

UNRAVELLING THE CORROSION PROTECTION MECHANISM OF SILYL ESTER BY COMBINED ELECTROCHEMISTRY AND X-RAY COMPUTED TOMOGRAPHY

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ABSTRACT

Recently, encapsulated silyl esters have been shown to act as efficient healing agents for self-healing anticorrosive coatings. While the positive protective effects were irrefutable, the actual protection mechanism has not been clarified yet. In this study, x-ray computed μ -tomography and electrochemical impedance spectroscopy have been employed to unravel the protection mechanisms for a coated AA7050 aluminium alloy.

The results show that the employed silyl ester protects the damaged coating-metal system by delaying the delamination initiation and growth kinetics while at the same time decreasing the underfilm pit area growth. The study also shows the potential of x-ray computed μ -tomography to follow the delamination front line and underfilm pits in coated metallic samples. The combination with EIS led to a major understanding of both EIS plots and the protection mechanisms offered by the silyl ester used.

1. INTRODUCTION

In the search of ideal self-healing systems using the microencapsulation route for corrosion protection, efforts have been recently put into the design of healing agents that do not require reacting with a second agent present in the coating matrix (i.e. second capsule or catalyst) but rather with species available in the environment (e.g. O₂, H₂O) [1]. In this direction previous studies have proposed the use of oils [2], silanes [3, 4] and silyl esters [5, 6]. In particular, the silyl ester concept, independently of the first chemistry used and published, involves a multifunctional action concept based on wetting, adhesion, hydrophobicity, reaction with humidity and metal surface, and time-dependent densification. At the same time, the oil linked to the silane group protects the silane from early reaction in the capsule proposing thus a multi-action agent. The first results with an encapsulated silyl ester showed by means of general [5] and local electrochemical techniques [6] long time corrosion protection of coated AA2024-T3 under immersion in mild NaCl solutions. In these previous studies, it was suggested that the main corrosion protection mechanism was due to the partial restoration of the barrier protection at a hand-made scratch.

In this study we combined two non-destructive techniques (x-ray computed micro-tomography and electrochemical impedance spectroscopy) to try to unravel the corrosion protection mechanism of silyl esters for high strength aluminium alloys. X-ray tomography was capable of quantifying underfilm corrosion processes (i.e. pit and delamination growth) supporting the impedance results.

2. MATERIALS

Hollow square tubes with rounded corners were machined from a hot rolled AA7050-T74. The tubes were 30mm long with an outer surface of 5×5mm² at cross section and 6mm diameter rounded corners. The inner diameter of the tube was 4mm. The tubes were abraded with Scotch Brite-3M “Clean N Finish grade A-VFN” followed by alkaline pretreatment in 2M NaOH for 10 seconds, rinsing with water and drying with pressurized air. The tubes were then dip-coated in an epoxy-amine bath to form a homogeneous coating, and allowed to cure at room temperature for one day followed by a 2h post-curing at 80°C. The dry thickness of the coatings was 100±10µm. After curing, a controlled 10mm long scratch was performed on one of the flat outer surfaces of each sample (Figure 1 schematically shows the longitudinal view and cross-section of the tubes).

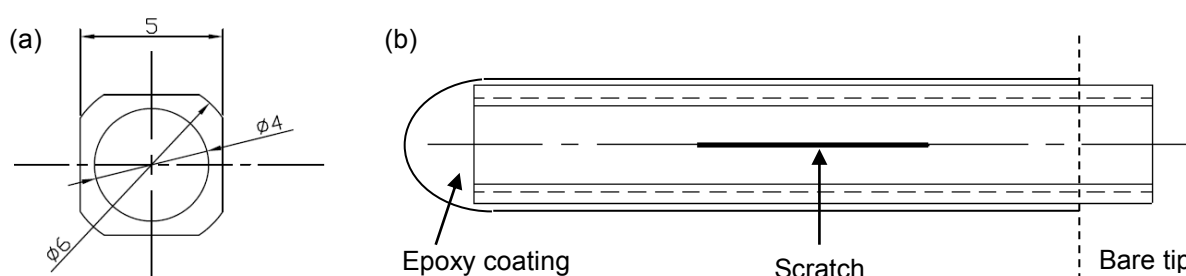


Figure 1: Cross-section of the square tube with round corners (a); longitudinal view of the coated and scratched tubes (b). Units in mm.

Prior to the start of the immersion tests, the scratch on one of the two samples was manually covered with liquid octyldimethylsilyloleate (silyl ester) synthesized as presented in [5]. The two samples (protected with silyl ester, and non-protected one) were then exposed overnight to ambient conditions before immersion and evaluation procedure started.

