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FABRICATION AND CHARACTERIZATION OF ADVANCED SELECTIVE PLATED COPPER COATINGS INCORPORATING NANOSIZED PARTICLES OF ZnO AND TiO_2

Deyan Veselinov[1]✉, Radostina Yankova[1], Hristo Skulev[1], Izabella Kwiecień[2], Joanna Wojewoda-Budka[2]

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Abstract

This study reports preliminary results on the fabrication and characterization of selective plated copper-based coatings with enhanced surface properties and durability through the incorporation of zinc oxide and titanium oxide particles. The coatings were produced using an electrolyte containing 3% wt. zinc oxide and 1% wt. titanium oxide particles, and their microstructures, phase compositions, and mechanical properties were investigated. The results show that the incorporation of ceramic particles leads to the formation of metal-matrix composite materials with finer grain structures, improved microhardness, and enhanced wear resistance. The coating incorporating ZnO particles exhibits superior wear resistance, maintaining stable roughness values and minimal material loss, while the coating with TiO_2 particles also shows improved wear resistance with moderate roughness increases.

Key words: selective plating, electrochemical deposition, surface modification, metal matrix composite coatings, nanoparticle reinforcement

Introduction. The demand for advanced materials with enhanced properties has led to significant research in the field of composite coatings. These coatings,

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which integrate various materials to form a composite layer, have shown remarkable improvements in mechanical strength, wear resistance, and overall durability compared to their pure counterparts [1–3].

Copper, known for its excellent electrical conductivity, thermal conductivity, and corrosion resistance, is widely used in various industrial applications. However, its relatively low hardness and wear resistance limit its use in environments where mechanical durability is critical. To overcome these limitations, researchers have explored the incorporation of nanosized ceramic particles, such as zinc oxide (ZnO) and titanium dioxide (TiO_2), into copper matrices to improve the mechanical and tribological properties of copper coatings [4–7].

Selective plating, also known as brush plating or electroplating, is a versatile technique for the deposition of metallic coatings to specific areas of a substrate. This process offers several advantages, including the ability to coat localized areas without masking, reduced material wastage, and the capability to deposit thick coatings. By integrating nanosized ceramic particles into the copper matrix during the selective plating process, it is possible to fabricate composite coatings with enhanced hardness, wear resistance, and potentially improved functional properties [8–10].

Zinc oxide and titanium dioxide are attractive choices for incorporation into copper coatings due to their distinct properties. ZnO is known for its high hardness, chemical stability, and antimicrobial properties, making it suitable for applications requiring wear resistance and hygienic surfaces. TiO_2, on the other hand, offers excellent hardness, chemical stability, and photocatalytic activity, making it beneficial for coatings exposed to harsh environments and requiring self-cleaning capabilities [11–14].

In this study, we focus on the fabrication and characterization of advanced selectively plated copper coatings incorporating nanosized particles of ZnO and TiO_2. The primary objective is to investigate the microstructural, mechanical, and tribological properties of these composite coatings. The incorporation of ZnO and TiO_2 particles into the copper matrix is expected to enhance the hardness, wear resistance, and overall durability of the coatings.

Materials and methods. Three types of selectively plated coatings were deposited on medical-grade stainless steel (SS) 1.4021 metal substrates. The samples, measuring $20 \times 30 \times 3$ mm, were cut from metal sheets using wire electrocutting.

For the selective plating, three electrolytes were used. One electrolyte was for depositing pure copper, prepared with 20% wt. copper sulphate pentahydrate ($CuSO_4.5H_2O$), 4% wt. sulphuric acid (H_2SO_4), and distilled water. The other two electrolytes, prepared using the same base, included 3% wt. copper-doped zinc oxide for the copper-zinc oxide (Cu-ZnO) composite and 1% copper-doped titanium dioxide for the copper-titanium dioxide (Cu-TiO_2) coating.

