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Characterization of electrochemically deposited silver coatings on different substrates at industrial scale

ABSTRACT

Electrochemical deposition of silver coatings on different substrates—namely copper and two types of steel—was performed on an industrial scale, followed by their characterization.The coatings were evaluated in terms of hardness, surface roughness, and adhesion, while current efficiency and coating thickness were calculated from the mass changes of the samples during electrodeposition. In addition to assessing the influence of substrate type on coating quality, the effect of current density on coating adhesion and morphology was also investigated. Steel 1 (WNR 1.7231), copper, and Steel 2 (WNR 1.0032) were used as cathode materials for silver electrodeposition. Their chemical composition was determined by XRF analysis. The results showed that both current density and substrate type significantly affect the properties of the obtained coatings. All coatings were matte white and provided complete surface coverage on all substrates. The highest surface roughness and hardness values were obtained for coatings deposited at a current density of 0.75 A/dm^2. The highest current efficiency was achieved at 0.5 A/dm^2, while the greatest coating thickness was obtained at 1.0 A/dm^2.

Keywords:*silver coatings, electrochemical deposition, current density, roughness, hardness.*

INTRODUCTION

Electrochemical deposition is a process in which a metallic coating is deposited onto a conductive surface through the application of an electric current. This technique has been extensively employed in various industries for over a century due to its ability to deposit uniform and homogeneous coatings and improve the physical, chemical, mechanical, and aesthetic properties of materials.Electroplating is widely used in different fields like electronics, automotive manufacturing, aerospace engineering, jewellery production, and corrosion protection technologies [1-5]. Silver is one of the most important metals because of its exceptional properties and its wide range of industrial applications. It possesses high electrical and thermal conductivity, making it particularly valuable in the production of electrical contacts, connectors, switches, and electronic components [6-9]. In addition, silver exhibits good corrosion resistance, high reflectivity, excellent solderability, and an attractive metallic appearance [10-12].

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These characteristics have led to its widespread use in both functional and decorative coatings. The principle of silver electrodeposition is based on electrochemical reduction reactions occurring at the cathode surface. When an electric current passes through an electrolyte containing silver ions, the positively charged silver ions migrate toward the cathode, where they gain electrons and are reduced to metallic silver. The deposited silver forms a thin layer on the substrate surface, whose thickness, morphology, adhesion, and uniformity depend on several operating parameters such as electrolyte composition, current density, temperature, pH, agitation, and deposition time [13-15]. The choice of substrate material plays a critical role in determining the quality of the deposited coating [16]. Copper is commonly used as a substrate because of its high electrical conductivity and relatively similar electrochemical behavior to silver, which promotes good adhesion and uniform coating formation. Silver-plated copper is extensively utilized in electrical and electronic applications where low contact resistance and high conductivity are required [17-19]. Steel is another important engineering material frequently subjected to silver

electroplating. Due to its high strength, durability, and low cost, steel is used in numerous industrial applications. However, unlike copper, steel is more susceptible to oxidation and corrosion, which can negatively affect coating adhesion and quality. Consequently, proper surface preparation, including cleaning, degreasing, and activation, is essential before the electrodeposition process. Silver coatings on steel can significantly improve corrosion resistance, antimicrobial properties, wear properties, electrical performance, and decorative appearance [20-22]. The electrochemical deposition process is governed by fundamental electrochemical laws, particularly those established by Faraday, which relate the amount of deposited material to the quantity of electric charge passed through the electrolyte. Understanding these principles allows for precise control of coating thickness and optimization of deposition efficiency. Furthermore, modern electrochemical techniques enable the investigation of nucleation, crystal growth, surface morphology, and microstructural characteristics of deposited silver layers [2].

This study focuses on the electrochemical deposition of silver onto steel and copper substrates in industrial scale. The objective is to investigate the deposition process, compare the behaviour of the two substrate materials, and evaluate the properties of the resulting silver coatings. Particular attention is given to the influence of substrate characteristics on coating adhesion, surface morphology, deposition efficiency, and overall coating quality. The findings contribute to a better understanding of silver electrodeposition mechanisms and provide valuable information for industrial applications where high-performance silver coatings are required.

