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Abstract

In the present study, the electrodeposition characteristics, microstructural development, and corrosion resistance of two advanced zinc-based ternary alloys, Zn-Fe-Mo and Zn-Fe-W, electrodeposited from sulphate baths with and without the presence of ammonium ions, have been investigated. The electrochemical characteristics of the alloys have been correlated with the bath composition and the current density of deposition.

Significant changes in the reduction potential of zinc and iron are indicated by cyclic voltammograms. The reduction potential of zinc changes from -1.12 to -1.2 and finally to -1.25 volts versus Ag/AgCl as the electrolyte changes from ammonium sulphate to sodium sulphate solution. Similarly, the iron reduction potential changes from -0.40 to -0.80 and finally to -1.25 volts versus Ag/AgCl as the electrolyte changes from ammonium sulphate to sodium sulphate solution. Co-reduction of molybdenum and tungsten with iron is also indicated by cyclic voltammograms due to the formation of complexes involving the above three metals along with ammonium ions and citrate ions. The presence of complexes is also supported by the UV-Vis spectra obtained from the electrolyte solutions. Continuous evolution of the electrolyte is indicated by spectra due to the complexation of metal ions, redox reactions, and the formation of polynuclear molybdate/tungstate complexes at around 650-880 nm, and depletion of iron is indicated at around 480 nm. The microstructural analysis revealed that the Zn-Fe-Mo coatings deposited within the range of current density used exhibited a compact, nanocrystalline columnar morphology with fibrous, oval-shaped crystallites of 20-40 nm size, whereas the morphology of the Zn-Fe-W coatings was found to be dependent on the current density used, with low current density values ranging from 10-15 mA cm^{-2} resulting in rough, powdery, and porous surfaces, whereas a dense, fine-grained morphology was achieved with a current density of 20 mA cm^{-2}, and a larger current density of 25 mA cm^{-2} resulted in a coarser, nodular morphology. The homogeneous elemental distribution for Zn–Fe–Mo coatings with an Mo content between 0.2 and 5.0 wt.% in the ammonium-containing electrolytes was confirmed by the EDX analysis, which indicated a reduction in the Mo content with an increase in the current density due to the selective deposition of Zn, while the Zn–Fe–W coatings demonstrated an increase in the Fe and W contents in the ammonium-containing electrolytes by the metal-ammonia and metal-citrate complexation mechanisms, with the maximum contents of W reaching 3 to 5 wt.% at a current density of 20 mA cm^{-2}, and the maximum content of Fe 11wt.% at 25 mA cm^{-2}. Surface roughness tests confirmed the SEM results, which found a smooth surface finish of the Zn–Fe–Mo coatings, while there was a reduction in Ra of the Zn–Fe–W coatings with increasing current density, though lower in ammonium-containing baths due to refinement in nucleation and growth. Cross-sectional analysis of both systems by FIB/SEM presented dense columnar microstructures, although localized interfacial microvoids were observed in Zn–Fe–W coatings prepared from ammonium-containing baths during early stages of deposition due to hydrogen evolution, whereas Zn–Fe–Mo coatings exhibited more uniform through-thickness integrity. The XRD analysis also showed that the Zn-Fe-Mo coatings remained nanocrystalline, with the texture being dependent on the ammonium ions, whereas the Zn-Fe-W coatings showed a phase transformation from Zn- to Fe-Zn intermetallic phases, dominated by the $Fe_{22}Zn_{78}$ phase, when the current density increased, without the presence of tungsten phases due to their low concentration. The electrochemical measurement showed the optimal corrosion behavior at intermediate to high current densities by both alloy systems. In particular, compact microstructures and balanced alloy compositions were achieved at 20 mA cm^{-2}. In the case of the Zn-Fe-Mo coatings, the low corrosion current densities (ranging from 0.3 to 1 μA cm^{-2}), Mo-assisted passivation at low current densities, and high impedance values (with the highest value being 75 kΩ·cm^2 in the case of the Na_2SO_4 derived coatings at 25 mA cm^{-2}) are achieved. In the case of the Zn-Fe-W coatings, the stable corrosion potentials (around -1000 mV vs. Ag|AgCl), the highest polarization resistance at 20 mA cm^{-2}, and the highest values of the barrier resistance (around 6.6 kΩ·cm^2) are achieved. Overall, the results demonstrate strong structure-composition-corrosion relationships in Zn-Fe-Mo as well as Zn-Fe-W, and confirm that optimization of the current density, in association with the ammonium-assisted complexation, is a requirement in order to produce dense, homogeneous, and corrosion-resistant Zn-based ternary alloy coatings.

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