The copper doping process was performed as follows: 18 g of nanosize particles (approximately 200 nm) were added to a beaker containing 200 ml of deionized

water and 0.4 g polyethylene glycol. The mixture was stirred for 30 min. In a separate beaker, 4 g of $CuSO_4.5H_2O$ were dissolved in 50 ml of deionized water. This copper sulphate solution was then slowly added to the stirred particle mixture. The pH was adjusted to 10 using a sodium hydroxide (NaOH) solution. Subsequently, 5 ml of 37% formaldehyde was added, and the solution was stirred for 2 h. The particles were then filtered, washed three times with deionized water and isopropanol, and dried in an oven at 60 °C for 12 h.

Before the selective plating process, several preparatory operations were performed, including substrate masking, electrochemical cleaning, electrochemical etching, and activating the masked surface. A bonding layer of nickel, 1 µm thick, was then deposited via selective plating. Finally, the three types of coatings were plated onto the surfaces. After plating, the samples were rinsed thoroughly with deionized water and carefully dried for subsequent analysis and evaluation. All chemical reagents, purchased from Chimtex Ltd. (Varna, Bulgaria), were of analytical grade, ensuring their reliability and accuracy.

The electrochemical selective plating processes were conducted using a DC power source, providing precise control over current and potential. A graphite electrode wrapped in white tuff wrap was used as the anode. The metal matrix composite coatings were deposited using different average current densities, depending on the electrolyte solution. All procedures were carried out under controlled laboratory conditions at room temperature, ensuring consistent and reliable results.

Upright metallurgical microscope (LM-308) was used to observe cross-sections of the selective plated coatings. The size of the initial powder particles, before copper doping was determined using transmission electron microscope PHILIPS CM20 (200 kV) TWIN with the EDAX Phoenix attachment for local chemical microanalysis intended for microstructure observations. The microstructure of the produced coatings was examined using a scanning electron microscope (SEM) HIROX SH-5500P equipped with an energy dispersive spectroscopy (EDS) module QUANTAX 100 Advanced – Bruker. Phase analysis was performed with an X-ray diffractometer (XRD) Tongda TDM-10 employing CuKa radiation. XRD patterns were acquired using continuous scan mode, covering the 2theta (2θ) angle range from 30 to 90 degrees at a scan speed of 1.5 degrees/min. The X'pert HighScore software by Malvern Panalytical was used for peak identification, matching, and comprehensive analysis of the acquired XRD data.

To determine the surface roughness of the coatings, a profilometer (model DGT-SRT200A, Baxit) was employed. The microhardness of the coatings was measured using cross-sections. Cross-sections of the plated samples were obtained with a low-speed cutting machine, model DTQ-5. These cross-sections were then molded in resin, ground with alumina sandpaper, and polished. Microhardness tests were conducted on a DVK-200A testing machine, equipped with a Knoop indenter, using a load of 0.01 kg.

The pin-on-flat method was employed to determine the ability of the coatings to withstand sliding wear under specific loading conditions using a Glomro BXT-MAR306 wear test bench. A cylindrical counter body made of rubber with a Shore 70A hardness, 7 mm diameter, and 38.5 mm^2 contact area was utilized. The counter body was loaded with a 0.5 kg weight and moved along a 60 mm trajectory. Five series of 2000 cycles were performed, totalling a wear distance of 600 m. The degree of wear was determined using the weight method with an analytical balance accurate to 0.0001 g. All test samples were cleaned, dried, and weighed at the beginning and end of each test series. The change in mass of the samples was used to calculate the wear dynamics.

Results and discussion. ***Surface microstructure and elemental analysis.*** After selective plating, the pure copper coatings and the copper coatings containing titanium oxide particles exhibited mirror finishes. Notably, the coatings with TiO_2 displayed a slightly brighter appearance, while those incorporating zinc oxide particles had a bright satin finish. The microstructures of the selectively plated copper coatings were thoroughly examined using optical microscopy and scanning electron microscopy. Optical micrographs of cross-sections revealed continuous, uniform, and defect-free deposition for all three types of coatings (Fig. 1), indicating that the selective plating process was highly effective.