EXPERIMENTAL

The substrates used in this study were steel WNR 1.7231 (Steel 1), copper, and steel WNR 1.0032 (Steel 2). The exposed cathodic surface area of each specimen was 0.5 dm^2. The chemical composition of the substrates was determined by X-ray fluorescence (XRF) spectroscopy using an X-MET 8000 analyzer.Prior to electrodeposition, all specimens underwent a chemical surface preparation procedure to ensure adequate cleanliness and coating adhesion. The first step consisted of degreasing in 1,1,1-trichloroethane at 76 °C for 7 min, followed by thorough rinsing. Subsequently, the steel substrates were pickled in hydrochloric acid to remove surface oxides and contaminants. Copper substrates were initially treated in chromic acid and then subjected to hydrochloric acid pickling. Following chemical pretreatment, the substrates were sequentially coated with nickel, copper, and silver thin layers before the final silver electrodeposition process.The dimensions of the working area of the plating bath is approximately 700 × 450 × 700 mm.These intermediate coatings promoted better adhesion and a more uniform deposition of the final silver coating.The composition of the silver-plating electrolyte and the operating conditions employed during deposition are summarized in Table 1.

Table 1. The composition of the plating baths and operating conditions used for silver electrodeposition

Parameters	Nickel film	Copper film	Silver film	Silver coating
Bath composition	350 g/L $NiCl_2 \cdot 6H_2O$ 30 g/L HCl	40 g/L Cu 30g/L KCN	4 g/L AgCN 75 g/L KCN	45 g/L AgCN 32 g/L KCN 12 g/L KOH 35 g/L K_2CO_3
Temperature (ºC)	22	60	20	20
Current density (A/dm^2)	4	2	2.2	1;0.75;0.5
Deposition time (min.)	3	2	2	15

Electrodeposition of silver coatings was conducted at three different current densities, 0.5; 0.75; 1.0 A/dm^2.Three replicate samples were used for each substrate type. The roughness, hardness, and adhesion of the deposited coatings were examined. Coatings morphology was examined by Leica DM600M metallurgical microscope. Surface roughness measurements were performed byMitutoyo surface profilometer. The hardness of the coatings was evaluated using the Vickers microhardness method, while coating adhesion was examined by bending test. In addition to these characterization techniques, current efficiency was calculated based on Faraday's law, and coating thickness was determined from the measured mass gain after electrodeposition.Initially, the samples were weighed to determine their initial mass. After this, the specimens underwent identical chemical preparation procedures, followed by the sequential deposition of nickel, copper, and silver thin films. Subsequently, the samples were dried for 15 minutes, after which the final mass was

measured. For each substrate, the mean mass change (Δm) was determined and used as a correction factor for the initial sample mass. This correction accounts for the mass contribution of previously deposited nickel, copper, and silver intermediate layers, ensuring that the final calculation reflects only the mass of the final silver coating. Accordingly, the corrected initial mass was obtained by adding Δm to the initial mass of the prepared substrates.The actual mass of the deposited silver coating was then determined as the difference between the final measured mass and the corrected initial mass of the specimen.

RESULTS AND DISCUSSION

Substrate composition

The composition of the used steels and copper substrates is presented in Tables 2-4.

Table 2. Steel 1 substrate composition

Element	Wt.%
Fe	96.84
Cr	1.02
Mn	0.97
Si	0.64
Cu	0.13
V	0.13
Ni	0.07
S	0.05
MO	0.03
P	0.02

Table 3. Copper substrate composition

Element	Wt.%
Cu	99.40
Si	0.28
Al	0.27
Fe	0.03
P	0.01
Zn	0.01
Ni	0.01

Morphology of the electrodeposited silver coatings

The photographs of the final electrochemically deposited silver coatings on all investigated substrates obtained at different current densities are presented at Fig. 1.

