offers several advantages over traditional electroplating methods. One of the main benefits is that it allows for precise and accurate deposition of coating on specific areas of a part, without affecting the surrounding surfaces. This

precision makes it ideal for repairing or refurbishing parts with localized corrosion, wear, or damage. Selective plating is also a cost-effective solution as it reduces the need for expensive and time-consuming disassembly and reassembly of large components. Additionally, the process can be carried out on-site, which eliminates transportation costs and downtime associated with off-site plating services [13, 14].

This study exhibits preliminary results on the microstructure, surface roughness, microhardness, wear resistance and corrosion resistance of selective plated copper coatings onto stainless steel and nickel alloy samples.

Experimental. In order to prepare samples for plating, $20 \times 60 \times 3$ mm sections were cut from sheets of austenitic stainless steel 316L and nickel alloy Nickel 201 using a low-speed cutting machine with a continuous supply of cooling fluid. Detailed information on the chemical composition and properties of these alloys can be found in [15] and [16], respectively. Once cut, the samples were thoroughly cleaned with acetone, rinsed with deionized (DI) water, and air-dried to remove any residual contaminants.

The selective plating process used in this study involved several operations, including surface preparation, deposition of a bonding layer, and the plating of a copper coating. The preparation sequence began with masking the substrate, followed by a series of electrochemical preparatory steps, such as electrochemical cleaning, electrochemical etching, and activating the surface. Next, a thin bonding layer of nickel, 1 µm in thickness, was deposited on the surface. Copper coating was then plated onto the nickel layer, with a predetermined thickness of 40 µm. To complete the process, the selective plated surfaces were thoroughly rinsed with DI water immediately after plating and air-dried.

The electrochemical selective plating processes were conducted using a DC power source, providing precise control over current and potential. A graphite electrode wrapped in a white tiffwrap was used as anode. The chemical solutions used in the process included active compounds as sodium hydroxide and citric acid for electrocleaning, sulphuric acid and ammonium sulphate for electrochemical etching and activating, nickel sulphate and nickel formate for the deposition of bonding layer, and copper sulphate for the copper coatings. Two different electrolyte solutions were used to selective plate copper layers: an acidic solution with a pH of 0.5 and an alkaline solution with a pH of 8.5. The copper coatings were deposited using different average current densities, depending on the electrolyte solution used. Specifically, for the acidic solution (pH 0.5), an average current density of 0.46 A/cm^2 was employed, while for the alkaline solution (pH 8.5), a higher average current density of 1.55 A/cm^2 was used. All procedures were carried out under controlled laboratory conditions at room temperature, ensuring consistent and reliable results.

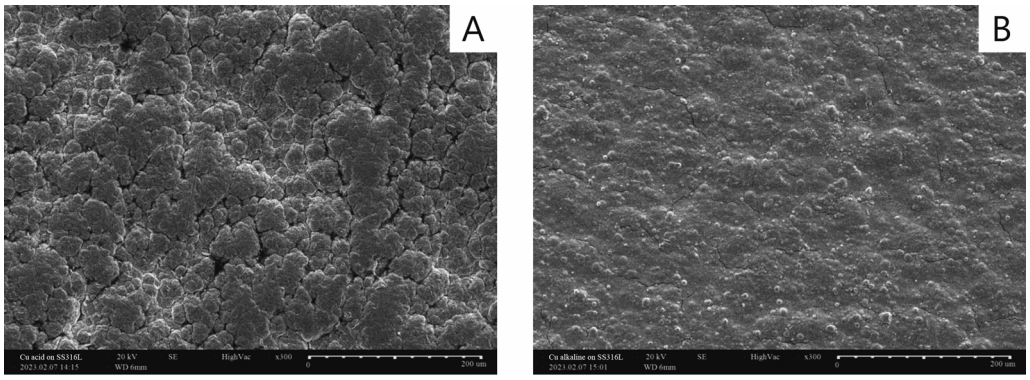
The microstructures and chemical composition of the plated samples were analyzed using a scanning electron microscope (SEM) HIROX SH-5500P equipped with an energy dispersive spectroscopy (EDS) module QUANTAX 100 Advanced

