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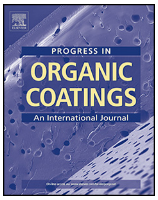

Influence of mass transport on the competition between corrosion and passivation by inhibitor release after coating breakdown

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ABSTRACT

Interactive combination of the properties of storage, release of pigments and transport of inhibitors are controlling the efficacy of inhibitive coatings deposited as primer on 2024 alloys subject to environments with a risk of atmospheric corrosion. A test method is proposed to characterize the competition between the triggering of localized microstructural corrosion and the passivation of a bare metal surface. The behaviour of a cut-edge electrode machined from a coated AA2024-T3 plate has been used to mimic the electrochemical response after a breakdown in the surface coating. In this work, the calibration of the described method is based on conventional chromate/dichromate inhibitors, assumed to be cathodic inhibitor. In situ pH imaging with an ion-selective microprobe was used to confirm the effect of the inhibiting pigment depletion inside the primer coating on the competition between corrosion and passivation. This test method is intended as useful for selection of chromate replacement.

1. Introduction

The conventional industrial solution for addressing corrosion protection of aluminium structures is provided by coatings doped with inhibiting pigments, in which the inhibitor release from the applied coating system enables active corrosion protection. Their efficacy depends on the local competition between the triggering of microstructural corrosion by local trenching around coarse intermetallic particles in absence of inhibitor ions and passivation induced by electrochemical and/or chemical evolution of the inhibitor ions released from the primer. It is typically the reaction mode of conventional chromate or dichromate inhibitors which were chosen to calibrate the proposed test method. In the context of this paper, the term “passivation” is used to characterize the effect of the reduction of Cr(VI) species which leads to the suppression of the oxygen reduction reaction (ORR) on the reactive areas of the 2024 surface.

Whatever the inhibitor, the combination of its storage release, its mass transport to the freshly exposed metallic area and its irreversible reaction providing passivation (chromium oxide formation in the case of chromate or dichromate primers) underlies the competition between triggering of corrosion and passivation which needs a sufficient quantity of inhibitor on demand after any kind of local breakdown of the protective coating.

Regarding literature, in most of previous works on chromate or dichromate ions, assumed to be cathodic inhibitors, their efficacy was tested by simple comparison of polarization curves. The suppression of the ORR in presence of Cr(VI) ions was a good predictor since the triggering of localized corrosion on 2024 alloy is typically under cathodic control.

Nevertheless, it appears that identification of alternative environmentally friendly inhibitors only by plotting polarization curves would be not sufficient.

Concerning chromate or dichromate based pigments, a lot of results concerning the rate of release from the polymeric matrix which clearly show different release regimes, are available in literature [1,2]. As function of the water permeability of the coating and of the solubility of the inhibitive pigments the release process leads to a steady state corresponding to the existence of a depletion zone inside primer. The existence of this depleted layer due to continuous exposition of the coating, for example, after a scratch has been recently imaged by X-rays or ESEM microtomography [3,4], but its effect upon the competition between corrosion triggering and passivation has been rarely experimentally investigated, even though some models describing the consecutive steps, release, transport and reaction of inhibitive ions have been proposed in literature [5–7].

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It must be noticed that the prevention of such depleted layer represents a critical issue in the development of more efficient corrosion protection systems for aluminium alloys, by developing self-repairing coatings [8].

In all these modelling approaches, the authors focused rather on the mass transport control of the release step, which is a well-documented step [9,10], than on the modelling of the transport of the released ions to the substrate surface. This can be explained by the fact that inhibitive coatings are designed to post-damage healing at short distances, typically inside a scratch (typically in the range of 100 μm). At this scale, transport can be assumed to be not a limiting step. But in aircraft structures, it could exist other defects (in service defects) which can initiate either at edges or around fasteners in assemblies [11] where, for example, some machining can remove the surface protection system in some areas (especially in drill holes), resulting in a wet assembly at the fastener. In this configuration the effectiveness of the release inhibitor will be controlled not only by the release rate but also by the transport of the inhibiting ions to the exposed metallic areas at a distance which can be evaluated in the range of millimetre. In this condition, all the more as the electrolyte will consist in a stagnant liquid and/or a trapped electrolyte, the effect of the mass transport in the electrolyte on the competition between corrosion and the release of inhibitors from the pigments trapped in the coating cannot be neglected.

Furman et al. studied in ref. [12,13] the corrosion sensitivity of damages in a chromate-inhibited paint system which are simulated by artificial defects (slots exposing fresh metal at the bottom of a machined scratch through the coating to the underlying aluminium alloy 2024-T3) of various size varying from 4 to 0.2 mm. The discussion of the obtained results raises the question of the efficacy of the mass transport of inhibitor species from the exposed painted wall to the centre of the slot. These latter results support the existence of a critical distance beyond which the chromate concentration is not sufficient to protect the surface of the alloy. This critical distance which characterize the competition between the corrosion triggering and the passivation of the metallic surface has been highlighted in the presence of an electrolyte resulting from a neutral salt spray (NSS) test. In an additional paper [14], the authors demonstrate that the number and size of pits in the artificial defects as function of time of exposure depend on the width of the slot, i.e. the smaller the slot the longer the time to produce the first pit. These results confirm the effect of the distance between the inhibitor source (the wall of the machined slot) towards the centre of the metallic exposed surface inside the slot.