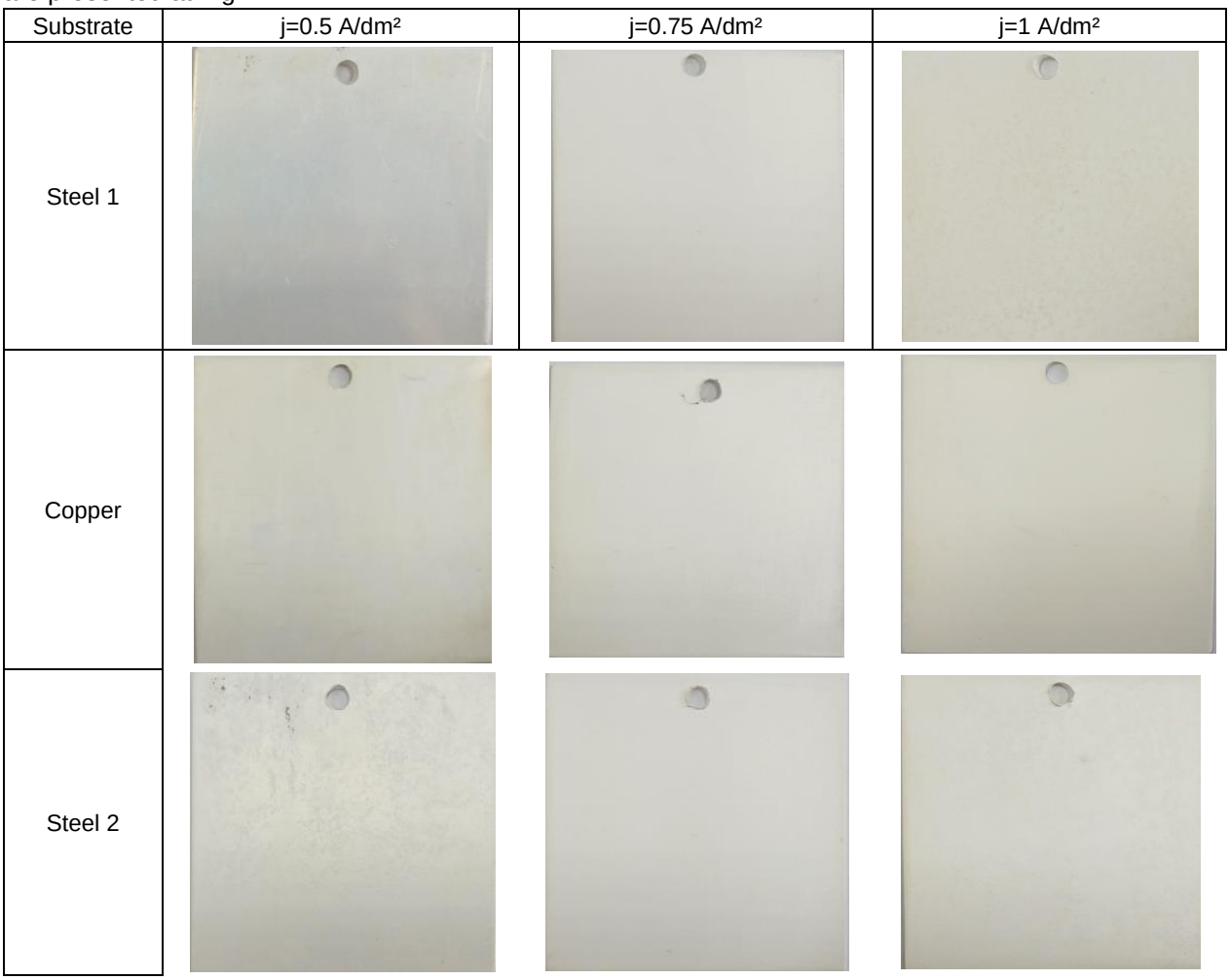

Figure 1. Photographs of obtained silver coatings on different substrates

Table 4. Steel 2 substrate composition

Element	Wt.%
Fe	98.90
Mn	0.37
Si	0.24
Cu	0.09
Cr	0.05
S	0.05
Ni	0.04
V	0.03
MO	0.01
P	0.01

