In-situ Measurement of Corrosion Kinetics of Aluminium Alloy 6063 under Chloride Bearing Droplet Deposits

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Summary

The goal of this paper is to advance our understanding of the corrosion of aluminium in marine enviroments where it is exposed to seawater and a combination of steel corrosion products. Pit nucleation, corrosion product development, and corrosion rate measurements were obtained using in-situ measurements and analyses carried out by X-ray computed tomography. Atmospheric corrosion tests under chloride bearing droplet deposits at 33% and 93% relative humidity were carried out. The use of x-ray tomography allows the evaluation of the pits and corrosion products in a non destructive manner. The surface was analysed post mortom using laser confocal microscopy. The formation of corrosion products resulting in the possible protection of aluminium from further corrosion was probed by exposing the samples to FeCl₃ and seawater. The effect of seawater and sea-water contaminated with FeCl₃ on the rate of corrosion product formation and its effect on the structural integrity of AA6063 is discussed.

Keywords: 6063 aluminium, X-ray tomography, CT, Corrosion.
**Introduction**

The versatility of corrosion resistant AA6063 is exploited by a range of industries from employment in window frames, to heat exchangers in air-conditioning units, to structural components. Its broad application as a building material results in exposure to a variety of environments. In particular, marine environments have high levels of salt and humidity in the air. Exposure of AA6063 to sea-salt containing droplet deposits can result in local corrosion damage in the form of large pits, with corrosion products often obscuring the depth and severity of attack[1].

The corrosion behaviour of AA6063 with exposure to sea-water and FeCl$_3$/sea-water containing deposits has been investigated using laser surface confocal microscopy and x-ray computed tomography (X-ray CT) analyses. The effect of FeCl$_3$ on corrosion product formation has been explored, with 3D corrosion kinetics obtained using a quasi in-situ X-ray CT approach.

**Experimental**

Extruded Aluminium alloy 6063-T5 with a chemical composition of wt %, 0.56% Si, 0.03% Mn, 0.20% Fe, 0.02% Ti, 0.02% Zn, 0.53 % Mg and 98.64% Al was used in this study. 20mm x 20mm x 0.5mm coupons of extruded aluminium alloy 6063-T5 were cut out of a heatsink. The sample surface was prepared by grinding to 4000 grit, followed by a diamond polish to a 1µm finish. After which the samples were electro polished in a perchloric/ethanol bath.

The material has a hardness value of 92 HV 1. The microstructure was characterised using a FEI quanta 650 SEM. The surface roughness and pit depths and characteristics were analysed using laser confocal microscopy. In-situ experiments were carried out in a XTH Nikon 320Kv scanner at a resolution of 5.9 µm x 5.9 µm x 5.9 µm.

The samples were exposed to a 35ul droplet of 4M FeCl$_3$ in seawater and then stored relative humidities of 33 % and 93% relative humidity. The humidity was controlled using saturated salt solutions (MgCl$_2$ used to give maintain a humidity of 33%, and KMnO$_4$ for a humidity of 93%)[2] where the exposed coupons were placed in airtight containers. The humidity was monitored inside the containers using a humidity logger. After having been exposed for 7 days, the aluminium coupons were scanned using the x-ray tomography scanner. The x-ray
beam was filtered using a 0.05mm copper filter and the x-ray energy applied at 140kv. After scanning, the sample was exposed to a second 35ul droplet of FeCl₃.

Figure 1: In-situ experiment procedure for corrosion testing

Pit volumes measured were compared with pit volume data from the Keyence laser confocal microscope on a cleaned sample after the final exposure. The Keyence laser confocal microscope uses a combinataion of white light and a laser light source to generate high resolution coloured images with high resolution topographical profiles. This analytical method is non destructive. The sample itself is placed directly below the lens and the area scanned allowing a detailed height map to be created.
Results

Figure 2: (a) Photo of corrosion site on aluminium surface (b) 3D view of Corrosion Product Formation on the aluminium surface after exposure to FeCl₃ (c) 3D view of pits below the aluminium surface, viewed after cleaning sample

The amount of corrosion products on the aluminium surface in Figure 2 were formed from the reaction of two 35 µl droplets. We can observe how the corrosion products build up to 2.67mm in height. The area affected has a diameter of 10mm.

The vast majority of pits in Figure 2 have depths less than 100µm with some very large pits having depths of up to 300 µm. The numbers of pits formed from this corrosion activity is visibly large, however the surface area affected is much greater than the depth therefore one can assume that there is more lateral corrosion than vertically. The pit size and depth distribution follows what has been observed in previous preliminary investigations. The corrosion rate and any changes to it which may be caused by the corrosion product deposits are under investigation.

Figure 3: (a) Corrosion after exposure to 35 µl of 4M FeCl₃ solution 1) Corrosion products 2) Bright regions representing iron 3) Aluminium coupon  (b) One hour after exposure to an additional 35 µl of 4M FeCl₃ solution

The brighter regions in Figure 3 represent heavier elements, in this instance the brightest areas are areas containing iron deposits. The oxidation state of these iron deposits is yet to be determined. We also observe how the central region in Figure 3 (a) with an iron cover has
broken down in (b). Additionally, the bright regions next to the surface are iron deposits on the aluminium surface. In Figure 3 going from a to b we can observe that the voids in the corrosion products are filled with more corrosion products. The effects of the humidity and temperature on a droplet have been reported in the literature by several groups[3][4].

![Image](image.png)

*Figure 4: X-ray CT image, the aluminium surface is a light grey, with the deposition of iron shown in blue, and areas where there is a mixture of aluminium and iron on surface in red and purple*

The observations being that at a lower humidity the droplets are more concentrated and can result in significantly higher rates of corrosion in comparison to higher humidities, however the concept of critical moisture is at play in that a minimum level of moisture is required for corrosion to occur [5]. Figure 4 details the compositional and corrosion product distribution. The outermost regions are surrounded by rings of aluminium based corrosion products and then iron deposits. On the central area which consisted of the droplet centre the iron deposits are seen to form on the top of the corrosion products and on the aluminium surface.

The use of tomography to carry out quasi in-situ experiments allows non destructive analysis of the complete corrosion process whilst also providing an understanding of the different compositional distributions that occur during corrosion. The reported work is part of a larger
effort to gain a complete understanding of corrosion on aluminium 6063-T5 and the factors that affect it.
References:


