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Short communication

Active self-healing coating for galvanically coupled multi-material assemblies

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ABSTRACT

A new "self-healing" coating concept for active corrosion protection on galvanically coupled multi-material structures is reported in the present work. The novel approach is based on the combination of two types of nanocontainers with two different inhibitors in the same coating system. The nanocontainers confer a triggered release of both inhibitors which act in a synergistic way when an aluminum alloy is galvanically coupled with carbon fiber reinforced plastic. The layered double hydroxide and bentonite were used as functional nanocarriers for 1,2,3-benzotriazole and Ce^{3+} inhibitors respectively. Scanning vibrating electrode technique has been applied for the monitoring of galvanic corrosion activities and kinetics of self-healing processes in confined defects. The effective inhibition of electrochemical activity in the defects on coated galvanically coupled aluminum alloy with carbon fiber reinforced plastic was demonstrated for the first time.

1. Introduction

The new light-weight strategies especially in transport industries call for wider utilization of hybrid structures consisting of joined dissimilar materials. The materials with very different electrochemical potential are often electrically connected creating high risk conditions for galvanic corrosion. For example the hybrid structures based on electrically connected aluminum alloys and carbon fiber reinforced plastic (CFRP) are considered for the new generation of cars and aircrafts. One of the aluminum alloys used in both mentioned applications is AA6061.

However, the presence of more noble components, such as carbon fiber reinforced plastic (CFRP), in electrical contact with active metals significantly accelerates their corrosion due to the galvanic coupling [1,2]. The current anti-corrosion approaches including the new self-healing coatings are mainly designed for protection of single materials [3]. To our knowledge there are no works published in the literature reporting on fault-tolerant active protection coatings which can be applied for galvanically coupled multi-material assemblies. However the demand of dedicated systems tailored for suppression of galvanic corrosion is also increasing.

Recently the synergistic combination of known corrosion inhibitors 1,2,3-benzotriazole (BTA) and $Ce(NO_3)_3$ has been demonstrated as an excellent active protective system for Zn/Fe galvanic couple in a chloride medium [4]. These successful results stimulated us to implement such a synergistic combination of corrosion inhibitors in a single coating formulation applied to dissimilar system composed by an aluminum alloy and CFRP. The idea is to introduce the inhibitors into the coating in a separate way being encapsulated in the form of nanocontainers in order to reduce any potential negative effects such as inhibitor deactivation, osmotic blistering, and uncontrollable spontaneous leaching [5,6].

In this work two types of functional nanocontainers were utilized: layer double hydroxides (LDH) and bentonite for BTA and cerium cations respectively. These nanocontainers confer a controllable delivery of inhibitors on demand triggered by the appearance of corrosion related species such as Cl^- or OH^- in the case of LDH [7,8] and Me^{n+} in the case of bentonite [9].

The localized corrosion monitoring approach with scanning vibrating electrode technique (SVET) suitable for galvanic multi-material tests [4,10,11] has been used to monitor corrosion current densities on blank and coated Al/CFRP electrodes.

2. Experimental

2.1. Inhibitor testing on bare galvanic couple

Testing of synergistic combination of free corrosion inhibitors was performed on Al/CFRP galvanic couple in chloride media. The BTA and $Ce(NO_3)_3$ inhibitors with concentration of 5 mM and the mixture of these inhibitors with 5 mM gross concentration (2.5 mM of each) in 0.05 M NaCl were tested. Previously introduced [4,10] multi-electrode cell set-up consisting of pure Al wire (Goodfellow) and aerospace grade PEEK based CFRP materials embedded into inert epoxy resin (Buehler) (see photo in Fig. 1a) was used. The surface of the electrodes

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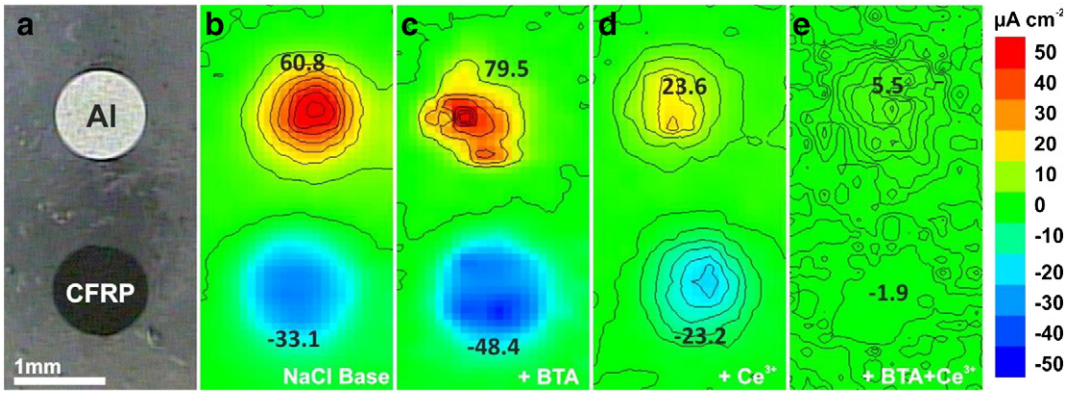

Fig. 1. Microphotograph of Al–CFRP galvanic test cell (a), SVET maps taken after 3 h of immersion in different inhibitor solutions with Al and CFRP electrodes electrically coupled in 0.05 M NaCl (b) and with addition of inhibitor 5 mM BTA (c), 5 mM $Ce(NO_3)_3$ (d) and the combination of inhibitors 2.5 mM BTA + 2.5 mM $Ce(NO_3)_3$ (e).

was renewed routinely before each experiment with 2500 grit SiC paper and rinsed with deionized water.