As can be seen from the Fig. 1, the surface of each substrate was completely covered by the silver coating at all applied current densities. At a current density of 0.5 A/dm^2, the deposited silver layers were relatively thin, allowing the surface topography of the underlying substrate to remain partially visible. This effect was particularly pronounced for Steel 1 and Steel 2, where the characteristic nonhomogeneous structure of the base material could still be observed through the coating. Despite the relatively small coating thickness at the lowest current density, continuous and uniform coverage of the substrate surface was achieved in all cases. The deposited silver coatings exhibited a white matte appearance across all substrates. Such a surface morphology was expected, as no post-deposition treatments, such as polishing, burnishing, or brightening, were performed following electrodeposition.Fig. 2 presents optical micrographs of the deposited silver coatings at three different current densities on two types of steel and copper.

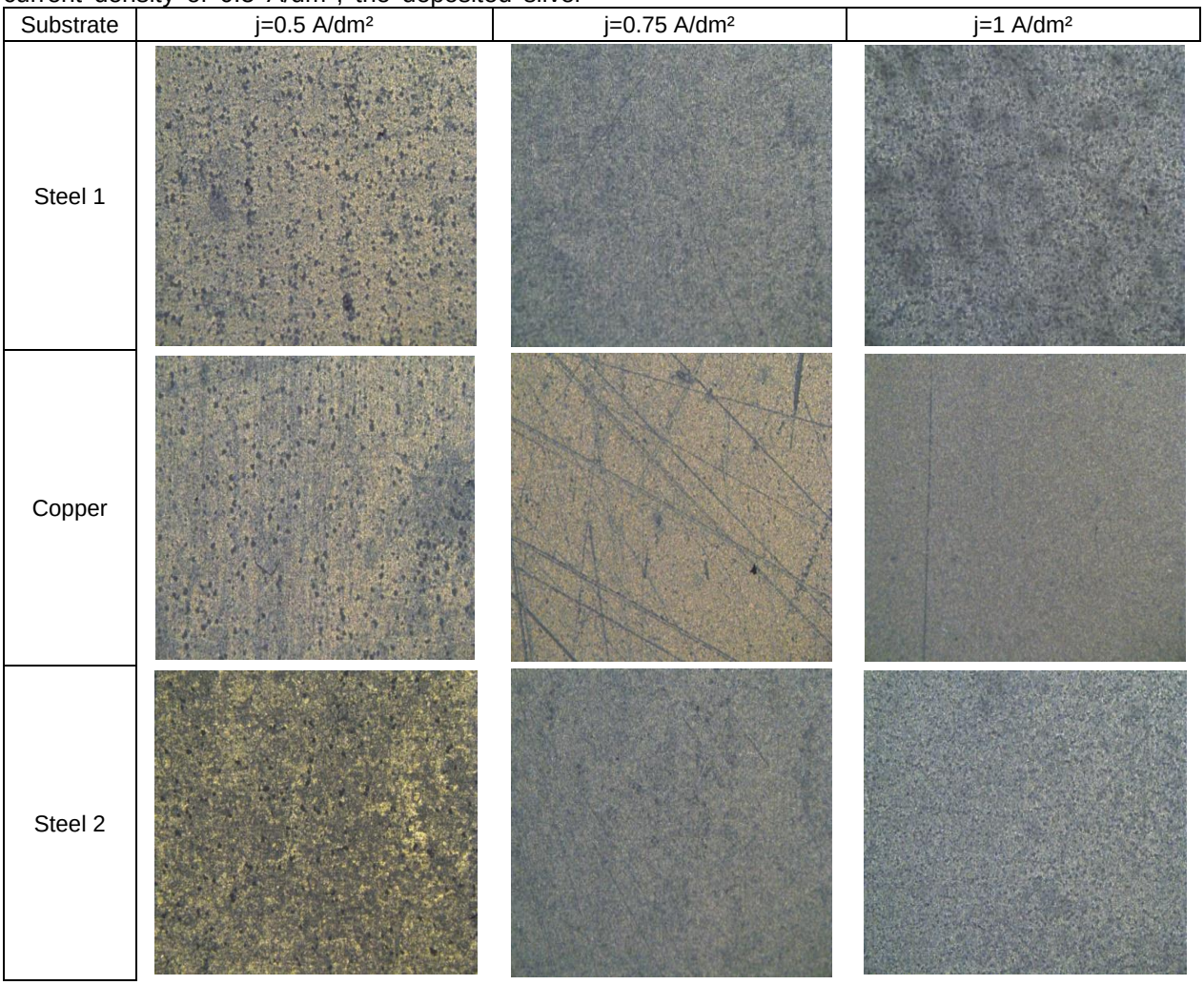

Figure 2. Morphology of the obtained silver coatings on different substrates

As shown in Fig.2, the silver coatings deposited at a current density of 0.5 A/dm^2 were relatively thin on all substrates, as evidenced by the visible nonhomogeneous and rough surface morphology of the underlying base metals. The topographical features of the substrates remained clearly

discernible through the deposited silver layer, indicating limited coating thickness at this current density. An increase in the current density to 0.75 A/dm^2 resulted in improved surface coverage on both Steel 1 and Steel 2 substrates. Consequently, the nonhomogeneous structure and roughness of the underlying materials became significantly less pronounced compared to the coatings deposited at 0.5 A/dm^2. In the case of the copper substrate, several surface irregularities and fine scratches remained visible. However, the silver coating was continuous and compact across the entire surface, suggesting that these features originated from the substrate itself rather than from defects in the deposited layer.At the highest investigated current density of 1.0 A/dm^2, thicker and more compact silver coatings were obtained on all substrates.

