"Smart" Anti-Corrosion Coatings Utilizing Conductive Polymers Doped With Inhibitor Molecules

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The need for anti-corrosion coatings, which are pinhole and scratch tolerant, coupled with growing environmental concerns involving heavy metals, such as hexavalent chromium, has led to new coating strategies employing inherently conductive polymers (ICPs) as a key component. The first documented observations of corrosion protection of steel by polyaniline (PANI) were reported in 1981 by Mengoli, et al.[1] Since then, numerous papers have been published on the corrosion protection of carbon steel[2], stainless steel[3], iron[4], titanium[5], copper[6] and aluminum alloys[7] with ICP's. Two comprehensive review articles have been published[8].

ICP's have been postulated to stabilize the potential of the metal in a passive regime, maintaining a protective oxide layer on the metal. In this model, oxygen reduction on the ICP film replenishes the polymer charge consumed by metal oxidation, thereby stabilizing the potential of the exposed metal in the passive regime and minimizing the rate of metal dissolution:

$$\mathbf{(1/n)M^{o} + (1/m)ICP^{m+}R^{-} + (y/n)H_2O \rightarrow (1/n)M(OH)_y^{(n-y)+} + (1/m)ICP^{o} + R^{-} + (y/n)H^{+} \quad (1)}$$

(ICP reduction/metal oxidation/dopant release)

$$\mathbf{(m/4)O_2 + (m/2)H_2O + ICP^{o} \rightarrow ICP^{m+} + mOH^{-} \quad (2)}$$

(ICP oxidation by molecular oxygen)

Where: M = metal, ICP = inherently conductive polymer, and R^- = dopant

From equation (1) it is important to note that dopant ion is released upon reduction of the ICP. Very little is known about the relative anti-corrosion effectiveness of PANI doped with organic acids other than sulfonic acids and phosphonic acids. In the case of carbon steel coated with phosphonic acid doped PANI, Fe^{2+} is proposed to react initially with dopant anion (supplied by the leuco-emeraldine salt equilibrium) in an anodic regime[2]. The insoluble iron-dopant salt formed then effectively passivates the exposed metal surface.

Two unique properties of ICPs that no other organic molecules possess is their ability to conduct electricity and bind and expel molecules or ions in response to an electrochemical potential. The switching of the ICP redox state may be triggered by local electrochemical reactions occurring on the surface of a metal which occur during a corrosion process. Through proper design, ICPs may be synthesized to contain inhibitor molecules or ions as dopants. When coated onto a metal, the ICP would then contain inhibitor molecules that would be released when a corrosion process (metal oxidation) occurs. The inhibitor would diffuse to the corroding site and shut down the anodic (or cathodic) corrosion reaction. In this sense these coatings are "smart", in that they release the inhibitor when a defect and corrosion chemistry occurs. Furthermore the change in state of the conducting polymer with the consequent color and resistivity change gives such coatings a visual self-diagnostic ability.

Localized Corrosion Protection of Aluminum Alloys

Aluminum alloy 2024-T3 is an inhomogeneous alloy containing intermetallic particles that are enriched in alloying elements vs. the alloy matrix. Intermetallic particles greater than 0.2 microns in size have been classified into four groups: Al_2CuMg (S-phase), $Al_6(CuMnFe)$, Al_7Cu_2Fe and $(AlCu)_6Mn$[9]. The increased susceptibility of the 2024-T3 alloy to pitting corrosion is centered upon the unique electrochemistry of these intermetallic inclusions.

The key to developing new anti-corrosion coatings for 2024-T3 lies in understanding the electrochemistry of the intermetallic particles. Al_2CuMg (S-phase) have open circuit potential (OCP) values negative of the alloy matrix and thus are initially anodic. The OCP of other intermetallic particles is positive vs. the alloy matrix, these particles becoming cathodes. Local galvanic coupling from the cathode reaction (oxygen or proton reduction) to the matrix metal immediately surrounding the particle results in localized pitting corrosion. In our protection model, the onset of corrosion triggers release of the inhibitor from the ICP through formation of a local galvanic couple. In the case of 2024-T3, ICP coating damage (by scratching) causes the potential of the intermetallic particles to become active with respect to the matrix metal.

Several inhibitor ions that are known to inhibit oxygen reduction on copper inclusions in AA 2024-T3 have been incorporated into PANI and subsequently coated onto AA 2024-T3 and 7075-T6 aluminum panels.

SRET and Salt Fog Results

Coated aluminum panels were scribed and evaluated using SRET (scanning reference electrode technique). SRET results will be presented which show a very rapid passivation of the scribed surface in dilute sodium chloride solution. 1000 hour salt fog results will also be presented which show excellent localized corrosion protection as well as adhesion and flexibility.

References

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