All coatings were produced under identical plating parameters, including voltage, current density, and other relevant conditions, maintained consistently for a predetermined number of ampere-hours. It was observed that the final thickness of the coatings was influenced by the presence of ceramic particles. Specifically, the measured thicknesses of the selectively plated deposits were approximately 40 µm for pure copper and 31 µm for coatings containing 3% wt. ZnO particles, and 33 µm for coatings containing 1% wt. TiO_2 particles. These measurements suggest that the incorporation of ceramic particles affects the deposition rate and overall thickness of the coatings.

Additionally, the surfaces of the coatings were examined using SEM and EDS. SEM images highlighted the fine integration of nanoparticles within the copper matrix, which played a crucial role in modifying surface properties and enhancing the performance of the coatings. The presence of nanoparticles contributed to improved mechanical properties, increased hardness, and enhanced wear resistance of the coatings.

EDS was employed to perform a detailed analysis of the elemental composition of the coatings. The EDS spectra confirmed the presence of copper, zinc, and titanium elements in their respective coatings, along with oxygen, indicating the successful incorporation of ZnO and TiO_2 nanoparticles. EDS mapping provided further confirmation by revealing the uniform distribution of the ceramic particles within the copper matrix, ensuring homogeneity and consistent properties throughout the coatings.

Furthermore, the influence of the incorporated nanoparticles on the microstructure and surface morphology of the coatings was evident. The nanoparticles

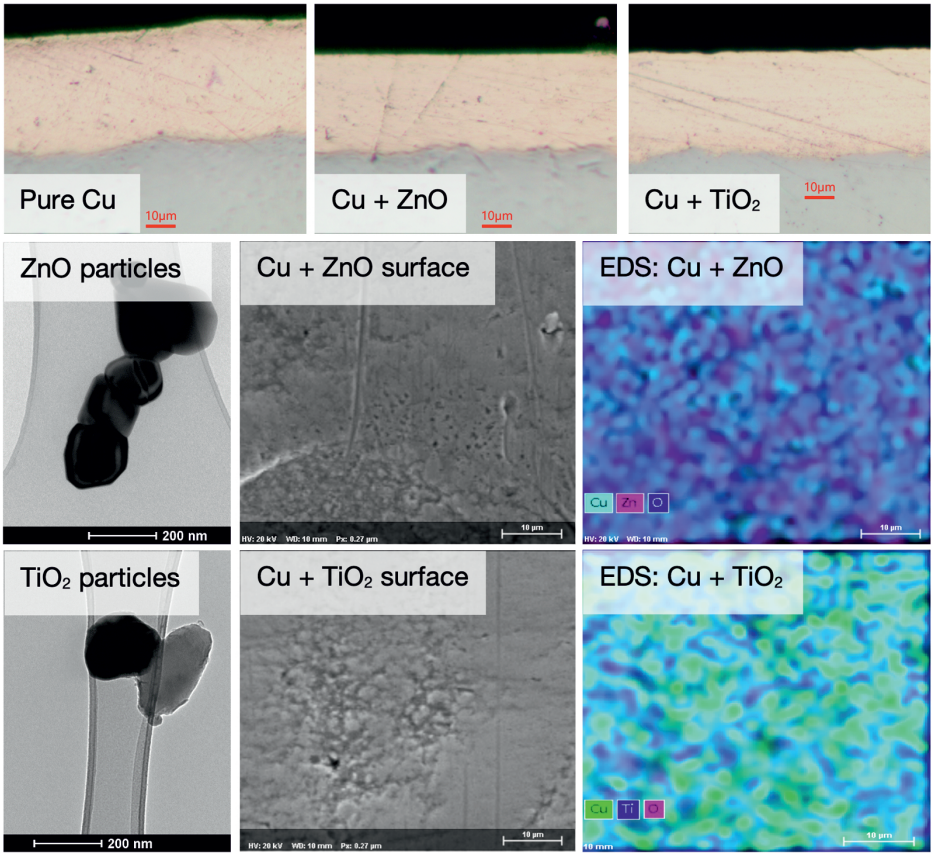


Fig. 1. Optical cross-section micrographs, surface SEM images, and EDS mapping of selective plated copper coatings containing ZnO and TiO_2

acted as nucleation sites during the electroplating process, promoting finer grain structures and enhancing the overall quality of the coatings. The incorporation of ZnO and TiO_2 particles also contributed to the improved aesthetic qualities of the coatings, as observed in their distinct finishes. Figure 1 illustrates some of the key findings from the conducted analyses, showcasing the continuous, uniform, and defect-free nature of the selectively plated copper coatings.

