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“SMART” protective ability of water based epoxy coatings loaded with $CaCO_3$ microbeads impregnated with corrosion inhibitors applied on AA2024 substrates

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ABSTRACT

Corrosion protection of aluminium alloys often relies on the application of a coating on the metallic surface. The coating normally combines a barrier effect that restricts the ingress of corrosive species, with an inhibitive role induced by corrosion inhibitor pigments added to the coating formulation. However, the direct addition of corrosion inhibitors to the coating can cause some detrimental interactions between components, as well as formation of preferential electrolyte pathways, compromising the barrier properties. Moreover, electrolyte uptake and ageing may result in leaching of those corrosion inhibitors. In order to extend the corrosion inhibition ability of organic coatings one possible solution is to store the inhibitors inside nano or microreservoirs compatible with the coating matrix and able to sense the local changes induced by the corrosion process. This strategy has led to the development of a new generation of “smart” coatings for anti-corrosion purposes. The aim of this work is to study the anti-corrosion properties of water-based epoxy coatings loaded with pH sensitive particles, acting as feedback active containers for corrosion inhibitors and applied on the aluminium alloy AA2024-T3. For this purpose micron size calcium carbonate beads were modified with different corrosion inhibitors: cerium nitrate, salicylaldoxime and 2,5-dimercapto-1,3,4-thiadiazolate. These particles act as pH sensitive reservoirs because they dissolve at acidic pH, releasing the corrosion inhibitor, which then suppresses the corrosion activity of the bare metal. Electrochemical impedance spectroscopy (EIS) was used to estimate the electrical parameters assigned to the barrier properties of the coating and corrosion inhibition ability in the presence of inhibitor loaded calcium carbonate beads. The most relevant corrosion inhibition effects were observed from $CaCO_3$ microbeads modified with cerium ions. The self healing potential of this new system was corroborated by localised electrochemical impedance measurements (LEIS).

1. Introduction

Aluminium alloys, including AA2024 are widely applied in the aeronautics and aerospace sectors because they offer excellent mechanical properties. However, AA2024 alloys are particularly susceptible to corrosion due to the presence of Cu rich precipitates [1]. One of the most widespread strategies for corrosion protection of aluminium alloys consists of the application of protective coatings, which generally consist of several layers, depending on the final application. Two of these layers, the pre-treatment and the primer have been prepared with chromates, which are known because of their powerful corrosion inhibition activity. However, hexavalent chromium is recognized as having carcinogen effects, and several efforts have been focused on its replacement with other friendly protection methods [2]. In addition to chromates replacement, another important aspect to take into account, when designing coatings for corrosion protection purposes, is the decrease of the volatile organic contents (VOC). Thus, the search of coatings with these characteristics has become a priority in many industrial sectors [3], including the aeronautical sector.

In order to enhance the protective properties of chromate free low VOC coatings, these can be modified with corrosion inhibiting species. In this way, the coating provides both passive barrier protection and ability to inhibit active corrosion sites when the coating is damaged. However, for improved performance it is necessary to ensure that the inhibitor does not have a detrimental effect on the barrier properties of the coating [4] and that the inhibitor is not leached, or depleted in the short term. If detrimental interactions occur between the coating and the inhibitor, then the barrier properties are disrupted and the corrosion protection ability of the modified coating decreases considerably [5,6]. Thus, in order to overcome these disadvantages, one of the most promising approaches to develop more effective anti-corrosion coatings is based on the use of confined inhibitors that are released by

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specific stimuli. Several systems can be used for this purpose [7–14]: microcapsules, porous microparticles or stratified layers made of pH sensitive polyelectrolytes. Although this strategy minimises the negative interactions between the inhibitor compounds and the coating, it also demands good compatibility between the guest reservoirs and the host coating matrix. When good compatibility is achieved, the most relevant advantage of this approach is that it prevents inhibitor leakage and short term diminution of the inhibitive performance.

In general, the protective systems based on inhibitor encapsulation, provide longer term corrosion protection ability (the so called active protection) due to the controlled delivery of the active inhibiting species. This delivery can be triggered by local changes induced either by the corrosion process or by other external stimuli. The various stimuli include local pH changes due to redox activity [5,9,15], UV irradiation [16] and presence of aggressive ions [17]. Thus, when the host containers sense these stimuli, the inhibitor is released to the active area and the corrosion process is inhibited. After cessation of the stimulus, the containers confine the inhibitor again, avoiding unnecessary leaching and ensuring longer term performance. The most promising systems rely on the use of pH sensitive nano/micro particles or nanocapsules, triggered by pH gradients created as consequence of the redox activity. In a previous works, other strategies were investigated in order to store effective corrosion inhibitors in pH sensitive inorganic based containers such as hydroxyapatite microparticles, with positive results [9]. Literature also reports some other interesting approaches based on the use of conductive polymers. The principle of active protection relies on the assumption that the high potential of the polymer is able to keep the metal surface in the passive state. Indeed some traces of healing ability were observed [18].