For Steel 1, the coating exhibited a somewhat coarser-grained and more pronounced surface morphology compared to the coating deposited at 0.75 A/dm^2. The coatings deposited on copper and Steel 2 at 1.0 A/dm^2 were characterized by improved compactness and homogeneity, with the underlying substrate structure becoming almost completely obscured. On the copper substrate, only a single fine scratch corresponding to a pre-existing scratch in the base material remained visible. Overall, the coatings produced at 1.0 A/dm^2 exhibited excellent surface coverage, high uniformity, and increased thickness. As a result, the appearance of the final silver coatings became very similar across all investigated substrates, reflecting the improved coverage, compactness, and homogeneity achieved at higher current densities.The observed increase in coating homogeneity with increasing current density can be attributed to changes in the kinetics of the electrodeposition process. At lower current densities, the deposition rate of silver is relatively slow, resulting in the formation of thin coatings that are insufficient to completely mask the surface irregularities and roughness of the underlying substrate. Consequently, the topographical features of the base material remain visible through the deposited layer.As the current density increases, the rate of electrochemical reduction of silver ions at the cathode surface also increases, as well as number of nucleation sites, leading to a higher deposition rate and a greater amount of silver deposited per unit time. This promotes rapid surface coverage and the progressive filling of surface irregularities, scratches, and other microdefects present on the substrate. The resulting coating becomes thicker and more continuous, thereby reducing the influence of the substrate morphology on the surface appearance of the deposit.Consequently, the surface roughness and topographical features of the substrate become progressively masked as the coating thickness increases. Similar observations have been reported in literature by different authors [13, 23, 24], demonstrating that increased nucleation density and surface coverage lead to more uniform electrodeposited metallic coatings.

Roughness and hardness of the silver coatings

The results of hardness and surface roughness measurements of the electrochemically deposited silver coatings are presented in Table 5. Table 5 summarizes the mean values of the measured surface roughness and microhardness for three specimens of silver coatings deposited at different current densities (0.5, 0.75, and 1.0 A/dm^2) on steel 1, copper and steel 2.

