



Inhibition of filiform corrosion on organic-coated AA2024-T3 by smart-release cation and anion-exchange pigments

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ARTICLE INFO

Article history:

Received 27 January 2012
Received in revised form 1 March 2012
Accepted 1 March 2012
Available online 9 March 2012

Keywords:

Scanning Kelvin probe
Filiform corrosion
Aluminium
Inhibition
Ion-exchange

ABSTRACT

In-coating cation and anion exchange pigments are studied with respect to their ability to inhibit chloride-induced filiform corrosion (FFC) on organic-coated AA2024-T3 aluminium alloy substrates. In-situ scanning Kelvin probe potentiometry is used to quantify both underfilm potentials associated with populations of propagating corrosion filaments and the kinetics of coating disbondment. Smart-release bentonite pigments containing exchangeable cerium (III) and yttrium (III) cations are shown to be largely ineffective in reducing rates of FFC propagation. The reasons for this are discussed in terms of the chemistry of the electrolyte-filled corrosion filament head. In contrast, anion-exchange hydrotalcite (HT) based pigments are highly effective inhibitors of FFC. A comparison of the extent of FFC observed for various inorganic exchangeable anions is made with as-received HT comprising carbonate anions. Of the anions evaluated, exchangeable chromate unsurprisingly provides the highest FFC inhibition efficiency. It is also demonstrated that exchanging the native carbonate ions for certain organic species which act as complexing agents for copper ions, gives rise to an equivalent level of FFC inhibition. The implication of these findings with respect to the mechanism of FFC on copper containing aluminium alloys is considered.

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1. Introduction

It has been known for many years that rare earth metal (REM) ions, added to a corrosive electrolyte are effective inhibitors of aluminium alloy corrosion under immersion conditions [1–3]. Rare earth cations such as cerium (III) and yttrium (III) act as cathodic precipitation inhibitors, reacting with OH⁻ ions produced via cathodic oxygen reduction, to precipitate insoluble hydroxides at the metal solution interface [4,5]. However, in the case of cerium which has multiple oxidation states, the oxidation of Ce(III) to Ce(VI) by hydrogen peroxide, formed as a side product of cathodic O₂ reduction, may also play a role. It has been proposed that this process promotes the formation of dense cerium (IV) oxide (CeO₂) films and contributes to the high efficiency of corrosion inhibition by Ce³⁺ [6]. Considerable efforts are currently being directed towards exploiting this high efficiency of inhibition by developing REM-based coating systems as chrome (VI)-free alternatives for the protection of aluminium surfaces [7–9]. Several groups have reported promising anti-corrosion properties for cerium (III) based conversion coatings [10–12], while others have employed sol-gel-based coatings as delivery systems for Ce³⁺ ions [13–16].

One of the most promising non-chromate technologies presently under investigation is the use of ion-exchange minerals as so-called “smart-release” pigments incorporated within an organic polymer binder. The appeal of such systems lies in the ability to release inhibitor species and sequester aggressive ions such as chloride or H⁺ only when a corrosive aqueous environment is encountered. In this work we have used bentonite cation exchange clays, modified to incorporate REM ions, as smart release pigments in an attempt to assess the anti-corrosion efficiency of in-coating Ce³⁺ and Y³⁺ on aluminium. Such an approach has been used successfully in previous work on galvanised steel to inhibit underfilm corrosion by a cathodic delamination mechanism [17]. Since there are few, if any sparingly soluble inorganic salts of REMs available to be processed into pigment form, the use of a cation exchange matrix to deliver REM cations from within an organic coating is particularly attractive. Here we have studied the protection of aerospace aluminium alloy AA2024-T3 by model coatings containing exchangeable Ce³⁺ and Y³⁺ ions, under well-defined atmospheric corrosion conditions, where filiform corrosion (FFC) predominates. FFC is characterized by “thread-like” deposits of corrosion product beneath the coating which propagate in the presence of oxygen, aggressive ions such as chloride (Cl⁻), and a high relative humidity [18,19]. Corrosion filaments, comprising an electrolyte filled “head” and a “tail” of dry corrosion product, propagate under the influence of differential aeration arising from facile mass transport of oxygen through the filament-tail. Hence cathodic

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oxygen reduction remains localized at the droplet trailing-edge while anodic metal dissolution is principally located at the droplet leading-edge. Aggressive anions (Cl^-) and water are conserved in the filament-head electrolyte.

