Abstract

The electrodeposition of copper-tin (Cu-Sn) alloys, commonly known as bronze, is a widely studied area due to the alloy's outstanding corrosion resistance, mechanical strength, and aesthetic appeal. However, achieving uniform and stable Cu-Sn coatings on stainless steel remains a challenge, particularly when acidic electrolyte baths are employed. In this study, we present a novel and cost-effective approach for depositing Cu-Sn alloy coatings using a stable, non-electroactive pyrophosphate-based bath. The developed electrolyte system exhibits high current efficiency (92%) and long-term stability, maintaining its integrity even after prolonged exposure to ambient conditions. To gain deeper insights into the deposition mechanisms, we utilised the Hyperquad simulation and speciation (HySS) software to calculate the concentration of Cu(II), Sn(IV), and pyrophosphate species as a function of pH, thereby facilitating accurate speciation analysis. Additionally, cyclic voltammetry (CV) and chronoamperometry studies were conducted to analyse the reduction and nucleation processes, which were interpreted using the Scharifker-Hills model. The results revealed that the deposition of Cu follows a progressive nucleation mechanism, while the Cu-Sn alloy deposition adheres to an instantaneous mode. X-ray diffraction (XRD) and scanning electron microscopy (SEM) confirmed the formation of $Cu_{13.7}Sn$ and ε-Cu_3Sn phases with minor β-Sn content, while profilometry measurements indicated a uniform coating thickness ranging from 7 to 13 µm.

The corrosion resistance of the Cu-Sn coatings was systematically investigated in aggressive sulfate (Na_2SO_4) and chloride (NaCl) environments using potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). The results revealed distinct corrosion mechanisms depending on the medium. In chloride environments, the Cu-rich phases showed complete dissolution, whereas tin preferentially dissolved in sulfate conditions. Notably, coatings deposited at 0.4 A demonstrated superior corrosion resistance in sulfate media, while those deposited at 0.5 A exhibited enhanced resistance in chloride media. Post-corrosion analysis using XRD and Rietveld refinement confirmed the formation of protective oxide layers, predominantly SnO_2 and CuO, which contribute to the stability of the coatings. Electrochemical analysis demonstrated that the primary corrosion protection is provided by the charge transfer resistance (R_{ct}), as observed from the EIS data. Furthermore, Nyquist plots revealed a mixed kinetic and

diffusion-controlled process in sulfate environments, whereas the chloride medium predominantly exhibited no diffusion control.

This research provides a comprehensive understanding of the electrodeposition and corrosion behaviour of Cu-Sn alloy coatings using a pyrophosphate-based bath. The findings demonstrate that the choice of deposition current and electrolyte composition has a significant influence on the microstructure and corrosion resistance of the coatings. The use of HySS software for speciation analysis further enhances the accuracy of understanding the electrochemical behaviour. These insights lay the groundwork for further improvements in the development of durable and aesthetically appealing bronze coatings for industrial applications.

Keywords: Pyrophosphate bath; Electrodeposition; Cyclic Voltammetry; Chronoamperometry; Corrosion.