Table 5. The roughness and hardness data of the electrodeposited silver coatings on different substrate

Substrate	Current density (A/dm^2)	Mean roughness value (μm)	Mean hardness value (HV 0.2)
Steel 1	0.5	0.39	204
	0.75	3.14	251
	1.0	2.30	208
Copper	0.5	1.86	153
	0.75	1.78	149
	1.0	4.20	127
Steel 2	0.5	2.58	134
	0.75	6.64	228
	1.0	3.61	152

Table 6. The dependence of the coating thickness and current efficiency of the deposition current density

Substrate	Current density (A/dm^2)	Mean current efficiency (%)	Mean thickness of the coating (HV 0.2)
Steel 1	0.5	89.3	4.3
	0.75	93.9	6.7
	1.0	97.4	7.8
Copper	0.5	97.6	4.7
	0.75	86.3	5.5
	1.0	90.0	7.3
Steel 2	0.5	96.2	4.6
	0.75	93.9	6.0
	1.0	90.4	7.3

The highest surface roughness values of the silver coatings were recorded for samples deposited at a current density of 0.75 A/dm^2 on both Steel 1 and Steel 2 substrates. In contrast, the lowest roughness values on these steel substrates were obtained at a current density of 0.5 A/dm^2, ranging from 0.39 to 2.58 µm.

For the copper substrate, the lowest surface roughness was observed at 0.75 A/dm^2, with an average value of 1.78 µm, while a slightly higher value of 1.86 µm was measured at 0.5 A/dm^2. The highest roughness on copper was recorded for coatings deposited at 1.0 A/dm^2, reaching 4.2 µm.The smallest variation in roughness values across measurements was observed for coatings deposited at 1.0 A/dm^2, ranging from 2.3 to 4.2 µm. This indicates that with increasing current density, and consequently increasing coating thickness, the deposited silver layers become more uniform, compact, and less influenced by the initial roughness of the substrate. As a result, the surface characteristics of the base material have a reduced effect on the final appearance and topography of the silver coating. Table 5 also shows the dependence of the average microhardness of the silver coatings on both the current density and the type of substrate. The observed relationship is well pronounced, indicating a strong influence of deposition parameters and substrate material on the mechanical properties of the coatings.The highest microhardness values for all investigated substrates were obtained at a current density of 0.75 A/dm^2. Among the tested materials, coatings deposited on Steel 1 exhibited the highest hardness across all current densities, with values ranging from 204 to 251 $HV_{0,2}$. In contrast, the lowest hardness values were recorded for coatings deposited on copper, ranging from 127 to 153 $HV_{0,2}$. For Steel 2 substrates, the microhardness values varied between 134 and 228 $HV_{0,2}$.These results clearly indicate that the measured hardness of the final silver coatings is strongly dependent on the nature of the substrate material, particularly its intrinsic hardness. In addition, the deposition current density significantly influences the microstructure of the coatings, with 0.75 A/dm^2 appearing to be the most favorable condition for achieving higher hardness values across all investigated substrates.

Coatings thickness and current efficiency

The current efficiency of the electrodeposition process was calculated based on the mass gain after deposition of the final silver coating, in accordance with Faraday's laws of electrolysis. The obtained results are presented in Table 6.

It can be observed that there are variations in current efficiency at identical current densities for different substrates. For Steel 1, a noticeable increase in current efficiency is observed with increasing current density. In contrast, Steel 2 exhibits an opposite trend, where current efficiency decreases as the current density increases.For the copper substrate, no clear monotonic dependence on current density is evident. The lowest current efficiency is recorded at 0.75 A/dm^2, while the highest value is obtained at 0.5 A/dm^2, which also represents the maximum overall efficiency of 97.6%. The average current efficiency for silver deposition on all investigated substrates ranges from 86.3% to 97.6%. The average coating thickness increases with increasing current density for all three investigated substrates. It can also be observed that the thickness values obtained at identical current densities are comparable across all substrates. This suggests that the applied current density has a more pronounced influence on the thickness of the deposited silver coating than the type of substrate itself.Following chemical surface preparation and the deposition of nickel, copper, and silver intermediate layers, the substrate surface exerts a reduced influence on the quality, morphology, and thickness of the final silver coating. The lowest coating thickness was obtained on Steel 1 at a current density of 0.5 A/dm^2, while the highest thickness was also recorded on Steel 1, but at 1.0 A/dm^2. These results clearly confirm the dominant role of current density in controlling the thickness of the electrodeposited silver layer.