3. METHODS

The tube samples were exposed to a cycle of X-ray μ -tomography imaging + immersion in 0.05M NaCl distilled water solution + evaluation by electrochemical impedance spectroscopy. The procedure was repeated for 19 days combining thus two non-destructive techniques. For the micro tomography tests a Phoenix Nanotom S micro-CT scanner was employed using an X-ray radiation of 75kV and 90µÅ. Image reconstruction was performed using the Phoenix reconstruction software package. The electrochemical impedance spectroscopy tests (EIS) were performed using a potentiostat-galvanostat Autolab-PGSTAT302N with frequency response analyzer and traditional three electrode set-up was employed using Ag/AgCl, KCl (saturated) as the reference electrode, platinum gauze as the counter electrode and the coated squared tubes as the working electrodes.

4. RESULTS

Image analysis to obtain delamination area, surface pit area, and pits volume was completed using Volume Graphics Studio MAX 2.0. Two layers were taken for the analysis depending on the quantification of the delamination or the pit area formation. The layer for delamination analysis was placed (in the computing software) 25µm above the estimated metal surface, while for the pit analysis the layer was placed 25µm below the same metal surface. The position of these layers was selected based on the limit of detection of the device and image optimization. This approach disregards very superficial pits at initiation stage as well as pits that go into the material less than 25µm, although it detects the general trend of corrosion (delamination and pits) of the metallic surface.

In Figure 2 it can be seen that there is a change in corrosion behaviour when adding the silyl ester to one of the scratched samples. The fitting of the delamination curves shows linear trends in both samples although with different slopes (delamination growth kinetics). It is clear from Figure 2 that the addition of silyl ester delays the delamination initiation time (from one day after immersion to 12 days) as well as restrains the delamination growth (three times slower growth kinetics when using silyl ester; from 0.92 to 0.34 mm²/day). This result suggests that one of the most relevant mechanisms of protection offered by the silyl ester is by prevention and delay of delamination. Moreover the results also confirmed (not shown here) that the silyl ester delayed pit formation and underfilm pit growth kinetics significantly. The results were confirmed by the EIS tests.

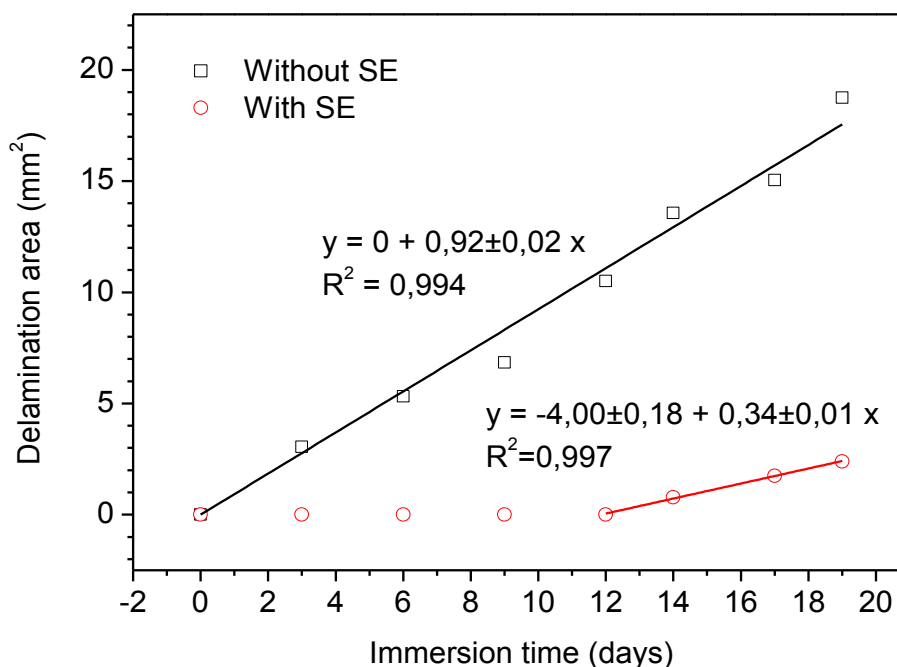


Figure 2: Evolution of delamination area with immersion time for non-protected (black-square) and protected with silyl ester (red circle). Plot includes regression.

5. CONCLUSIONS

This work highlights the potential of using combined tomography and electrochemical tools to gain major understanding of underfilm corrosion processes (pitting and delamination) and their inhibition. It is foreseen that the approach here employed will be of importance for the field of self-healing anticorrosive coatings and paints as more quantified information can be obtained from the approach here presented. Moreover, the combination of tomography and EIS allows also a direct link between the trend changes in EIS and corrosion phenomena such as pitting and delamination. The results confirmed that the silyl ester reduced delamination initiation and growth kinetics while decreasing underfilm pit area growth. Pit area growth followed different kinetics for the protected with silyl ester and the non-protected sample. These results confirm the potential use of silyl esters and related chemistries to reduce general degradation by a combined effect of barrier and coating-metal interface restoration.

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