by Bruker. To determine the surface roughness of the copper coatings, a profilometer (model DGT-SRT200A, Baxit) was used. The microhardness of the coatings was measured using cross-sections. A low-speed cutting machine model DTQ-5 was used to obtain cross-sections of the plated samples. The cross-sections were moulded in black resin, ground with alumina sandpaper and polished. The microhardness tests were performed on a DVK-200A testing machine, equipped with a Vickers indenter, using a load of 0.025 kg. To evaluate the wear resistance of the plated copper coatings, "Pin-on-flat" tests were carried out using a commercial Glomro BXT-MAR306 wear testing stand. During the wear test, a 7 mm diameter silicone rubber counterbody was loaded with 0.5 kg and moved along a 50 mm path for 5000 cycles. The degree of wear of the copper coatings was quantified using profilograms recorded before and after the wear test in a given section. By measuring the alteration of the roughness parameter Rz before and after the wear test, it was possible to assess the extent of wear on the surface of the copper coatings.

To assess the corrosion properties of the copper coatings, a Corrtest CS350 potentiostat/galvanostat was utilized. The test involved a three-electrode configuration consisting of a Pt counter electrode, an Ag/AgCl reference electrode, and the coated test sample as the working electrode. A 3.5% wt. solution of sodium chloride (NaCl) was used as a corrosive media. The surface area exposed to the salt solution was limited to 1 cm^2. After attaining a stable open circuit potential (OCP), potentiodynamic polarization was conducted. The experiments were performed using freshly prepared solutions at room temperature.

Results and discussion. ***Surface microstructure and elemental distribution.*** Surface microstructure and elemental distribution of the selective plated copper coatings were examined using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The analysis revealed that the selective plated copper coatings exhibited a uniform and continuous deposition across the surface. Notably, the studied samples revealed a flawless surface appearance with no visible irregularities or structural imperfections, attesting to the exceptional quality and integrity of the selective plated copper coatings. These findings highlight the effectiveness and reliability of the selective plating process in producing homogeneous and defect-free copper coatings on the studied surfaces. The thickness of the coatings was measured by examining the cross-sections and it was found to be in agreement with the precalculated values of approximately 40 µm for both the acidic and alkaline solutions plated on the 316L and the Ni201 substrate materials. Figure 1 illustrates some of the results obtained during the conducted analysis.

Microhardness. The microhardness of both substrate metal materials and their respective electroplated coatings was measured on their surfaces as well as in cross-sections. To ensure accuracy, five tests were conducted for each sample, and the reported values are their average. A significant difference in the measured

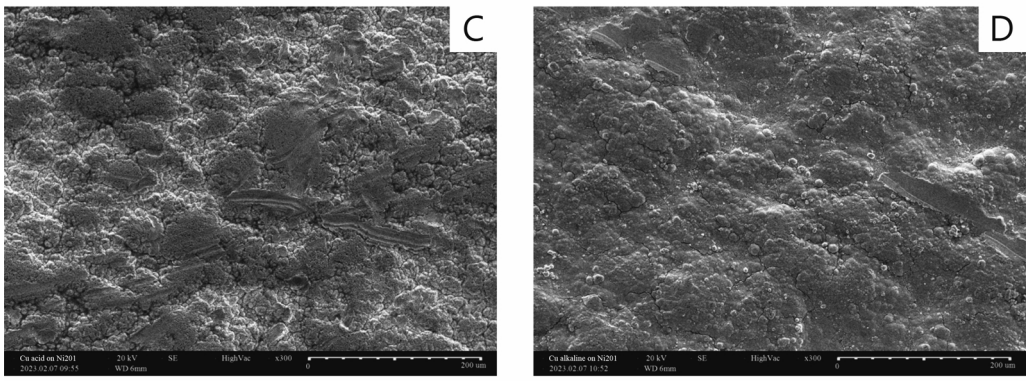


Cu acid on SS 316L

Element	At. No.	Netto	Mass [%]	Mass Norm [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Cu	29	6756	84.12	99.20	97.61	4.51	2.78
O	8	57	0.68	0.80	2.39	0.45	66.56
		Sum	**84.80**	**100**	**100**		

