

## Mechanisms of Li Leaching from a LiCO<sub>3</sub> Based Primer / Topcoat Paint System

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The search for alternatives to chromate-based inhibitors for corrosion protection of defects in paint coatings in the aerospace industry is still an active area of research. Studying a Li<sub>2</sub>CO<sub>3</sub>-containing primer *without* topcoat paint system, Marcoen and Co-Workers have shown that Li-based inhibitors provide good protection to aluminium alloys [1] although the Li release into solution is complex [2]. A model for this was developed based on leaching through particle clusters. These clusters were connected by a network of channels created when ingress of electrolyte caused particles to either completely or partially dissolve and subsequent swelling resulted in mechanical rupture of the binder. As immersion time increases, so too do the voids and channels for leaching. Initially, this is confined to Li<sub>2</sub>CO<sub>3</sub> particles and clusters, but after longer times, can develop around other types of inorganic particles in the primer too.

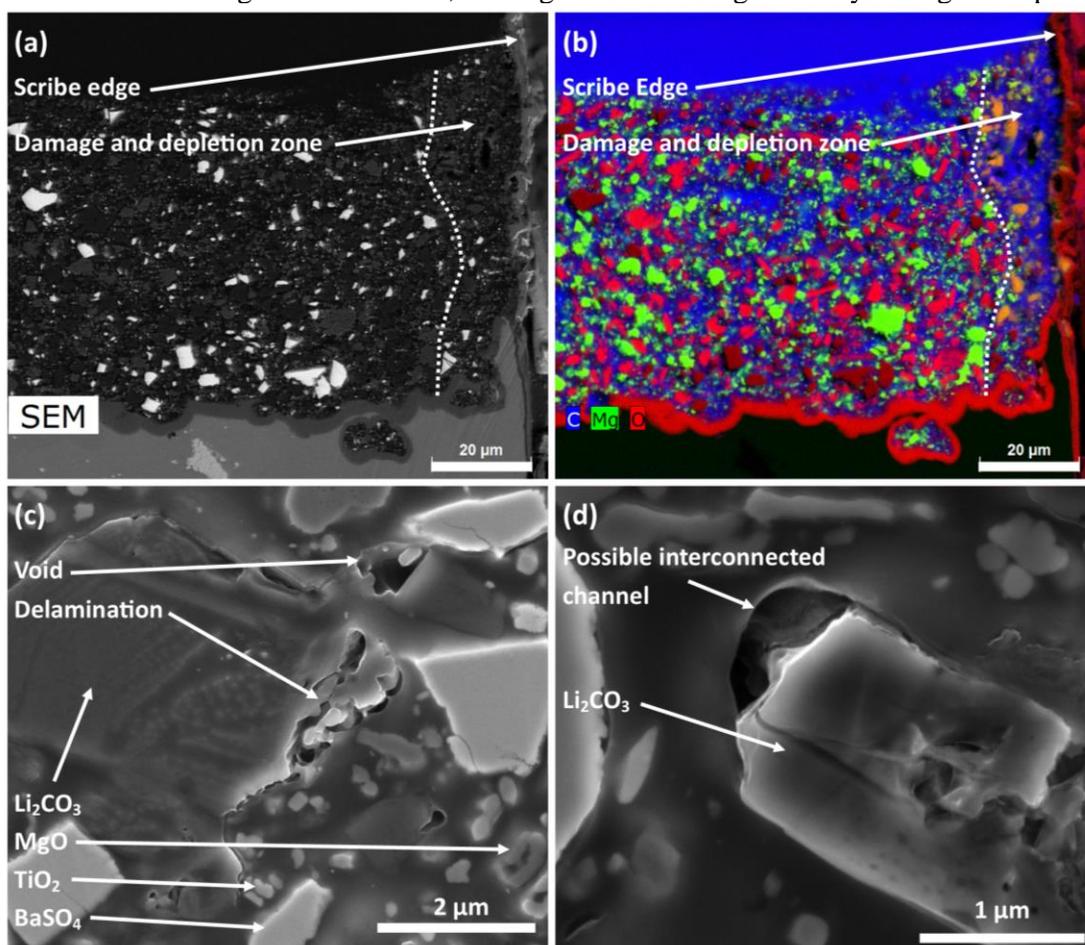
While some previous leaching studies of Li<sub>2</sub>CO<sub>3</sub> based coating systems looked at primer *without* topcoat [1], this study looks at a primer *with* topcoat system. We examine leaching of inhibitor into a scribed region, machined into the coating (designed to simulate a scratch or other defect in a real world painted aluminium alloy). The presence of the topcoat implies that, initially at least, leaching can only occur for clusters that form a network connected to the scribed edge. We characterise inhibitor depletion at this edge, tracking the changes that occur during the leaching process. This is an area that has not been widely investigated by other research groups for Li<sub>2</sub>CO<sub>3</sub> primer systems [3].

To this end, samples of coated Al-alloy 2024-T3 were prepared according to the procedure outlined in [4]. The primer contained particles of Li<sub>2</sub>CO<sub>3</sub> as inhibitor, MgO and BaSO<sub>4</sub> as fillers and TiO<sub>2</sub> as pigment. Scribes measuring 1mm wide and 100 μm deep were machined into the panels. This depth ensured that the scribe extended through the paint into the substrate below. The panels were exposed to neutral salt spray solution (NSS) for times ranging from 0 to 500 hrs. Samples were analysed using scanning electron microscopy and energy dispersive x-ray analysis (SEM/EDS); and particle induced x-ray and gamma-ray analysis (PIXE/PIGE) to characterise the Li depletion. Cross-sectional samples, through the paint layer at the scribe edge were prepared using traditional mechanical sample preparation techniques as well as Ar-ion beam slope cutting in a Technoorg-Linda SC2000 ion beam slope cutter/polisher. Details of instrumental setups used for sample preparation and analysis are given elsewhere [4].

