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CORROSION-WEAR TRADE-OFF IN HIERARCHICAL Cu-Ag BRUSH-PLATED COATINGS: EFFECT OF ELECTROLYTE pH

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Abstract

Hierarchical Cu-Ag composite coatings were deposited on AISI 316L stainless steel by brush plating from acidic and alkaline electrolytes, and their corrosion resistance, wear behavior, and wettability were systematically compared. Both coating types integrate a sub-micron columnar copper matrix (750 nm-1 μm) with bimodal silver particles. Electrochemical testing in 3.5% NaCl revealed that alkaline-deposited coatings exhibit substantially superior corrosion resistance (corrosion rate 0.028 - 0.039 mm/y) compared to acidic counterparts (0.090-0.103 mm/y), associated with more positive corrosion potentials (-0.079 to -0.118 V vs. -0.132 to 0.144 V) and lower anodic Tafel slopes. In contrast, for composite coatings, acidic deposition resulted in higher microhardness (CuAC+Ag: ~175 HK 0.01) and better wear resistance (mass loss ~1.1 mg at S = 600 m) compared to alkaline counterparts (CuALK+Ag: ~165 HK 0.01; mass loss ~4.0 mg). Pure copper coatings (both acidic and alkaline) exhibited the lowest mass loss (~0.5 - 0.6 mg) and the highest hardness (CuALK: ~215 HK; CuAC: ~200 HK), indicating that silver incorporation reduces wear resistance regardless of electrolyte pH. Water contact angle measurements showed hydrophilic behavior for all coatings (69.7°– 82.6°), with acidic coatings exhibiting higher angles despite inferior corrosion resistance, confirming that wettability alone does not govern electrochemical stability. These results reveal a clear application-specific trade-off: acidic deposition optimizes mechanical durability of composite coatings, while alkaline conditions favor corrosion protection, providing a rational basis for electrolyte selection in biomedical and industrial applications.

Keywords: brush plating; Cu-Ag composite; corrosion resistance; wear resistance; electrolyte pH; surface engineering

INTRODUCTION

Functional metallic coatings for biomedical and industrial applications must simultaneously satisfy multiple, often conflicting, performance requirements. While antibacterial activity is critical for medical devices, mechanical durability under sliding contact and corrosion resistance in physiological or aggressive environments are equally vital for long-term reliability [1,2]. Copper-silver (Cu-Ag) systems have attracted considerable attention due to their complementary antimicrobial properties [3-5], but the influence of deposition conditions on their mechanical and electrochemical behavior remains insufficiently explored.

Brush plating - a localized, dynamic electrodeposition technique - offers unique advantages for tailoring coating microstructure through non-equilibrium growth conditions [6-8]. While previous work has demonstrated the antibacterial potential and hierarchical microstructure of brush-plated Cu-Ag coatings [9], the effect of electrolyte pH on their corrosion and wear

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behavior has not been systematically addressed in the context of functional trade-offs.

Electrolyte pH is known to influence deposition kinetics, phase composition, surface roughness, and ultimately the functional performance of electrodeposited coatings [10,11]. Acidic conditions typically promote denser grain packing and higher hardness, while alkaline environments may favor more uniform, less porous deposits with improved passivation behavior [12,13]. However, the quantitative trade-off between mechanical durability and corrosion resistance in these specific hierarchical Cu-Ag systems has not been established.

This work investigates the effect of electrolyte pH (acidic vs. alkaline) on the corrosion resistance, wear behavior, and wettability of hierarchical Cu-Ag brush-plated coatings. The goal is to provide a rational basis for application-specific optimization, identifying which deposition conditions are most suitable for environments dominated by either wear or corrosion.

EXPOSITION

Experiment and characterization

Austenitic stainless steel AISI 316L coupons (20×60×3 mm) were mechanically polished, ultrasonically cleaned, and air-dried. Coatings were applied using a portable SIFCO ASC POWER PACK (60A/30V) with a graphite anode traversing the substrate at 15 m/min. Deposition was carried out at 3-12V, 30-45°C and a current density of 0.46A/cm² for 255-262s, targeting a nominal thickness of ~10 μm (verified by profilometry: 9.8 μm ±0.7 μm, n=5).

Six coating types were prepared by varying electrolyte pH and silver particle size:

- CuAC: pure copper from acidic electrolyte (pH 0.5)
- CuALK: pure copper from alkaline electrolyte
- CuAcid+Ag3μm: acidic electrolyte + 3-5 μm Ag microparticles (3-5 wt.%)
- CuAcid+Ag20nm: acidic electrolyte + 20-30 nm Ag nanoparticles (37-39 wt.%)
- CuAlk+Ag3μm: alkaline electrolyte + 3-5 μm Ag microparticles
- CuAlk+Ag20nm: alkaline electrolyte + 20-30 nm Ag nanoparticles

Detailed microstructural and antibacterial characterization of this hierarchical architecture is reported in a companion study [9].

Microhardness was measured on polished cross-sections using the Knoop method under a 0.01 kgf load. Surface roughness (Rz) was quantified by profilometry over five independent scan lengths.

Wear resistance was evaluated using a pin-on-flat configuration (Glomro BXT-MAR306). A cylindrical rubber counterbody (Shore 70A, 7 mm diameter) was loaded with 0.5 kg and reciprocated over a 60 mm trajectory. Five series of 2000 cycles were performed (total sliding distance S = 600 m). Mass loss (Δm) was recorded after each series using an analytical balance (0.0001 g accuracy).

Electrochemical corrosion behavior was assessed in 3.5% NaCl solution at room temperature using a potentiostat/galvanostat (Cortest CS350). The three-electrode configuration consisted of a Pt counter electrode, Ag/AgCl reference electrode, and the coated sample (1 cm² working area). After achieving stable open-circuit potential (OCP), potentiodynamic polarization tests were conducted to extract corrosion parameters: anodic (ba) and cathodic (bc) Tafel slopes, corrosion potential (E_0), corrosion current density (i_0), and corrosion rate.

Wettability was evaluated by water contact angle measurements using a droplet analyzer with 5μL deionized water drops (n=5).

Mechanical properties and surface topography

Microhardness measurements revealed a more complex picture than initially expected (Fig. 1a). For pure copper coatings, alkaline deposition resulted in higher hardness (CuALK: ~215 HK 0.01) compared to acidic

deposition (CuAC: ~200 HK 0.01). However, for the composite coatings, the trend was reversed: acidic deposition yielded higher average hardness (CuAC+Ag: ~175 HK 0.01) than alkaline deposition (CuALK+Ag: ~165 HK 0.01). These values represent the meaning of the micro- and nano-particle variants within each pH group, as the mechanical properties were found to be similar between the 3 µm and 20 nm Ag reinforcements. This indicates that the effect of electrolyte pH on hardness is primarily governed by the matrix structure rather than the specific size of the silver particles.

Surface roughness remained low for acidic coatings (Rz=2.77 µm - 2.89 µm), whereas alkaline formulations exhibited pronounced particle agglomeration and significantly higher roughness (Rz > 7.9 µm).

Table 1. *Microhardness and roughness of brush-plated Cu-based coatings (n = 5).*

Coating	Microhardness (HK 0.01)	Surface Roughnes, Rz (µm)
CuAC (Pure Cu, acidic)	~200 ± 5	2.89 ± 0.3
CuALK (Pure Cu, alkaline)	~215 ± 5	>7.9 ±0.5
CuAC+Ag* (Acidic comp.)	~175 ± 5	2.77 ±0.2
CuALK+Ag* (Alkaline comp)	~165 ± 5	>7.9 ±0.6

**Note: The values for CuAC+Ag and CuALK+Ag represent the average mechanical properties of the composite coatings containing either 3–5 µm Ag microparticles or 20–30 nm Ag nanoparticles. The micro- and nano-variants within each pH group exhibited similar hardness and roughness values, hence the combined presentation. In contrast, their distinct electrochemical behaviors (corrosion rates, potentials, and contact angles) are detailed separately in Table 2.*

Wear tests demonstrated that for the composite coatings, the acidic variants (CuAC+Ag, averaged across 3 µm and 20 nm Ag reinforcements) maintained superior resistance (mass loss ~1.1 mg at S = 600 m) compared to the alkaline counterparts (CuALK+Ag: mass loss ~4.0 mg) (Fig. 1b). The improved tribological performance of acidic composites correlates with lower roughness, reduced stress concentrations, and the presence of hard AgO phases detected in prior phase analyses of acidic brush-plated layers [14]. Higher surface roughness in alkaline coatings directly accelerated wear dynamics.