Phase analysis. The X-ray diffraction (XRD) patterns depicted in Fig. 2 provide a comprehensive analysis of the crystalline phases present in three distinct copper-based coatings: pure copper (Cu coating), copper-zinc oxide (Cu-ZnO), and copper-titanium oxide (Cu-TiO_2).

The top panel shows the pure copper coating, where XRD analysis reveals four significant peaks at 43.69°, 50.98°, 74.46°, and 75.26° 2θ. The highest intensity peak at 50.98° 2θ, with a relative intensity of 100%, confirms the high purity and crystalline nature of the copper coating, as matched to reference patterns (96-431-3204 and 00-003-1015).

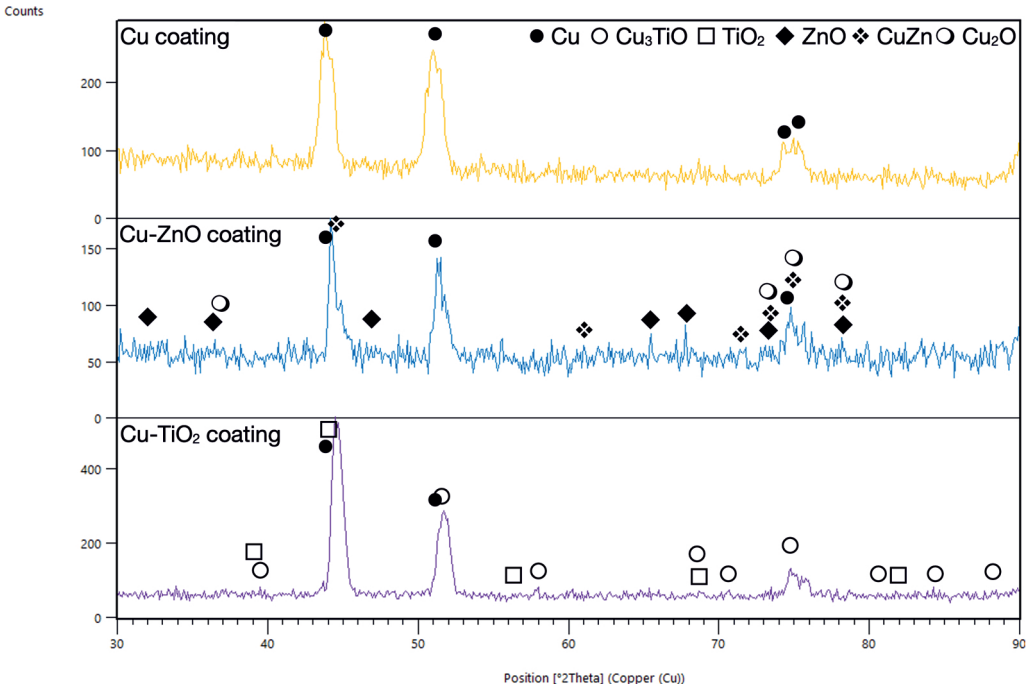


Fig. 2. XRD data of the selective plated copper coatings with ZnO and TiO_2 particles

In the middle panel, significant peaks observed at approximately 32° 2θ and 36.5° 2θ can be attributed to zinc oxide, as matched with the reference pattern (00-001-1136). This indicates that the ZnO particles have retained their crystalline structure during the plating process, which is expected given the initial composition of the electrolyte. The most intense peak at 44.30° 2θ, with a relative intensity of 100%, corresponds to copper, as supported by the reference pattern (96-410-5041).

Additionally, peaks at 51.46° 2θ and 74.85° 2θ suggest the formation of a Cu-Zn alloy phase, matched by the reference pattern (00-019-0179). The presence of this alloy phase indicates some degree of interdiffusion between the deposited copper and the incorporated ZnO particles. This is an expected outcome given the electrochemical environment and the selective plating process, which can facilitate such interactions. Overall, the XRD results are consistent with the electrolyte composition and the plating process, confirming the successful incorporation of ZnO particles within the copper matrix and the formation of a well-integrated composite material with distinct crystalline phases.

The bottom panel, representing the Cu-TiO_2 coating, reveals the presence of copper, TiO_2, and titanium copper oxide phases. The significant peaks observed at 44.42° 2θ and 51.82° 2θ, with the highest relative intensity at 44.42° 2θ (100%), match well with the reference patterns for copper (96-431-3204) and titanium

oxide (01-085-2084). This indicates a dominant presence of crystalline copper in the coating.

Additionally, the peaks at 39.19° 2θ, 56.63° 2θ, and 74.86° 2θ correspond to titanium oxide (00-034-0180) and titanium copper oxide (01-081-1612), suggesting the successful incorporation of TiO_2 particles within the copper matrix. The presence of these peaks is expected due to the inclusion of copper-coated TiO_2 particles in the electrolyte. The formation of titanium copper oxide phases indicates interactions between copper and TiO_2 during the plating process, leading to the creation of complex oxide phases such as Cu_3TiO. This incorporation of TiO_2 and the formation of copper-titanium oxide phases suggest a well-integrated composite material. The distinct and well-defined crystalline phases observed in the XRD patterns confirm the expected outcomes based on the electrolyte composition. The results demonstrate that the selective plating process effectively incorporates TiO_2 particles into the copper matrix, resulting in a composite coating with complex phase interactions and enhanced material properties.

Microhardness. The surface and cross-section microhardness measurements provide insights into the mechanical properties of these coatings. The data presented in Fig. 3 reveals significant variations in microhardness between the different copper-based coatings.

For the pure copper coating, the surface microhardness ranges from a minimum of 75.9 HK0.01 to a maximum of 94 HK0.01, with an average surface hardness of 87.7 HK0.01. The cross-section hardness values range from 82.9 HK0.01 to 96.5 HK0.01, averaging at 89.3 HK0.01. These values reflect the inherent softness of pure copper, which is expected due to its ductile nature.

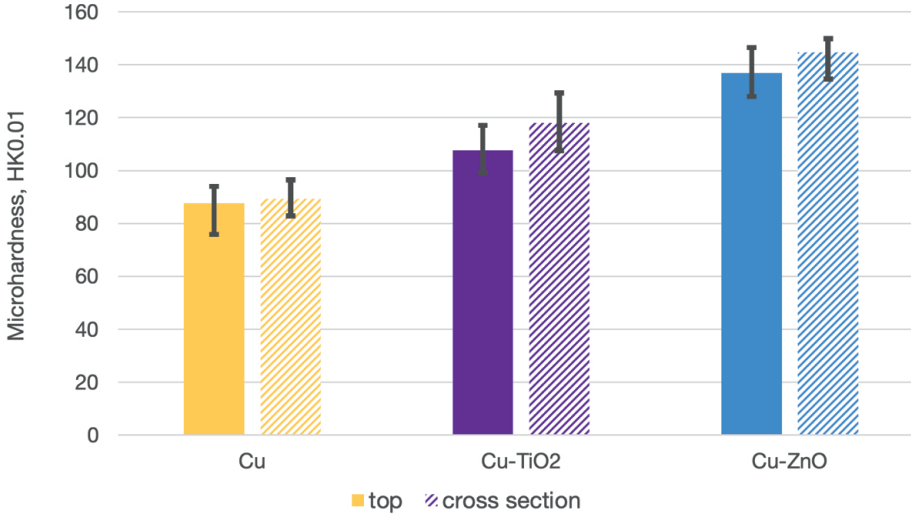


Fig. 3. Microhardness of the three types of coatings measured on the surface (top) and using cross-sections

The Cu-TiO_2 coatings exhibit higher microhardness values compared to pure copper. The surface hardness ranges from 99.1 HK0.01 to 117.1 HK0.01, with an average of 107.6 HK0.01. The cross-section hardness is even higher, ranging from 107.5 HK0.01 to 129.3 HK0.01, with an average of 118.0 HK0.01. This increase in hardness is attributed to the incorporation of TiO_2 particles, which are known to enhance the mechanical properties of the composite by providing reinforcement and improving the wear resistance.