Cu alkaline on SS 316L

Element	At. No.	Netto	Mass [%]	Mass Norm [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Cu	29	54167	90.94	99.34	98.11	2.29	2.74
O	8	374	0.60	0.66	1.89	0.21	34.94
		Sum	**91.54**	**100**	**100**		



Cu acid on Ni201

Element	At. No.	Netto	Mass [%]	Mass Norm [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Cu	29	25130	85.18	98.65	94.84	2.38	2.79
O	8	382	1.17	1.35	5.16	0.38	32.59
		Sum	**86.35**	**100**	**100**		

Cu alkaline on Ni201

Element	At. No.	Netto	Mass [%]	Mass Norm [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Cu	29	23605	86.74	98.35	95.35	2.22	2.80
O	8	416	1.46	1.65	4.65	0.46	31.32
		Sum	**88.20**	**100**	**100**		

Fig. 1. SEM images and EDS analysis of selective plated copper coatings using: A – acidic solution on 316L, B – alkaline solution on 316L, C – acidic solution on Ni201, D – alkaline solution on Ni201

values was not observed, regardless of whether the measurements were conducted on the surface or in a cross-sectional analysis. The acquired results are displayed in Fig. 2.

The surface microhardness values for the two substrates, stainless steel 316L and nickel alloy Ni201, were found to be 279 $HV_{0.025}$ for 316L and 267 $HV_{0.025}$, respectively. This indicates that the stainless steel substrate is slightly harder than the nickel substrate. In terms of coatings, the copper coatings, electroplated from acidic solution, on both substrate materials have similar microhardness values of 130 $HV_{0.025}$ for 316L and 133 $HV_{0.025}$ for Ni201, while the coatings deposited using

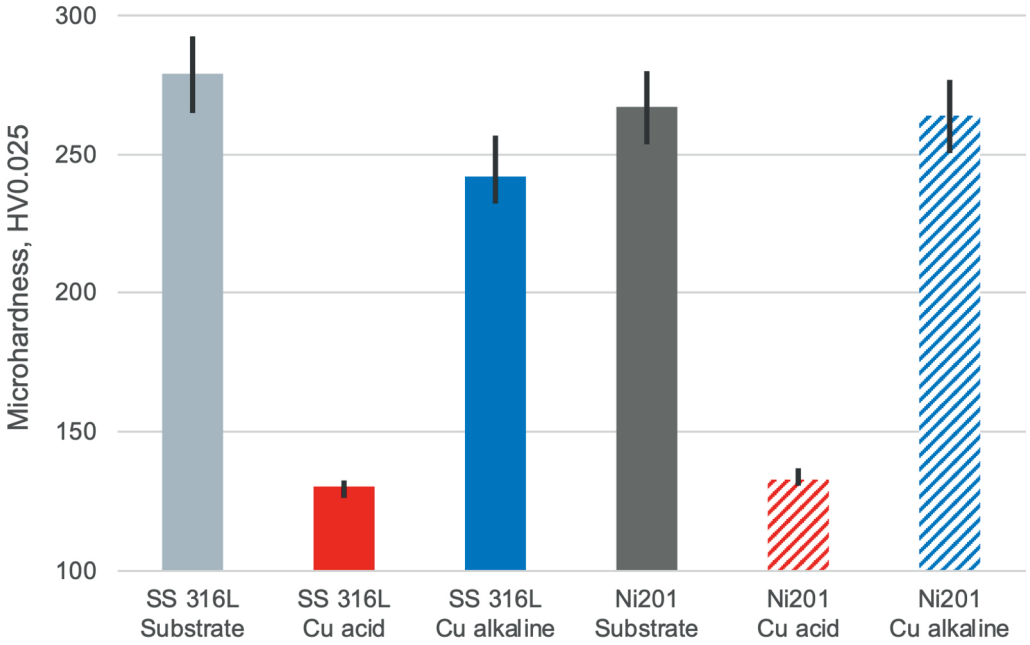


Fig. 2. Microhardness of stainless steel (SS 316L), nickel alloy (Ni201) substrate materials and selective plated copper coatings on them using acidic (Cu acid) and alkaline (Cu alkaline) electrolyte solution