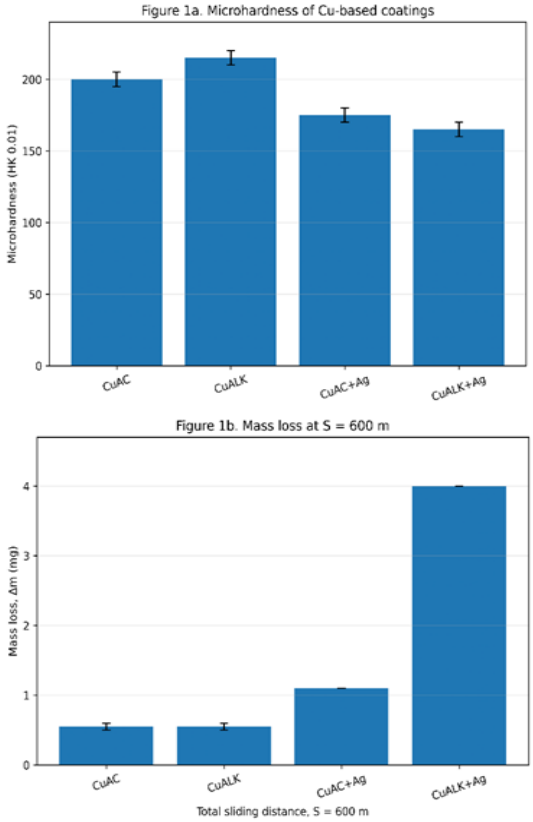


Fig. 1. *Mechanical properties and wear behavior (a) Microhardness (b) Mass loss at S = 600 m.*

However, an important observation is that pure copper coatings (both CuAC and CuALK) exhibited the lowest mass loss (~0.5 mg - 0.6 mg at S = 600 m), indicating that silver incorporation reduces wear resistance regardless of electrolyte pH. This suggests that the presence of Ag particles-particularly microparticles that agglomerate in alkaline conditions-disrupts the continuity of the copper matrix and accelerates material removal under sliding contact.

Corrosion resistance

Electrochemical characterization in 3.5% NaCl revealed significant differences between acidic and alkaline Cu-Ag coatings (Fig. 2, Table 2). The OCP measurements indicated distinct electrochemical behavior depending on electrolyte pH and silver particle size. Among the investigated coatings, CuAlk+Ag3µm exhibited the most positive OCP response, increasing during the measurement and stabilizing at approximately -0.055 V, which is consistent with a tendency toward a more stable passive state. In contrast, CuAlk+Ag20nm showed a gradual decrease in OCP from approximately -0.12 to -0.13 V, indicating that the incorporation of nanoscale Ag does not necessarily promote the same passivation behavior as the microparticle-containing alkaline coating.

Table 2. *Electrochemical corrosion parameters and water contact angles for Cu-Ag coatings (n = 5).*

Coating	b_a (mV)	b_c (mV)	i_0 (A/cm²) × 10^{-6}	E_0 (V)	Corr. Rate (mm/y)	Contact angle (°)
CuAcid + Ag3µm	83.3	105.2	8.76	-0.144	**0.103**	**77.9**
CuAcid + Ag20nm	76.2	138.1	7.66	-0.132	**0.090**	**82.6**
CuAlk + Ag3µm	58.5	65.7	3.29	-0.079	**0.039**	**72.0**
CuAlk + Ag20nm	52.4	179.0	2.46	-0.118	**0.028**	**69.7**

The OCP observations are consistent with the corrosion potentials obtained from potentiodynamic polarization (Table 2). The corrosion potentials of the alkaline coatings were more positive (-0.079 to -0.118 V) than those of the acidic coatings (-0.132 to -0.144 V), indicating a more favourable electrochemical state under the tested conditions.