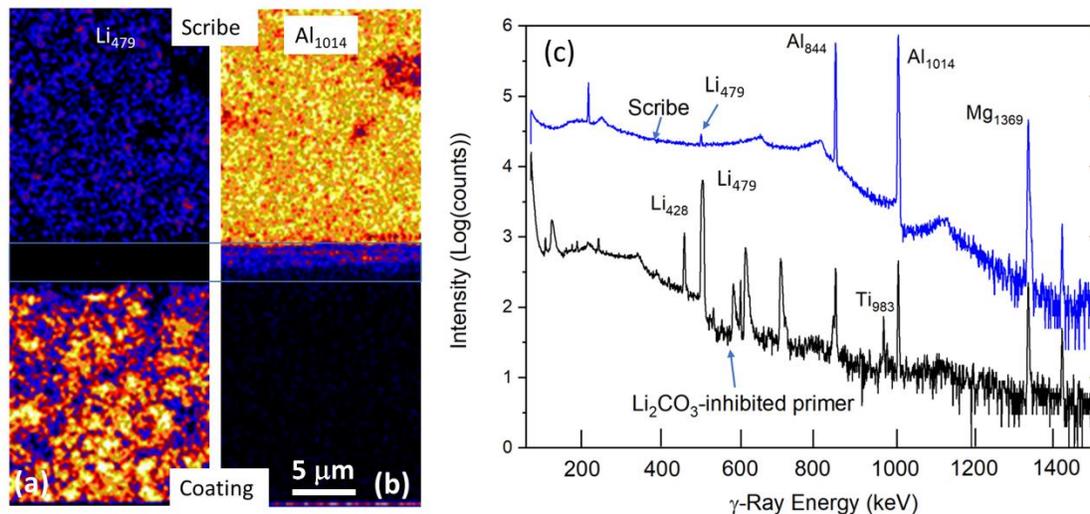
Figure 1(a) and (b) show a backscattered electron image and an EDS map of the sample exposed to NSS for 48 hrs. The bright particles in 1(a) are BaSO<sub>4</sub>, the medium grey particles are MgO and the darkest particles are Li<sub>2</sub>CO<sub>3</sub>. Figure 1 (b) shows the same three particles in dark red, green and bright red, respectively. These two images also show evidence of a depletion zone next to the scribe as well as mechanical damage resulting from the scribe. The depletion zone is indicated by the absence of the bright red Li<sub>2</sub>CO<sub>3</sub> particles near scribe edge. For longer NSS exposure times (>96 h) this depletion zone did not develop any deeper than the scribe damaged region suggesting that the mechanical damage due to scribing exacerbated or facilitated leaching of the inhibitor particles into the scribe. Figures 1(c) and (d) shows the same sample (48 Hr NSS) at higher

magnification. The primer constituents are identified in 1(c). At short NSS times small voids were formed within  $\text{Li}_2\text{CO}_3$  particles well away from the scribe (100 to 260  $\mu\text{m}$ ). At longer NSS times a mixture of voids and detachment from the binder were observed in and around  $\text{Li}_2\text{CO}_3$  particle. The detachment was assumed to be part of a channel network within clusters of particles. This channel network is believed to facilitate leaching of the inhibitor into the scribe (defect in a real-world sample).

Figure 2(a), (b) and (c) shows PIGE analysis of the boundary between the coating and the scribe. The 3MeV protons penetrate to a depth of between 10 and 20  $\mu\text{m}$ , allowing them to pass through the topcoat and reach the primer. Figure 2(a) shows the lithium  $\gamma$ -ray map and 2(b) shows the aluminium map. The top half of each map shows the scribe area and the bottom half shows the coating. Sum spectra for the top (scribe) and bottom (coating) half of the mapped area are shown in 2(c) in blue and black, respectively. The blue pixels in the scribe area of the Li map confirm that Li has leached out of the primer into the scribe after 48 Hrs NSS. The Li peak is labelled in the blue spectrum. From the species measured during the leaching experiments, Li was found to have the highest release rate, although this varied significantly during the experiment.



**Figure 1.** SEM/EDS results for 48 hrs exposure to NSS. (a) Low magnification BSE image of primer at the scribe edge. The dotted line shows the depletion zone which has been exacerbated or facilitated by the mechanical damage in this region. (b) EDS Map showing  $\text{Li}_2\text{CO}_3$  as red,  $\text{MgO}$  as green,  $\text{BaSO}_4$  as dark red. The absence of bright red particles in the depletion zone is apparent. (c) SE image showing the inorganic particles in the primer as well as an example of voids formed next to a  $\text{Li}_2\text{CO}_3$  particle and delamination between  $\text{Li}_2\text{CO}_3$  particle and the binder. (d) Large void next to a  $\text{Li}_2\text{CO}_3$  particle, possibly forming an interconnected channel.



**Figure 2.** PIGE results showing the presence of Li in the scribe after 500 h exposure to NSS. (a) Li map from the 479 KeV peak. The blue pixels in the “scribe” section of the map indicates that Li was detected in this region of the sample. (b) Al map from the 1014 keV peak and (c) respective spectra from the primer (under the topcoat) and the scribe. The band between the two pale dashed lines in the centre of the maps indicates where there is an edge effect at the scribe. This is due to charge build-up in the coating.

#### References

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- [3] Laird, J.S., et al., *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 2017. **404**: p. 167-172.
- [4] Visser, P., et al., *Li Leaching from Li carbonate-primer: Transport pathway development from the scribe edge of a primer/topcoat system*. Submitted to *Corrosion Science*, 2021.