

SELF-HEALING ANTICORROSIVE ORGANIC COATING BASED ON THE RELEASE OF A REACTIVE SILYL ESTER: USE OF LOCAL ELECTROCHEMICAL TECHNIQUES

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Keywords: local electrochemical techniques, coating, corrosion, capsules, silyl ester

ABSTRACT

Anticorrosive coatings offer passive (i.e. barrier to aggressive species) and active (i.e. release of active species) protection to underlying metals. Upon damage of the protective system the active release of species, like corrosion inhibitors, to the damaged site is the main protective mechanism. This mechanism of release of anticorrosive species has been used since the beginning of the 20th century by incorporation of chromium VI based inhibitors, but not defined as a self-healing mechanism until the mid-90s.

The implementation of self-healing concepts into protective coatings is of great interest due to the high probability of incurring damage in these systems and the crucial importance of maintaining the potential of protection of the underlying metallic substrate. In this sense, several groups have focused on different approaches: developing and understanding the effects of new environmentally friendly corrosion inhibitors, developing (nano)carriers for corrosion inhibitors, and focusing on the implementation of recovery of the barrier coatings using, amongst others, encapsulated systems.

The later approach (encapsulation) has mainly been approached by the use of two-agent systems (i.e. resin and crosslinker or catalyst) where the two agents are encapsulated together in a double capsule system, [1] separately in two different types of capsules, [2] or, the most common one, with one component encapsulated and the second one dispersed in the matrix. [3]

The authors have recently developed and published [4] a new concept for metal-protective organic coatings that involves an encapsulated agent (namely silyl ester) that is released upon fracture (i.e. scratch), perfectly wetting both metal and coating and immediately reacting with the underlying metallic surface and ambient humidity (no need of catalyst or crosslinker) creating a highly adhesive protective hydrophobic layer that offers extended protection to the underlying metal upon damage of the coating. The concept was tested and proved in [4] by using non destructive electrochemical techniques as electrochemical impedance spectroscopy (EIS) and, for the first time for self-healing coatings, scanning vibrating electrode technique (SVET), showing the high protection and potential of the new system.

While EIS offers overall information about the level of protection, in long-exposure tests it is complicated to discern between information coming from the repaired damage itself and that one

coming from the normal coating degradation. SVET offers more detailed and localized information about the precise protective effect and degradation of the released silyl ester at the scratch, complementing thus the information obtained by EIS. Figure 1a, shows the current density maps at the defect of a capsule containing coating, where activity can be detected at one hour immersion but disappears completely after 1day immersion in corrosive media (0.05M NaCl), showing high corrosion protection.

In order to further complement the obtained results, scanning electrochemical microscope (SECM) was used for the first time to evaluate healing of encapsulated systems obtaining very interesting results too. Figure 1b, shows a scratched coating without healing agent (left) and a coating with healing agent (right) immersed one day in corrosive solution (0.05M NaCl) showing the reduction of the cathodic reaction (oxygen reduction) and thus a sign of the good corrosion protection offered by the designed silyl ester.

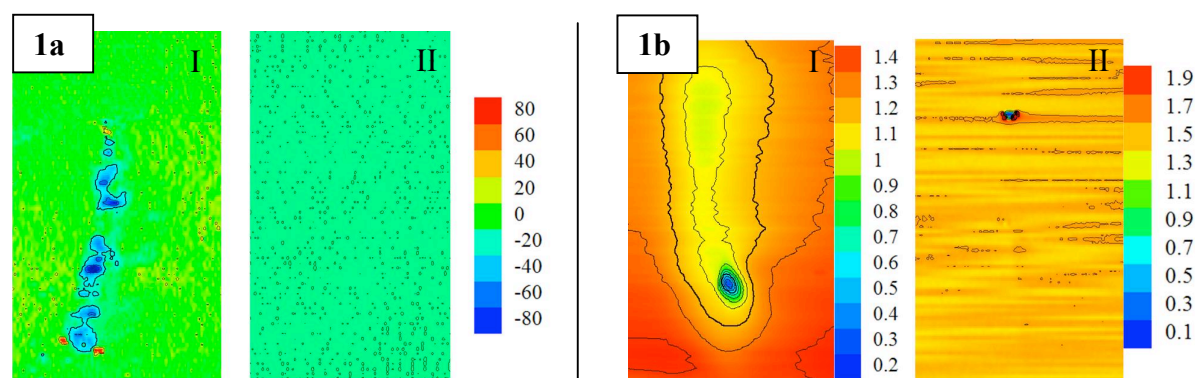


Figure 1: a) SVET current-density maps at the defect of a capsules-containing coating on AA2024-T3 after (I) 1 h, (II) 1 day immersion in 0.05M NaCl solution. Scanned area: $2 \times 3.5 \text{ mm}^2$. Current density legend: $\mu\text{A}/\text{cm}^2$;

b) SECM after 1day of immersion in 0.05M NaCl solution of scratched coatings applied on AA2024T3. (I) epoxy clearcoat without healing agent; (II) encapsulated silyl-ester containing coating. Color scale: current at the tip, nA. Image dimension: $0.9 \times 1.9 \text{ mm}^2$

In this work we demonstrate that the combination of local electrochemical techniques (SECM and SVET) with general electrochemical techniques (EIS) is a powerful mix of techniques for the evaluation of self-healing protective coatings. Furthermore, the results with SECM further support the previous results obtained by the authors with respect to the high corrosion protection offered by the designed silyl ester [4].

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