Potentiodynamic polarization analysis further confirmed the superior corrosion performance of the alkaline coatings. The CuAlk+Ag20nm coating exhibited the lowest corrosion current density, $i_0 = 2.46 \times 10^{-6}$ A/cm², and the lowest corrosion rate, 0.028 mm/y. CuAlk+Ag3µm also showed substantially reduced corrosion activity, with $i_0 = 3.29 \times 10^{-6}$ A/cm² and a corrosion rate of 0.039 mm/y. These values were considerably lower than those obtained for the acidic coatings, for which corrosion rates were 0.103 and 0.090 mm/y, respectively.

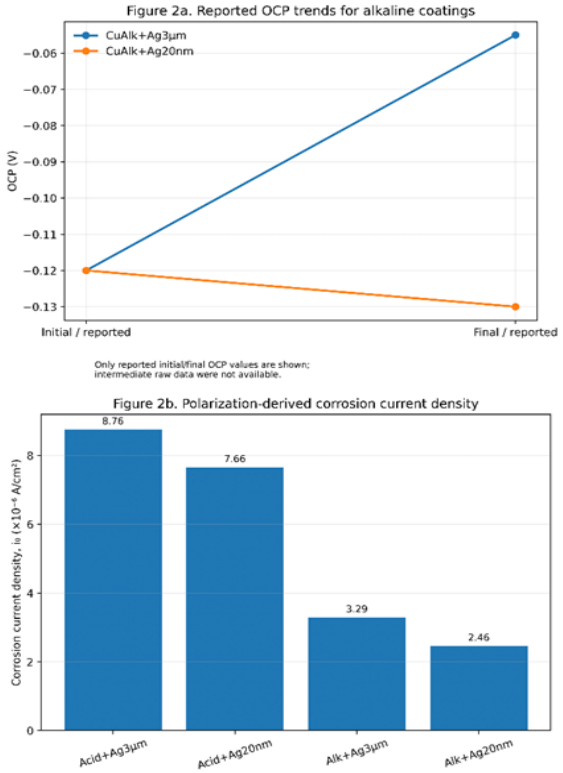


Fig. 2. *Electrochemical corrosion behaviour of Cu-Ag coatings in 3.5% NaCl solution. (a) Reported OCP behaviour of the alkaline coatings, highlighting the increasing/stabilizing response of CuAlk+Ag3µm and the gradual decrease observed for CuAlk+Ag20nm. (b) Corrosion current density i_0 obtained from potentiodynamic polarization.*

The Tafel parameters provide additional evidence for the different electrochemical behaviour of the two deposition conditions.

The alkaline coatings exhibited lower anodic Tafel slopes (52.4 - 58.5 mV) than the acidic coatings (76.2 - 83.3 mV), suggesting lower anodic dissolution rates and a more effective barrier response. The incorporation of 20 nm Ag nanoparticles also reduced the corrosion current density and corrosion rate within both electrolyte groups, indicating a beneficial effect of nanoscale Ag on the electrochemical uniformity of the composite coatings.

Overall, the available OCP observations and potentiodynamic polarization parameters consistently indicate that alkaline deposition provides superior corrosion protection, whereas the detailed electrochemical response depends on the size of the incorporated Ag particles.

Wettability and the Corrosion-Wear Trade-off

Water contact angle measurements indicated hydrophilic behavior for all coatings (69.7°- 82.6°) (Fig. 3a).

Interestingly, acidic coatings showed higher contact angles, with the highest value of 82.6° for CuAcid+Ag20nm, but inferior corrosion resistance. This demonstrates that wettability alone does not determine electrochemical stability. While a higher contact angle may limit initial electrolyte wetting, it does not prevent electron transfer or anodic activity, particularly in coatings containing highly conductive Ag particles. Overall protective behavior is therefore more strongly governed by microstructural uniformity and the electrochemical stability of the surface under the tested conditions.

