



Study of the formation of a protective layer in a defect from lithium-leaching organic coatings



P. Visser^{a,b,*}, A. Lutz^c, J.M.C. Mol^a, H. Terryn^{a,c}

^a Delft University of Technology, Department of Materials Science and Engineering, Mekelweg 2, 2628CD, Delft, The Netherlands, The Netherlands

^b AkzoNobel, Specialty Coatings, Rijksweg 31, 2171 AJ, Sassenheim, The Netherlands, The Netherlands

^c Vrije Universiteit Brussel, Group of Electrochemistry and Surface Engineering (SURF), Pleinlaan 2, 1050, Brussels, Belgium

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ABSTRACT

Lithium salts were investigated as leachable corrosion inhibitor and potential replacement for hexavalent chromium in organic coatings. Coatings loaded with lithium carbonate or lithium oxalate demonstrated active corrosion inhibition by the formation of a protective layer in a damaged area. The present paper provides more insight into the formation and composition of the protective layer in a damaged area generated from the lithium salt loaded coatings when exposed to neutral salt spray testing conditions (ASTM B-117). Lithium-ion leaching from the coating matrix was demonstrated with atomic absorption spectroscopy and the pH conditions in the damaged area were determined with a scanning ion-selective electrode technique. Additionally, the formation of the protective layer was studied with microscopic and surface analytical techniques. Scanning electron micrographs and Auger electron spectroscopy depth profiles revealed the process of coverage and growth of the protective layer in the damaged area. Furthermore, X-ray photoelectron spectroscopy analysis indicated that the protective layer likely consists of a hydrated oxide in the form of a (pseudo) boehmite with lithium distributed in its matrix.

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1. Introduction

Aluminium alloys such as AA2024 or AA7075 are high strength aluminium alloys that are extensively used in the aerospace industry. However, these alloys are susceptible to localized corrosion such as pitting corrosion and intergranular corrosion. Especially, AA2024-T3 aluminium alloys are susceptible for pitting corrosion due to the presence of copper-rich intermetallic particles in the matrix [1–5]. The different electrochemical nature of the particles and matrix results in the formation of micro-galvanic cells within the substrate and may initiate pitting corrosion [1–3,6].

Corrosion control is an important aspect in the aerospace industry [7]. Therefore, active protective coatings are an essential part of the corrosion protection scheme within the aircraft design. The typical corrosion protective scheme for the protection of the aluminium alloy substrate comprises a chemical conversion coating or anodic film, corrosion inhibiting primer and in certain areas a topcoat [8,9]. Such a scheme provides two modes of protection: barrier protection (passive) when the system is intact and inhibitor based passivation (active protection) when the coating is damaged

[10]. This active protection relies on a leaching mechanism. This is a complex process where in case of a damage, the inhibitor is released from the coating and migrates to the corroding sites and passivates the substrate at the coating defect area [11–13].

Traditionally, strontium chromate is used as leaching corrosion inhibiting pigment in coatings to protect the aluminium structures of aircraft and its exceptional corrosion protection was demonstrated in many research programs [14,15]. Despite their unique properties and performance, these hexavalent chromium-containing inhibitors need to be replaced. They are known carcinogenic compounds and their use is expected to be restricted due to new regulations [16,17]. Much research is conducted to find alternative inhibitors that perform equal or better compared to hexavalent chromium containing inhibitors [18–24].

Lithium salts have become of interest as an alternative corrosion inhibitor to protect aluminium alloys after reports of passivity of aluminium in alkaline lithium salt solutions [25,26]. Buchheit et al. studied lithium carbonate solutions as hexavalent chromium free chemical conversion coatings, generating a lithium aluminium carbonate hydroxide hydrate ($\text{Li}_2[\text{Al}_2(\text{OH})_6]_2 \cdot \text{CO}_3 \cdot n\text{H}_2\text{O}$) coatings on aluminium alloys under alkaline conditions [27]. The composition, structure and performance were studied in relation to processing and bath chemistries [28]. Their work demonstrated that the generated hydrotalcite coatings exhibit similar protective properties

* Corresponding author.

E-mail address: p.visser-1@tudelft.nl (P. Visser).

Table 1
Composition of lithium doped model coatings.

	Supplier	Lithium carbonate	Lithium oxalate
Component A			
N-Butylacetate	Sigma Aldrich	75.0 g	75.0 g
Desmophen 650MPA	Bayer Materials science	47.7 g	47.7 g
Lithium carbonate	Sigma Aldrich	23.6 g	
Lithium oxalate	Sigma Aldrich		32.0 g
Magnesium oxide	Sigma Aldrich	16.4 g	16.4 g
Tioxide TR 92	Huntsman	5.9 g	5.9 g
Blanc Fixe N (Ba(SO ₄))	Sachtleben	15.4 g	15.4 g
Component B			
Tolonate HDB 75 MX	Vencorex	28.5 g	28.5 g
Dynasilan Glymo	Evonik	5.2 g	5.2 g

as traditional conversion coatings. Rangel et al. used cyclic voltammetry and electrochemical impedance spectroscopy to study the protective properties of these lithium-based conversion coatings generated under these alkaline conditions [29]. From this work it was suggested that the formed layer comprised a dual structure; a porous layer and pore filler. In addition, cyclic voltammetry experiments suggested the initial formation of an aluminium hydroxide layer before the lithium incorporation [22].