One of the principal aims of this work is to evaluate REM cations as inhibitors of FFC on organic coated AA2024-T3. Although several previous studies have shown that coatings which have been impregnated with REM based salts can provide effective corrosion protection of AA2024-T3 substrates when immersed in corrosive aqueous electrolytes [13–16], little is currently known about the resistance of such coatings to FFC in atmospheric corrosion conditions. A second aim is to compare the efficiency of FFC inhibition by in-coating REM-exchanged bentonites with that of hydrotalcite (HT)-based, anion-exchange pigments, which have already been demonstrated to be highly efficient inhibitors of FFC [20,21]. In this work further developments in FFC inhibition on an AA2024 surface by HT pigments containing alternative inorganic anions to those previously evaluated [21] are presented. In addition, improvements in the performance of HT-containing coatings, via the incorporation of anionic organic reagents which interact specifically with copper cations, will also be described.

2. Experimental details

Polyvinyl butyral-co-vinyl alcohol-co-vinyl acetate and hydrotalcite powder ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) were obtained from the Aldrich Chemical Co. Aluminium alloy AA2024-T3 sheet of 1.5 mm thickness and composition by weight: 0.5% Si, 0.5% Fe, 3.8–4.9% Cu, 0.3–0.9% Mn, 1.2–1.8% Mg, 0.1% Cr, 0.25% Zn was provided by BAE systems Ltd. Wyoming Bentonite (grade GG, cation exchange capacity 0.7 meq g^{-1}) was obtained from Steetley Bentonites and Absorbents. Bentonite samples were exhaustively exchanged with trivalent rare earth (Ce^{3+} , Y^{3+}) cations from aqueous solutions of rare earth chlorides (99.9% purity, Aldrich) using a literature method [22]. The resulting cation exchanged bentonites were then washed by repeated cycles of centrifugation and re-dispersion in fresh distilled water until Cl^- ions could no longer be detected in the washing liquor using silver nitrate solution. Finally, the bentonites were washed with ethanol, dried in an oven at 70°C for 4 h, and the resulting powder ground to give a particle size of $<20 \mu\text{m}$ diameter. Chemical analysis of the Ce^{3+} bentonite pigment, carried out by digestion in aqua regia followed by inductively coupled plasma/mass spectrometry, gave a 3.2% w/w cerium composition.

Anion-exchanged HT pigments were prepared by heating 10 g quantities of HT at 450°C for 3 h prior to dispersion in 100 cm^3 of 0.5 M aqueous solutions containing the sodium salt of the target exchangeable anions as described previously [20,21]. Subsequently, HT pigments were washed by repeated cycles of centrifugation and re-dispersion in fresh distilled, dried in air, and ground to give a particle size of $<20 \mu\text{m}$ diameter. The anion-exchange capacity of the calcined HT has been measured previously [20] and found to be 0.7 meq g^{-1} . AA2024-T3 Samples were cut into 35 mm square coupons and abrasively cleaned using an aqueous slurry of 5 μm polishing alumina, followed by degreasing in acetone. Polyvinyl butyral (PVB) solutions were prepared in ethanol (15.5% w/w) and any required amount of exchanged bentonite or hydrotalcite powders added as an ethanolic slurry. The components were mixed thoroughly using a high shear blender. Pigmented PVB solutions were bar cast on to the clean sample surface and allowed to dry in air. This procedure gave a dried film thickness of $30 \mu\text{m}$ as measured using a micrometer screw gauge.