Comprehensive characterization reveals a clear application-specific trade-off between corrosion protection and wear resistance (Fig. 3b).

For composite coatings, acidic deposition conditions produced lower mass loss at S = 600 m (~1.1 mg), but higher corrosion rates (0.090 - 0.103 mm/y). In contrast, alkaline deposition resulted in substantially lower corrosion rates (0.028-0.039 mm/y), but higher mass loss (~4.0 mg). Thus, the two deposition conditions provide distinct performance advantages rather than a single optimum: acidic deposition favors mechanical durability, whereas alkaline deposition favors electrochemical protection. Pure copper coatings (CuAC and CuALK) exhibited the lowest mass loss (~0.5 - 0.6 mg) but were not included in the composite corrosion-wear trade-off comparison because corresponding corrosion parameters were not available.

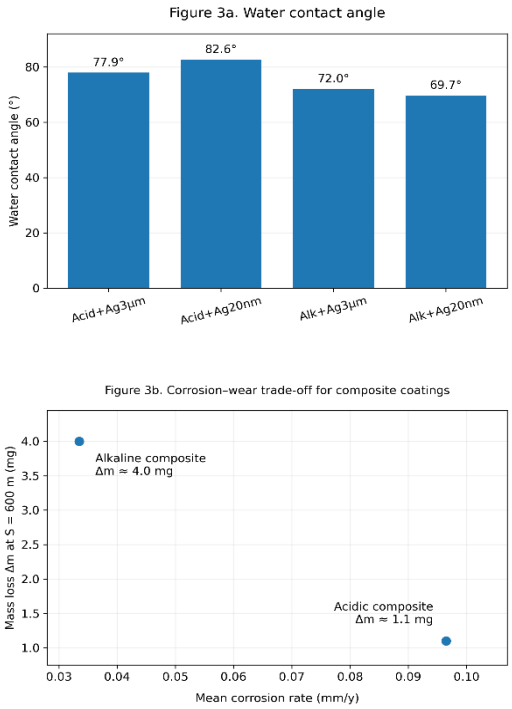


Fig.3. *Wettability and corrosion-wear trade-off of Cu-Ag coatings: (a) water contact angles; (b) mean corrosion rate versus mass loss at S = 600 m.*

This trade-off is associated with differences in coating microstructure. Acidic conditions promote denser columnar packing and were previously associated with the formation of hard AgO phases, enhancing the mechanical performance of the composites [14]. Alkaline conditions favor improved electrochemical stability and lower corrosion rates, but the investigated alkaline formulations also exhibited pronounced Ag particle agglomeration and higher surface roughness, which were associated with increased wear.

CONCLUSION

Hierarchical Cu-Ag composite coatings were deposited on AISI 316L stainless steel via brush plating using acidic and alkaline electrolytes. The influence of electrolyte pH on corrosion resistance, wear behavior, and wettability was investigated.

Alkaline-deposited composites exhibited superior corrosion resistance (0.028-0.039 mm/y) compared to acidic coatings (0.090-0.103 mm/y), with more positive corrosion potentials and lower anodic Tafel slopes. OCP observations indicated particle-size-dependent behavior, with CuAlk+Ag3μm showing a more positive and stable response than CuAlk+Ag20nm.

Conversely, acidic composites demonstrated higher microhardness (~175 vs. ~165 HK) and better wear resistance (~1.1 vs. ~4.0 mg mass loss at S = 600 m), associated with lower roughness and favorable microstructural characteristics. Pure copper coatings exhibited the lowest mass loss (~0.5–0.6 mg) and highest hardness (CuALK: ~215 HK; CuAC: ~200 HK), confirming that Ag incorporation reduces wear resistance regardless of pH.

All coatings were hydrophilic (69.7°–82.6°), with acidic deposits showing higher contact angles despite lower corrosion resistance, indicating that wettability alone does not determine electrochemical stability.

Overall, acidic deposition favors mechanical durability, whereas alkaline deposition enhances corrosion protection. These findings guide electrolyte selection for biomedical and industrial applications based on the dominant degradation mechanism.

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