alkaline solution have significantly higher microhardness of 242 $HV_{0.025}$ for 316L and 264 $HV_{0.025}$ for Ni201. In general, the results suggest that the alkaline copper coating provides a much harder surface compared to the acid coating regardless of the substrate materials.

Surface roughness and wear resistance. Surface roughness measurement can be a useful tool for quantifying wear and evaluating the performance of different materials and coatings in tribological applications. By comparing the surface roughness of a material before and after it has been subjected to wear, it is possible to estimate the degree of material loss that has occurred. A common method for measuring roughness is to use a profilometer, which measures the height variations of a surface at a microscopic level. By taking measurements of the surface roughness before and after the wear process, it is possible to calculate the difference in roughness, which can be used as a measure of the degree of wear.

The difference in roughness can be expressed in a variety of ways, such as Ra or Rz. These parameters represent different aspects of the surface roughness, such as the average height of peaks and valleys (Ra) or the maximum height difference within a given length (Rz). When a surface is subjected to wear its roughness usually increases because the wear process removes material from the surface of the sample, which creates a rougher surface. When the surface is rougher, there are more peaks and valleys, which increase the Rz value. The degree of wear is

Sample	Ra initial	Rz initial	Ra after wear	Rz after wear
SS 316L Substrate	1.406	8.667	1.565	9.396
SS 316L Cu acid	1.222	8.034	1.472	8.671
SS 316L Cu alkaline	0.856	4.956	1.013	5.712
Ni201 Substrate	2.684	14.881	3.133	16.163
Ni201 Cu acid	2.803	14.341	3.310	14.904
Ni201 Cu alkaline	3.337	15.558	3.526	16.288

Fig. 3. Calculated surface roughness of substrates and coatings before and after wear testing

determined by comparing the Rz value before and after the wear process. A higher Rz value after wear indicates a greater degree of wear and a rougher surface.

For each of the tested samples in this study, a total of five independent profile measurements were performed. Based on the five measurements, the average calculated values for the surface roughness parameters Ra and Rz are available in Fig. 3.

The acquired data indicates that the surface roughness values for both Ra and Rz increase after wear for all samples and coatings, indicating that the wear has caused an increase in surface roughness for all tested substrates and coatings. In terms of the initial surface roughness values of the base materials, it can be observed that the Ni201 substrate has higher Ra and Rz values than the SS 316L substrate, indicating that the surface of the nickel substrate is rougher initially.

When comparing the effects of different coatings on the same substrate material, it can be seen that the electroplated copper coatings using an alkaline solution result in a lower initial Ra and Rz value compared to those deposited from the acidic solution for both SS 316L and Ni201 substrates. This indicates that the alkaline copper coating provides a smoother surface finish compared to the acidic copper coating.

Moreover, after the wear tests, the alkaline copper coating still has a lower Ra and Rz value compared to the acidic copper coating, suggesting that the alkaline coating is more resistant to wear. Overall, the data suggests that the Cu alkaline coating provides a better combination of initial surface finish and wear resistance for both SS 316L and Ni201 substrates.