In NSS exposure conditions, it can be assumed that this effect of the distance is controlled by the availability of the corrosion inhibitor as the surface of the tested coupons is continually washed. Consequently any inhibitor that has leached into a drop can be periodically removed preventing the inhibitors ions to reach easily the metallic exposed surface: it is clear this depends on the distance. This confirms the main result obtained with large size scratches, i.e. the larger the scratch the higher lack of passivation from the released inhibiting ions.

Even if properties of storage, release, transport and reaction of inhibitive ions from coatings are frequently combined, it appears that mass transport in solution has not been frequently used as a selective parameter to support the benchmarking of selected inhibitors, probably because it was not easy to monitor any physico-chemical process quantifying the competition between corrosion triggering in open-circuit potential conditions and the release of inhibitors from the pigments trapped in the coating. For example, in a recent paper [15], an original experimental approach of the efficacy of inhibitors (cerium salts) supplied after the onset of corrosion was supported by a numerical approach of transport of inhibitors through the solution.

The study described in this paper is intended as a test method for the assessment of chromate replacement, based on detection of microstructural corrosion by surface pH probing of the metallic surface which will be controlled by all the steps involved in the mass transport of inhibitors species from the inner part of the primer to the freshly exposed metallic area. All experiments dedicated to corrosion protection efficiency analysis were performed in open-circuit potential conditions to highlight the role of dichromate ions on the cathodic reaction which controls the triggering of the localized microstructural corrosion. This is an important feature as mentioned by Frankel and coworkers [16] which suggest, in a simple way of testing alternative inhibitors (and the required concentrations), to limit the identification to a critical limiting cathodic current density (or nominal corrosion current density) below which stable pitting does not occur.

In this paper, we tried to illustrate that such a simple comparison of polarization curves is not a sufficient predictor of the corrosion or passivation behaviour.

2. Experimental

2.1. Materials and solutions

Specimens are based on cut-edge electrodes machined from rolled plates (100 mm × 70 mm × 4 mm) of an aluminium alloy (AA2024-T3). The cut-edge geometry (Fig. 1a) was chosen to mimic a breakdown of the primer coating, which can be compared to the experiments conducted on artificial defects of various widths [14].

In a first part of the study, experiments were performed on uncoated AA2024-T3 to study the electrochemical behaviour of the alloy in an aggressive environment with or without addition of inhibitors species in bulk solution.

In a second part of the study, AA2024-T3 plates were coated on both ST-L sides (ST = short transverse and L = longitudinal directions). The exposed area (4 mm × 10 mm) in contact with the corrosive electrolyte corresponds to the ST-SL (SL = long transverse direction) face of the machined plate and was used to study the effect of the release of the inhibitors species on the corrosion damage of the aluminium alloy.

The cut-edge electrodes were mechanically ground with successively finer grades of SiC papers lubricated with alcohol. Finally the specimens were polished with a 3 μm diamond paste on cloth preventing the selective dissolution of the coarse intermetallic particles of which the reactivity will be studied.

In this work, most of the experiments related to the evaluation of the corrosion damages as function of the presence of inhibiting ions (whatever their origin) were performed in a 0.5 M NaCl neutral solution (pH 6.5). To study some specific features of the local corrosion response of a coarse intermetallic particle and to define the kinetic of passivation on a damaged surface the

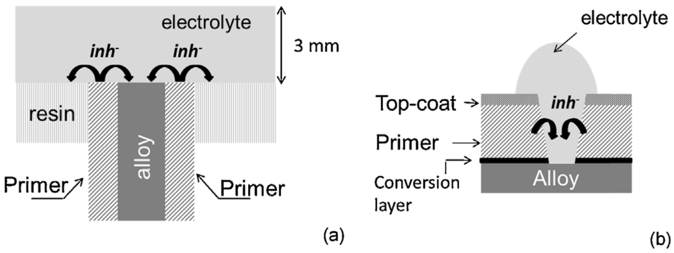

Fig. 1. Schematic illustration of (a) the cut-edge electrode designed to mimic the chemical and electrochemical reactions encountered in the real case of a scratch on an industrial paint system (b). The exposed area (4 mm × 10 mm) in contact with the corrosive electrolyte corresponds to the ST-SL (SL = long transverse direction) face. The L-SL faces were coated with the primer. The volume of the electrolyte above the cut-edge electrode is 5.5 × 3.1 × 0.3 cm^3 = 4.65 cm^3