Applicable Electronics Inc. (USA) instrumentation controlled with the ASET software from ScienceWares was used for SVET measurement of localized corrosion current densities. The vibrating microelectrode had about 10–20 μm spherical platinum black tip and vibrated with 20 μm amplitude at the distance of 200 μm above the sample surface.

2.2. Preparation of inhibitor loaded nanocontainers

LDHs were synthesized according to the experimental procedure previously described [7,8,12] and the intercalation of the inhibitor was performed by anion-exchange method.

The cationic exchange reaction was used in order to impregnate bentonite particles with Ce^{3+} [8]. The chemicals: $Al(NO_3)_3 \cdot 9H_2O$ (≥98,5%), $Mg(NO_3)_2 \cdot 6H_2O$ (99%), NaOH (≥98%), $NaNO_3$ (≥99.5%), $Ce(NO_3)_3$ (99%), hydrophilic bentonite obtained from Sigma-Aldrich and 1,2,3-benzotriazole (BTA >99%) obtained from Riedel-de-Haën were used in functional nanocontainer preparation.

2.3. Localized electrochemical study on coated galvanic couple

The set-up for testing of active corrosion protection coating is presented in Fig. 2a. Electrically coupled AA6061 and aerospace grade PEEK based unidirectional CFRP square-shaped electrodes (11 mm * 11 mm) were embedded in an inert epoxy mount. The cell was polished with SiC paper (grit 2500) and rinsed with deionized water and ethanol before application of active protection coating.

The commercially available bi-component epoxy resin (SEEVENAX, Mankiewicz) impregnated with a mixture of nanocontainers was used

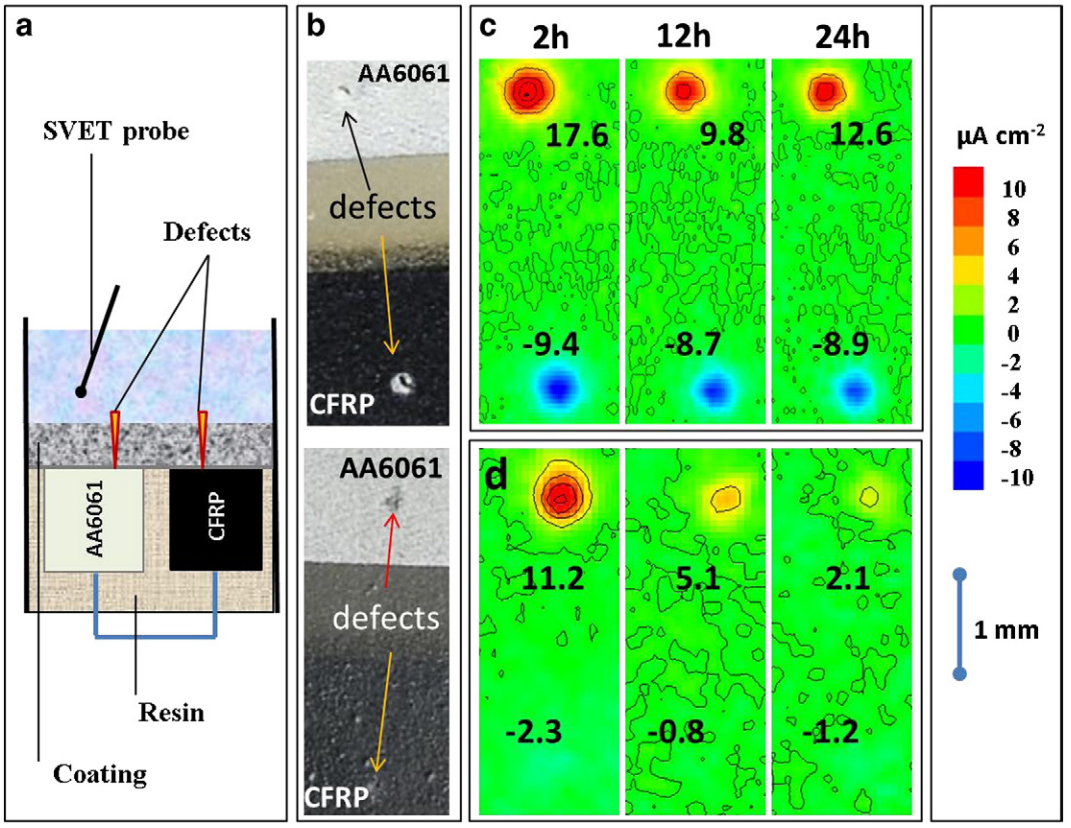

Fig. 2. Schema of AA6061 + CFRP microelectrode concept (a), microphotographs of coated galvanic cell concept with artificial defects (b). The SVET maps for the sample with blank coating (c) and for the coating loaded with combination of nanocontainers (LDH-BTA + bentonite-Ce^{3+}) (d) obtained after 2 h, 12 h and 24 h of immersion in 0.05 M NaCl.