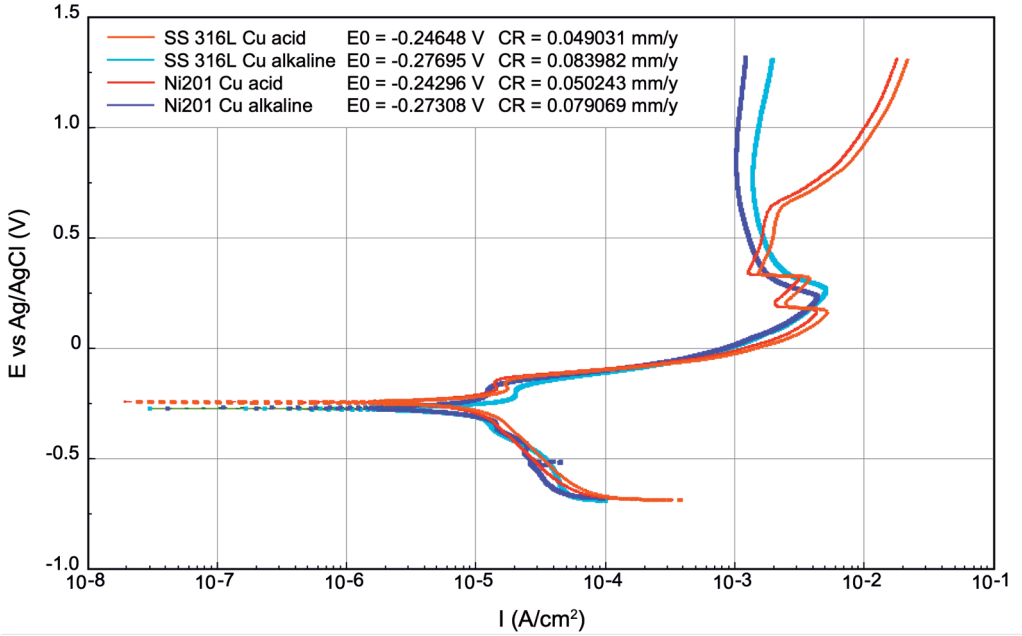


Fig. 4. Potentiodynamic polarization data of selective plated copper coatings deposited on stainless steel 316L and nickel alloy Ni201 samples tested in 3.5% NaCl

Corrosion resistance. The corrosion resistance of the selective plated copper coatings was assessed through potentiodynamic polarization tests in a 3.5% NaCl solution at room temperature. The corrosion parameters extracted from the obtained polarization curves are available in Fig. 4.

Based on the acquired data, it can be concluded that the copper coatings deposited using an alkaline solution on both substrates have a more negative open circuit potential (E0) compared to the coatings obtained with an acidic solution. This suggests that the alkaline copper coatings have a higher tendency to corrode than the acidic coatings. Additionally, the corrosion rate (CR) of the alkaline copper coatings is higher than that of the acidic coatings, further confirming their higher susceptibility to corrosion.

In terms of the relative corrosion resistance of the coatings, the copper coating deposited on the stainless steel substrate has the highest corrosion resistance, followed by the acidic copper coating deposited on the nickel alloy, the alkaline copper coating deposited on Ni201, and the alkaline coating deposited on SS 316L in decreasing order. However, all of the deposited copper coatings exhibit similar corrosion resistance, typical for copper metals.

Conclusion. The selective plated copper coatings exhibited a uniform and continuous deposition with no visible irregularities or structural imperfections, demonstrating the exceptional quality and integrity of the selective plated copper coatings. The thickness of the coatings matched the precalculated values,

indicating the accuracy of the plating process. Regarding microhardness, both substrate materials and their respective copper coatings were evaluated. The alkaline copper coatings displayed significantly higher microhardness compared to the acidic copper coatings, regardless of the substrate materials. Surface roughness measurements showed an increase in roughness after wear testing for all samples and coatings, with the alkaline copper coatings exhibiting lower initial roughness values and better wear resistance compared to the acidic coatings. Concerning corrosion resistance, the alkaline copper coatings demonstrated a higher tendency to corrode than the acidic coatings. However, all the copper coatings exhibited similar corrosion resistance, typical for copper metals. Overall, these findings emphasize the effectiveness of the selective plating process in producing high-quality, uniform, and defect-free copper coatings with desirable properties such as hardness, wear resistance, and corrosion resistance on stainless steel and nickel alloy substrates.

