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Abstract

Unveiling the Self-Healing Effect of Cerium Ions in PMMA-Silica Coatings on AA7075: A Comparative Study of Ce(III) and Ce(IV) †

Andressa Trentin *, Samarah V. Harb, Mayara C. Uvida and Peter Hammer

Institute of Chemitry, Department of Pysical Chemistry, São Paulo State University, Rua Prof. Francisco Degni 55, Araraquara 14800-060, SP, Brazil; s.harb@unesp.br (S.V.H.); mayara.uvida@unesp.br (M.C.U.); peter.hammer@unesp.br (P.H.)

* Correspondence: andressa.trentin@unesp.br

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Abstract: Cerium salts in the form of ammonium cerium(IV) nitrate and cerium(III) nitrate hexahydrate are widely used as corrosion inhibitors due to their ability to provide active protection against corrosion. When incorporated into polymeric, ceramic or hybrid coatings, cerium ions modify their structure and impart beneficial or adverse effects on barrier features, depending on the concentration and type of salt added. In this study, we compare the effect of varying amounts of Ce(III) and Ce(IV) ions on the structure and anti-corrosion properties of poly(methyl methacrylate) (PMMA)-silica hybrid coatings deposited on AA7075 aluminum alloy. The PMMA-silica coatings provided for both additives a long-term protection of AA7075 due to the highly cross-linked structure and a less defective polymeric network; however, the self-healing ability as a key feature was achieved only by Ce(IV) ions. Electrochemical impedance spectroscopy essays combined with time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy and energy dispersive X-ray spectroscopy revealed the corrosion inhibition mechanisms occurring in corrosion-induced and artificial defects. It was found that intermediate Ce(IV) loadings (500 and 1000 ppm) proved to be more effective in providing a high corrosion resistance with an active barrier property, extending the service time up to 720 days in 3.5% NaCl solution. The regenerative action of Ce(IV) can be associated with the faster formation of oxides and hydroxides mainly at intermetallic particle sites of AA7075 at pH ~ 3, compared to those from Ce(III) formed at pH ~ 9. These results link an optimized hybrid structure provided by cerium ions with their self-healing ability, making PMMA-silica-Ce(IV) hybrids very attractive as low-cost, high-performance and smart chromium-free coatings.

Keywords: PMMA-silica hybrid; organic-inorganic coatings; corrosion protection; Ce(IV) and Ce(III); self-healing

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