Adhesion of the coatings to substrate

The results of the adhesion tests are presented in Fig. 3, which shows photographic images of the specimens after the bending test. These images illustrate the condition of the coatings following plastic deformation of the plated plates and provide a qualitative assessment of the adhesion strength between the coating and the substrate under mechanical loading.

After bending, no cracking, peeling, or delamination of the silver coatings was observed on any of the investigated specimens, indicating excellent adhesion performance that meets the required acceptance criteria.Due to the use of different bending tools during testing, distinct bright lines were observed on the Steel 1 (WNR 1.7231) specimens. However, these features are not associated with coating damage. In this case, deformation was performed using a tensile testing machine, and the observed shiny marks are attributed to frictional contact between the specimen surface and the loading tool during mechanical deformation, rather than to coating failure or detachment.

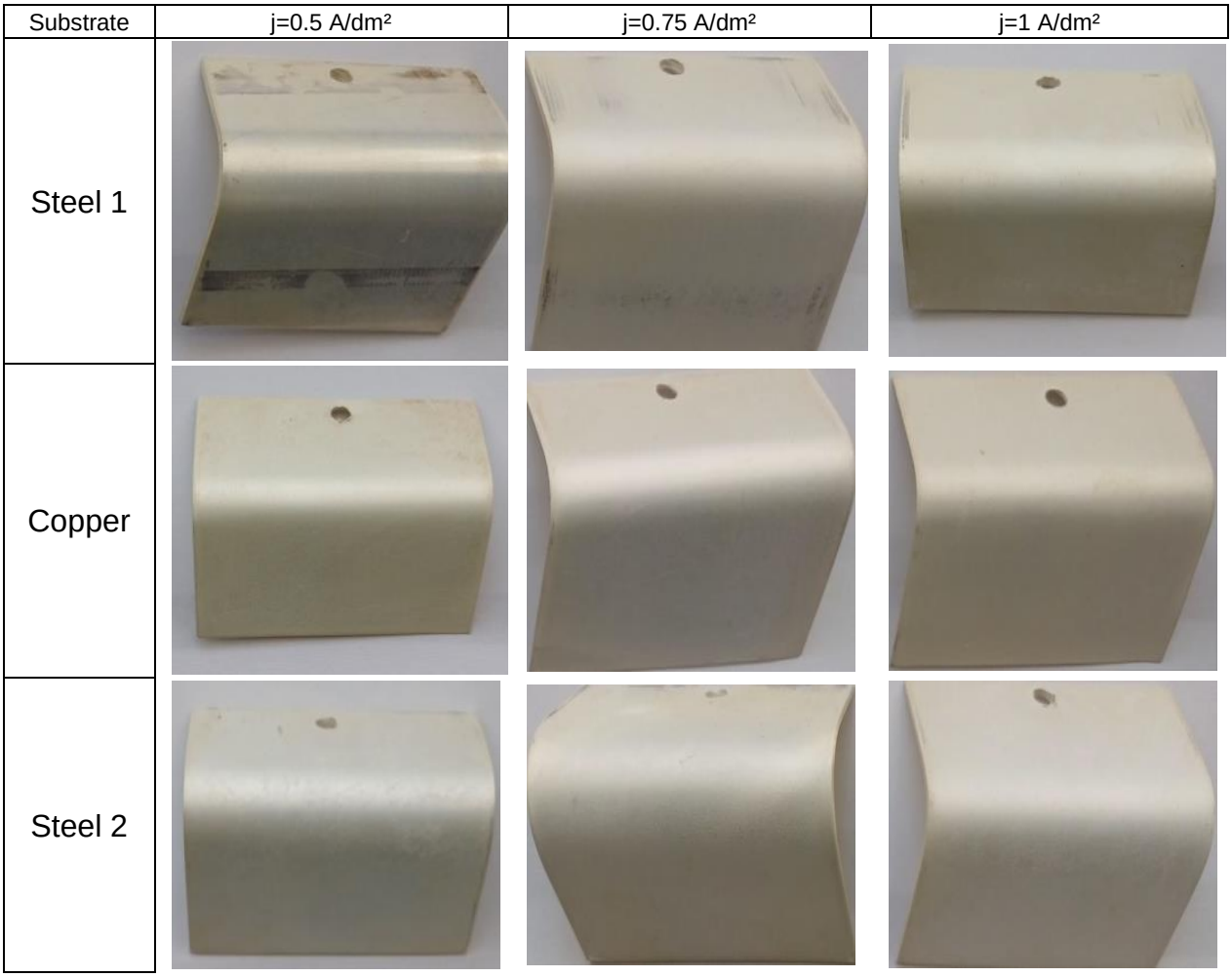

Figure 3. Photographs of the silver coatings after bending test

After bending, no cracking, peeling, or delamination of the silver coatings was observed on any of the investigated specimens, indicating excellent adhesion performance that meets the required acceptance criteria.Due to the use of different bending tools during testing, distinct bright lines were observed on the Steel 1 (WNR 1.7231) specimens. However, these features are not associated with coating damage. In this case, deformation was performed using a tensile testing machine, and the observed shiny marks are attributed to frictional contact between the specimen surface and the loading tool during mechanical deformation, rather than to coating failure or detachment.

CONCLUSIONS

Electrochemical silver coatings were successfully deposited on different substrates at various current densities using a scale-up electroplating system and systematically characterized. As expected, both the current density and the substrate material significantly influenced the properties of the deposited coatings. Visually, all silver coatings exhibited a matte white appearance and completely covered the substrate surface.Complete surface coverage was achieved on all substrates. At a current density of 0.5 A/dm^2, the silver coatings were