The Cu-ZnO coating demonstrates the highest hardness values among the three coatings. The surface hardness ranges from 128 HK0.01 to 146.6 HK0.01, with an average of 136.9 HK0.01. The cross-section hardness values range from 134.7 HK0.01 to 149.8 HK0.01, averaging at 144.8 HK0.01. The significant increase in hardness is most likely due to the presence of ZnO particles, which contribute to the overall strengthening of the composite material. The high hardness values indicate improved mechanical properties and potential for enhanced wear resistance and durability.

Summarizing the microhardness data, it is evident that the incorporation of TiO_2 and ZnO particles into the copper matrix significantly enhances the hardness of the coatings. These results suggest that the Cu-ZnO and Cu-TiO_2 coatings are likely to provide superior mechanical performance and durability compared to pure copper.

Surface roughness and wear resistance. Surface roughness and wear resistance are critical parameters for evaluating the performance and durability of coatings. In this study, surface roughness measurements were conducted using a profilometer, a precise instrument that scans the surface to detect variations in height. Two key parameters were measured: Ra, which represents the average roughness, and Rz, the average maximum height of the profile. Five independent profile measurements were performed for each type of coating to ensure statistical reliability and to account for any surface heterogeneity.

Wear resistance was assessed using the pin-on-flat method, a widely adopted technique for evaluating the tribological performance of materials. In this method, a pin is pressed against the flat surface of the coated sample under a controlled load and moved back and forth for a specific number of cycles. The amount of material removed from the coating, along with the wear track depth and width, is measured to determine the wear rate. This test simulates real-world wear conditions, providing valuable data on the coatings' durability and resistance to abrasion. By correlating surface roughness parameters with wear resistance results, we can gain insights into how surface texture influences the coatings' performance under mechanical stress. The summarized results are displayed in Fig. 4.

For surface roughness, values of Ra and Rz were measured at different sliding distances, and each sample underwent five independent profile measurements. The pure copper coating shows an increase in roughness with sliding distance, with Rz rising from 0.552 µm at 0 m to 1.359 µm at 600 m and Ra from 0.079 µm to

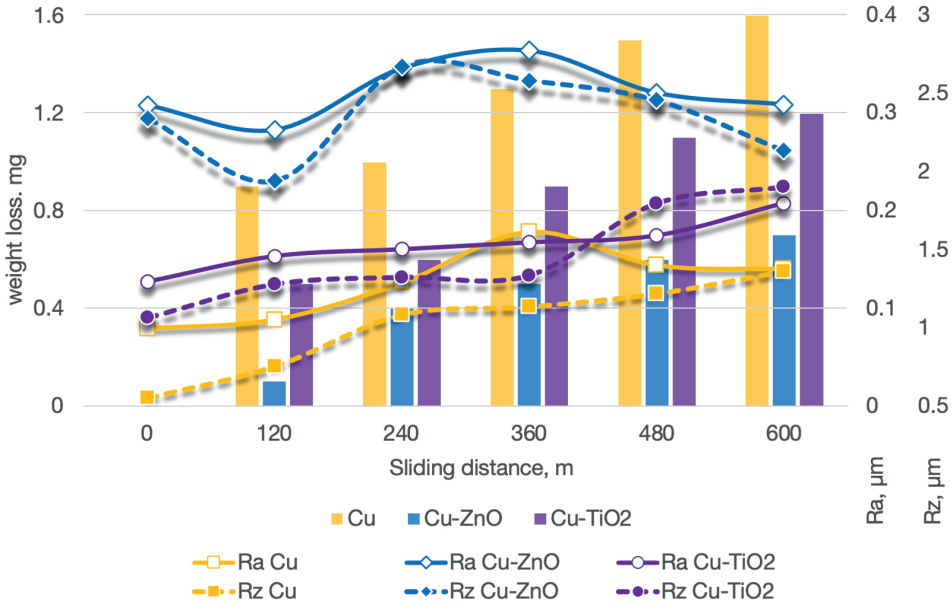


Fig. 4. Wear loss and surface roughness of the copper-based coatings for sliding wear of 600 meters