REFERENCES

[1] Facciolà A., G. F. Pellicanò, G. Visalli, I. A. Paolucci, E. Venanzi Rullo et al. (2019) The role of the hospital environment in the healthcare-associated infections: a general review of the literature, Eur. Rev. Med. Pharmacol. Sci., **23**(3), 1266–1278. https://doi.org/10.26355/eurrev_201902_17020.

[2] Canciu A., A. Cernat, M. Tertis, F. Graur, C. Cristea (2023) Tackling the issue of healthcare associated infections through point-of-care devices, Trends Analyt. Chem., **161**, 116983, https://doi.org/10.1016/j.trac.2023.116983.

[3] Cruz-López F., A. Martínez-Meléndez, E. Garza-González (2023) How does hospital microbiota contribute to healthcare-associated infections?, Microorganisms, **11**, 192, https://doi.org/10.3390/microorganisms11010192.

[4] Stachel A., L. T. Keegan, S. Blumberg (2021) Modeling transmission of pathogens in healthcare settings, Curr. Opin. Infect. Dis., **34**, 333–338, https://doi.org/10.1097/QCO.0000000000000742.

[5] Global Report on Infection Prevention and Control (n.d.) https://www.who.int/publications/i/item/9789240051164 (accessed June 1, 2023).

[6] Report on the Burden of Endemic Health Care-associated Infection Worldwide (n.d.) https://apps.who.int/iris/handle/10665/80135 (accessed June 1, 2023).

[7] Kişla D., G. G. Gökmen, G. Akdemir Evrendilek, T. Akan, T. Vlčko et al. (2023) Recent developments in antimicrobial surface coatings: Various deposition techniques with nanosized particles, their application and environmental concerns, Trends Food Sci. Technol., **135**, 144–172, https://doi.org/10.1016/j.tifs.2023.03.019.

[8] Lazar F. S., M. Colin, G. Carré, N. Bachelard, J.-P. Chopart et al. (2023) Effects of ageing in disinfectant solution on the corrosion resistance and antimicrobial behavior of copper alloys, Molecules, **28**, 981, https://doi.org/10.3390/molecules28030981.

[9] Arendsen L. P., R. Thakar, A. H. Sultan (2019) The use of copper as an antimicrobial agent in health care, including obstetrics and gynecology, Clin. Microbiol. Rev., **32**, https://doi.org/10.1128/CMR.00125-18.
[10] Jose A., M. Gizdavic-Nikolaidis, S. Swift (2023) Antimicrobial coatings: Reviewing options for healthcare applications, Appl. Microbiol., **3**, 145–174, https://doi.org/10.3390/applmicrobiol3010012.
[11] Bharadishettar N., K. U. Bhat, D. Bhat Panemangalore (2021) Coating technologies for copper based antimicrobial active surfaces: A perspective review, Metals (Basel), **11**, 711, https://doi.org/10.3390/met11050711.
[12] Veselinov D. (2022) Titanium for biomedical applications: Surface treatment and anodizing, 1st edn, Sofia, Prof. Marin Drinov Publ. House of Bulg. Acad. of Sci., ISBN: 978-619-245-265-0.
[13] Kilgore D. (2020) The benefits of automated selective plating, NASF Surface Technology White Papers, **84**(8), 11–18, https://www.pfonline.com/cdn/cms/2006_Printable_Version.pdf (accessed October 8, 2023).
[14] Cotell C. M., J. A. Sprague, F. A. Smidt (1994) Selective (brush) plating. In: ASM Handbook, Vol. 5: Surface Engineering, ASM Int., 277–281, https://doi.org/10.31399/asm.hb.v05.a0001261.
[15] Matweb. AISI Type 316L Stainless Steel (n.d.) https://www.matweb.com/search/datasheet_print.aspx?matguid=a2d0107bf958442e9f8db6dc9933fe31 (accessed June 8, 2023).
[16] BSWMetals. Nickel 200/201 (n.d.) http://bswmetals.bg/fise-produse/Ni%20200.pdf (accessed June 8, 2023).

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