Filiform corrosion was initiated by applying a $1 \mu\text{l}$ volume of aqueous HCl (0.5 mol dm^{-3}) along the length of a 10 mm defect, scribed in the centre of the coated sample using a scalpel blade. In each case it was ensured that the direction of the scribe was normal

to that of substrate rolling direction. After allowing any excess water to evaporate, the sample was placed in the environmental chamber of the scanning Kelvin microprobe (SKP) apparatus and held at a constant temperature of 20°C and relative humidity of 93%. Repetitive scans were carried out every 4 h on a 1 cm^2 area of the coated AA2024-T3 alloy sample encompassing the scribe, using a data point density of 10 points/mm and a mean probe to sample height of $100 \mu\text{m}$. In separate experiments, duplicate samples were initiated by the same procedure and placed in a separate environment chamber maintained at a constant relative humidity of 93%. After a period of 1 week following initiation, these samples were removed and photographic images of any corroded regions were recorded. Full descriptions of the analysis of both photographic images and SKP-derived Volta potential maps to give quantitative measures of delaminated coating area are given elsewhere [20,23]. For selected samples, at the end of the experimental period, the PVB coating was manually peeled off and the substrate surface analysed by secondary ion mass-spectroscopy (SIMS). SIMS analysis was carried out with a lateral resolution of $10 \mu\text{m}$ and a mass resolution of ± 0.1 Dalton using a Millbrook Instruments MC300 (Mk II) Chemical microscope fitted with a gallium ion source. Full details of the SKP instrument used in this work and the procedures used for calibration can be found in previous publications [24,25].

3. Results and discussion

3.1. REM-exchange FFC inhibition

The influence of Ce^{3+} and Y^{3+} exchanged bentonite-pigments, dispersed within a model PVB coating, on FFC kinetics was investigated by using in situ SKP scanning. The technique allows dynamic changes in E_{CORR} patterns associated with FFC propagation to be visualised, and enables the area of coating delamination as a function of time to be determined. This latter procedure has been described in detail elsewhere and exploits the observation that E_{CORR} values measured over an area of intact undelaminated coating differ significantly, typically by hundreds of mV, from those measured over a region where coating delamination has occurred [23]. The influence of pigment volume fraction (ϕ_{pt}) for both Ce^{3+} and Y^{3+} exchanged bentonite-pigments on the rate of propagation of a population of corrosion filaments was studied over the range $0 \leq \phi_{\text{pt}} \leq 0.2$.

Fig. 1 shows characteristic E_{CORR} distribution maps obtained 80 h after FFC initiation and subsequent holding at a constant relative humidity of 93% at 20°C . The square regions indicated by dashed lines on the corresponding visual images indicate the region over which the scans were recorded. It is evident from these results that the extent of FFC attack and E_{CORR} values associated with individual filaments, observed in the presence of both Ce^{3+} and Y^{3+} based pigments, remain similar to the unpigmented case (see Fig. 1a). Profiles of E_{CORR} as a function of distance, recorded for individual filaments propagating under both Ce^{3+} - and Y^{3+} -bentonite coatings, were similar to those reported previously for PVB-coated AA2024-T3 samples in the absence of inhibitor pigment. SKP-derived E_{CORR} vs. distance plots recorded for a Ce^{3+} -bentonite containing coating at $\phi_{\text{pt}} = 0.2$, showing representative E_{CORR} values of -0.15 , -0.5 and $+0.1 \text{ V vs. SHE}$ for the intact coated metal, filament head and tail regions respectively, are given in Fig. 2. The similarity of these plots to others published elsewhere for PVB coated AA2024 under identical conditions [23], implies that any REM cations exchanging into the filament head electrolyte produce little or no polarization of potentials in either anodic or cathodic regions of the local corrosion cell. This is in contrast to previous findings obtained using strontium chromate-pigmented PVB [26] where significant depression of both filament tail and intact coating E_{CORR} values was observed.

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