0.14 µm. This progressive increase suggests significant wear, indicating that pure copper becomes rougher over time.

In contrast, the Cu-ZnO coating, which starts with higher initial roughness values (Rz at 2.336 µm and Ra at 0.307 µm), shows relatively stable roughness measurements across the sliding distances, with Rz slightly decreasing to 2.132 µm and Ra remaining around 0.308 µm. This stability suggests that the hard ZnO particles enhance the wear resistance of the coating, preventing significant changes in surface roughness. Similarly, the Cu-TiO_2 coating exhibits an increase in roughness with Rz rising from 1.063 µm to 1.898 µm and Ra from 0.127 µm to 0.207 µm, indicating wear but starting from a smoother surface compared to Cu-ZnO.

Wear resistance was assessed by measuring material loss at various sliding distances. Pure copper displayed the highest material loss, increasing from 0 mg at 0 m to 1.6 mg at 600 m, confirming it as the least wear-resistant coating. The Cu-ZnO coating had a significantly lower material loss, starting at 0 mg and rising to only 0.7 mg at 600 m, demonstrating superior wear resistance due to the incorporation of ZnO particles. The Cu-TiO_2 coating showed moderate wear resistance with material loss increasing from 0 mg to 1.2 mg at 600 m, indicating better performance than pure copper but not as high as Cu-ZnO.

In summary, the surface roughness and wear resistance data reveal that Cu-ZnO and Cu-TiO_2 coatings offer enhanced performance over pure copper. The Cu-ZnO coating exhibits the highest wear resistance, maintaining stable roughness values and minimal material loss, while the Cu-TiO_2 coating also shows im-

proved wear resistance with moderate roughness increases. Pure copper, despite its initial smoothness, undergoes significant roughness and material loss, making it the least favourable for wear-resistant applications. These findings underscore the effectiveness of incorporating ZnO and TiO_2 particles into copper matrices to enhance surface properties and durability.

Conclusion. This study has successfully demonstrated the fabrication of selective plated copper-based coatings with enhanced surface properties and durability through the incorporation of zinc oxide and titanium oxide particles. The results show that the incorporation of these ceramic particles leads to the formation of composite materials with distinct crystalline phases, finer grain structures, and improved mechanical properties. The Cu-ZnO and Cu-TiO_2 coatings exhibit significantly higher microhardness values compared to pure copper, indicating enhanced wear resistance and durability. Furthermore, the surface roughness and wear resistance tests reveal that the Cu-ZnO coating offers superior wear resistance, maintaining stable roughness values and minimal material loss, while the Cu-TiO_2 coating also shows improved wear resistance with moderate roughness increases.

Notably, the incorporation of zinc oxide particles at a concentration of 3% wt. and titanium oxide particles at a concentration of 1% wt. has a significant impact on the coatings' properties, highlighting the potential for optimizing particle concentrations to achieve specific performance enhancements. These findings have important implications for the development of wear-resistant coatings for various industrial applications. The ability to tailor the surface properties and durability of copper-based coatings through the incorporation of ceramic particles opens up new opportunities for the design of advanced materials with improved performance and longevity. Future studies can build upon these results to explore the effects of varying particle concentrations, sizes, and types on the properties of these composite coatings, as well as investigate their potential applications in real-world scenarios.

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[1]*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: dveselinov@ims.bas.bg, radyankova@ims.bas.bg, skulev@ims.bas.bg

[2]*Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Krakow, Poland*
e-mails: i.kwiecien@imim.pl, j.wojewoda@imim.pl