In the present work, a new smart anticorrosion system for AA2024, consisting of a water based epoxy matrix loaded with calcium carbonate microbeads modified with various corrosion inhibitors is proposed. This modified coating is expected to store the corrosion inhibitor until damages and subsequent corrosion events appear. As consequence of the electrochemical activity of the bare aluminium alloy, the pH at the anodic sites decreases [9] and the $CaCO_3$ microbeads start to dissolve, releasing the corrosion inhibitor, which heals the corrosion activity of aluminium. When this happens, the pH gradient vanishes and the inhibitor is no longer released from the $CaCO_3$ microbeads.

The main advantages of $CaCO_3$ microbeads are their easy and cheap production methodology and their ability to sense local acidification. To achieve the desired anti-corrosion properties, the $CaCO_3$ microbeads were impregnated with various anti-corrosion species known as effective towards AA2024 corrosion: cerium ions (Ce^{3+} from cerium nitrate) [19], salicylaldoxime (Sal) [1] and 2,5-dimercapto-1,3,4-thiadiazolate (DMTD) [20]. The $CaCO_3$ microbeads loaded with the corrosion inhibitors were added to water-based epoxy coating formulations, which were applied on AA2024 coupons by dip coating. The $CaCO_3$ microbeads used in this work were prepared and characterized as described elsewhere [21].

The corrosion inhibition performance of coated AA2024 coupons was assessed by electrochemical impedance spectroscopy (EIS) during immersion in NaCl electrolytes. The local inhibition ability was studied by localised electrochemical impedance (LEIS) over an artificial defect formed in the coating. Complementary experiments were also performed using scanning electron microscopy coupled with energy dispersive spectroscopy and X-ray diffraction. The results revealed that effective corrosion protection ability can be achieved with this new approach, which is a step further in the development of water based anti-corrosion smart coatings.

2. Experimental

2.1. Synthesis of $CaCO_3$

Calcium carbonate microbeads were prepared according to the procedure reported by Tong et al. [21]. The colloidal aggregation method was used, after mixing equal amounts of 0.2 M $CaCl_2$ (provided by Merk, >99.5%) and 0.2 M Na_2CO_3 (provided by Sigma–Aldrich, >99.5%) solutions at 37 °C. L-Aspartic acid 0.12 g (provided by Sigma–Aldrich, >99.0%) was used as an organic template for inducing the nucleation of calcium carbonate. The $CaCO_3$ particles were separated from the solution by filtration through a 0.22-μm Millipore filter and dried in desiccators.

$CaCO_3$ microbeads containing the corrosion inhibitors were prepared as follows: 0.2 M of Na_2CO_3 solution containing 0.036 M of inhibitor compound was mixed with 0.2 M $CaCl_2$ at 37 °C together with 0.12 g L-Asp. Three different inhibitors were used: cerium(III) nitrate (Ce^{3+}), salicylaldoxime (Sal) and 2,5-dimercapto-1,3,4-thiadiazolate (DMTD). After 1 min of soaking, the suspension was filtered using a 0.22-μm Millipore filter and washed with millipore water. After preparing, the inhibitor doped beads were kept in desiccators.

2.2. Preparation of AA2024 coupons

The AA2024-T3 aluminium alloy (composition as described [1]), was used as substrate to assess the anticorrosion properties of the coating modified with the $CaCO_3$ particles loaded with different corrosion inhibitors. The coupons of AA2024 were chemically etched, using a three-step cleaning procedure as generally applied in the aeronautical industry. The specific treatment was carried out as follows: alkaline cleaning in Metaclean T2001® at 60–70 °C for 15–25 min, followed by alkaline etching in TURCO Liquid Aluminetch N2® at 60 ± 5 °C for 30–60 s and acidic etching in TURCO Liquid Smutgo NC® at 30 ± 5 °C for 5–10 min. The coupons were briefly immersed (<1 min) in millipore water after each step to remove the reaction products.

2.3. Preparation of the water based epoxy coating

The coating was a commercially available model two-component water-based paint commonly used as an anticorrosive primer. The epoxy coating was supplied by a coating manufacturer and it is a simplified model of a commercial primer for AA2024 used in the aeronautical industry. The solution for coating preparation was loaded with 5 wt% (relative to the weight of the coating solution) of inhibitor-modified $CaCO_3$ microbeads and stirred for 10 min. A coating solution without $CaCO_3$ addition was also prepared as reference. The epoxy mixture loaded with $CaCO_3$ microbeads was applied on the aluminium coupons by dip-coating. The withdrawal rate was 18 cm/min and the immersion time in the coating solution was 100 s. In order to obtain the required thickness five consecutive dips were performed. All the coupons were cured at 50 °C for 7 h in air for further cross-linking and water evaporation. To assess the influence of the inhibitors on the barrier and active properties of the coating, three different formulations of coating solutions directly loaded with corrosion inhibitors (without $CaCO_3$ microbeads) were prepared. The inhibitors were added to the coating solution after mixing the two components – resin and hardener and stirred for 10 min.

Seven epoxy coatings were prepared: a blank coating (without additives), 3 coatings loaded with inhibitor-modified $CaCO_3$ particles (cerium nitrate, salicylaldoxime and 2,5-dimercapto-1,3,4-thiadiazolate) and 3 coatings directly loaded with these corrosion inhibitors.