Building on this conversion coating work, lithium salts were proposed as leaching inhibitor for coatings to protect aluminium alloys [30]. Organic coatings loaded with lithium salts provided fast and effective corrosion protection in an artificial damage when exposed to neutral salt spray conditions (ASTM B-117) [31]. It was found that lithium ions were able to leach from the organic coating and generate a layer with corrosion protective properties in the scribed area. This layer comprised barrier, porous and columnar morphologies and consisted mainly of aluminium, oxygen, and lithium. A multi-step mechanism has been proposed for the formation of such a layer involving a competitive growth and dissolution process at the aluminium alloy surface [31]. This previous work described the first observations and characterization of these protective layers generated from a coating loaded with lithium salts as leaching inhibitor.

The objective of this work is to study the formation of these protective layers in a coating defect on AA2024-T3 in more detail and obtain a deeper understanding of the lithium-ion leaching kinetics, the conditions in the defect area and the lateral and in-thickness formation process of the protective layer. Therefore, polyurethane model coatings were loaded with lithium-salts as leaching inhibitor. Leaching of lithium-ions from the coatings was measured with atomic absorption spectroscopy (AAS). The coated AA2024-T3 substrates were scribed. The Scanning Ion-selective Electrode Technique (SIET) was used to measure the pH in the scribed area when the defect is exposed to a corrosive environment. The samples were exposed to neutral salt spray (NSS) conditions and the formation and development of the layer was analyzed with field emission scanning electron microscopy (FESEM) and surface analytical techniques. Auger spectroscopy depth profiling (AES) and X-ray photoelectron spectroscopy (XPS) were used to study the thickness and chemical composition of the protective layer as a function of formation time. Based on this information, the formation mechanism of the protective layer has been elucidated in further detail.

2. Experimental

2.1. Materials and sample preparation

Organic model coatings (Table 1) based on polyurethane binder chemistry containing well defined quantities of lithium carbonate and oxalate have been prepared as previously described [31].

The coatings were applied on Tartaric–Sulfuric Acid (TSA) anodized AA2024-T3 unclad sheets of 0.8 mm thickness. The AA2024-T3 substrate was purchased from Alcoa (2024-T3QQ-A250/5) and the TSA pretreatment (thickness anodic film: 3–3.5 μm) was performed according to aerospace requirements (AIPI 02-01-003) at Premium AEROTEC, Bremen Germany. The coatings were applied with a HVLP spray gun and cured at 80° C for 16 h, after 1-h flash-off at 23° C. The measured dry film thickness of the coatings was typically about 20–25 μm. A mechanical milling device was used to artificially damage the coating with a U-shaped scribe, before exposing the samples to a neutral salt spray (NSS) test (ASTM- B117). The panels (7 cm x 7 cm) were scribed from corner to corner, leaving a 1 mm wide scribe that penetrated 100–150 μm deep into the metal. The samples were covered with tape on the backside and exposed to the neutral salt spray (ASTM-B117) test for varying periods from 30 min up to 168 h. After exposure, the process was quenched by a 2-min rinse with flowing demineralized water to remove any residual chlorides and the panels were air-dried. Separate panels were used for each exposure period.

For XPS analysis and comparison purposes, reference samples with a pseudo-boehmite and lithium based conversion coating were prepared on AA2024-T3 bare aluminium alloy panels. Before the treatment, the aluminium panels were cleaned with acetone. The hydrated aluminium oxide (pseudo-boehmite) coating was prepared by treating the panel with deionized water at 95–100° C for 1 h according to the method of Gorman et. al [32]. The lithium based layered double hydroxide (Li-LDH) conversion coating was prepared using the conversion coating process as described by Buchheit et al., by immersing a AA2024-T3 panel in a 0.1 M lithium carbonate solution (pH = 11.3) for 15 min [27]. Following the treatments the panels were rinsed with demi water for 5 min and dried at the air.

2.2. Lithium ion leaching measurements (AAS)

The release of lithium from the coating matrix was measured by immersion of unscribed coated panels (3.5 cm x 5 cm) in 90 ml demineralized water and at each measurement interval the solution was replaced with fresh demineralized water. The lithium containing solutions were acidified with 10 ml 20% nitric acid and lithium concentrations were measured with a Varian AA 640 atomic absorption spectrophotometer. A calibration curve from 0 to 5 μg/L was prepared from a 1000 μg/L lithium nitrate standard solution for Merck. The concentrations of released lithium ions in μg/cm² were normalized to a film thickness of 25 μm and accumulated. The leaching curves were performed in triplicate.

2.3. Scribe condition measurements (SIET)

The pH within the scribed area was measured using the Scanning Ion-selective Electrode Technique (SIET). The measurements

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