relatively thin, allowing the underlying substrate topography to remain visible. Increasing the current density resulted in thicker and more compact silver coatings.The highest surface roughness was observed for the silver coatings deposited at a current density of 0.75 A/dm^2 on Steel 1 and Steel 2 substrates, whereas the lowest roughness values for both steels were obtained at 0.5 A/dm^2.The average hardness of the silver coatings was strongly dependent on both the deposition current density and the substrate material. The highest hardness values were achieved at a current density of 0.75 A/dm^2 for all investigated substrates. Among the examined materials, coatings deposited on Steel 1 exhibited the highest hardness at all current densities. The average current efficiency ranged from 86.3% to

97.6%.All deposited silver coatings exhibited satisfactory adhesion. No coating delamination was observed on any of the tested specimens, regardless of the substrate material or deposition current density.

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IZVOD

KARAKTERIZACIJA ELEKTROHEMIJSKI NANESENIH SREBRNIH PREMAZA NA RAZLIČITIM PODLOGAMA U INDUSTRIJSKIM RAZMERIMA

Elektrohemijsko deponovanje srebrnih premaza na različitim podlogama - naime bakru i dve vrste čelika - izvršeno je u industrijskim razmerama, nakon čega je izvršena njihova karakterizacija. Premazi su procenjeni u pogledu tvrdoće, površinske hrapavosti i adhezije, dok su efikasnost struje i debljina premaza izračunate iz promena mase uzoraka tokom elektrodepozicije. Pored procene uticaja tipa podloge na kvalitet premaza, ispitivan je i uticaj gustine struje na adheziju i morfologiju premaza. Čelik 1 (WNR 1.7231), bakar i čelik 2 (WNR 1.0032) korišćeni su kao katodni materijali za elektrodepoziciju srebra. Njihov hemijski sastav je određen XRF analizom. Rezultati su pokazali da i gustina struje i tip podloge značajno utiču na svojstva dobijenih premaza. Svi premazi su bili mat bele boje i pružali su potpunu pokrivenost površine na svim podlogama. Najveće vrednosti površinske hrapavosti i tvrdoće dobijene su za premaze deponovane pri gustini struje od 0,75 A/dm2. Najveća strujna efikasnost postignuta je pri 0,5 A/dm², dok je najveća debljina premaza dobijena pri 1,0 A/dm².

***Ključne reči**: srebrni premazi, elektrohemijsko taloženje, gustina struje, hrapavost, tvrdoća.*

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