

The role of RE in Zn and Zn-Co alloy composites

Anđela Simović¹, Marija Mitrović², Milorad Tomić^{2,3}, Jelena Baiat⁴

¹University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia

²University of East Sarajevo, Faculty of Technology Zvornik, 75400 Zvornik, Republic of Srpska, Bosnia and Herzegovina

³Engineering Academy of Serbia, Belgrade, Serbia

⁴University of Belgrade, Faculty of Tehnology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia

Although rare earth (RE)-based conversion coatings have become a viable green substitute for hazardous chromium-coated ones, research in academia and industry is still ongoing to determine how they provide corrosive resistance. Numerous smart coatings incorporate nanoparticles of metal and metal oxides, offering diverse functional attributes and improved performance. In areas of the substrate that have been harmed by mechanical action or chemical interaction in a corrosion environment, these coatings may allow the substrate to heal itself [1-3]. One way to do self-healing is to incorporate inhibitor species into the coating formulation directly or encapsulate them in containers that are responsive to certain external stimuli. The corrosion protection afforded by the RE element and the small-scale phenomenon of corrosion inhibition conferred by RE doped pure Zn and Zn-Co alloy coatings are the main subjects of this work, with the aim of determining the RE contribution in corrosion protection either alone or in synergy with Co. Both Zn and Zn-Co alloy coatings are designed to modify the steel surface and offer effective corrosion protection, often as a stand-alone coating or as a base layer for organic top coats.

The chloride plating solutions containing Ce, Nd, or Sm were used to electrodeposit the Zn-RE and Zn-Co-RE protective composite coatings. As the primary drawback in the particle inclusion via electro-codeposition methods, particle agglomeration was minimized by adding RE to the plating solutions through synthetic RE-thioglycolate complexes and bath stability was determined as opposed to oxide containing or commercial powder containing ones. The protective qualities and self-healing capability were observed to be influenced by the type of RE, its reservoir, solubility in the composite coating, and surface morphology. The impact of these parameters was evaluated and compared using a multi-analytical approach, which involved dynamic light scattering, attenuated total reflectance, Fourier-transform infrared spectroscopy with ATR, nuclear magnetic resonance, Scanning Kelvin Probe Force Microscopy, open circuit potential measurements, and electrochemical impedance spectroscopy. It was shown that adjusting various electrodeposition parameters such as deposition current density, type of electrolyte agitation, and the source of rare earth elements can influence the RE content within the coating. The inclusion of rare earth elements in both Zn and Zn-Co coatings was demonstrated to reinforce to a different extent the barrier characteristics of composite coatings, consequently, possibly prolonging their durability in a 3 % NaCl solution. Moreover, a thorough investigation into the varying inhibition patterns displayed by bifunctional RE-complexes is clarified via theoretical computations. Predictions derived from density functional theory/molecular dynamics simulations indicate the possible development of various inhibitory compounds within the electrolyte. The corrosion inhibition mechanism hypothesized for RE-thioglycolates is based on both electrochemical and theoretical understandings, further corroborated through surface analysis techniques. Although significant, the RE loading within a coating does not singularly dictate the corrosion stability of composite coatings. The protective properties and self-healing capability were discovered also to result from an intricate interplay among the type of rare earth, its origin, solubility within the composite coating, and surface morphology.

Acknowledgement: This study was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contract No. 451-03-47/2023-01/200135).

References

1. C. Li, X. Guo, G.S. Frankel, *npj Mater. Degrad.* **54** (2021) 54 <https://doi.org/10.1038/s41529-021-00203-3>
2. M.F. Montemor, *Surf. Coatings Technol.* **258** (2014) 17-37 <https://doi.org/10.1016/j.surfcoat.2014.06.031>
3. A. A. Nazeer, M. Madkour, *J. Mol. Liq.* **253** (2018) 11-22 <https://doi.org/10.1016/j.molliq.2018.01.027>