

Corrosion of Aluminium in Chloride Environments

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Abstract

In order to obtain further insights into the mode of protection afforded by conversion coatings on aluminium substrates, Scanning and Transmission Electron microscopy techniques and potential measurements was employed to monitor variously treated aluminium specimens in chloride environments. Examinations revealed that conversion coated aluminium with top lacquer coatings and subsequently subjected to Chloride environments prevented pitting of the substrate. However, pits were observed on 'bare' aluminium and those with top lacquer coatings after being exposed to similar environments. The 'bare' chromate coated specimen revealed pits plugged by corrosion products suspected to be hydrated Cr III oxide and/or hydroxide formed through the reduction of Cr VI species present in the coating. Such a capability was not observed for the 'bare' chromate-phosphate specimen.

Key words: SEM, TEM, EDX, Chromate, Pitting corrosion, Aluminium.

1. INTRODUCTION

As a result of environmental and health considerations, considerable efforts are focussed on formulating conversion coating chemicals devoid of chromates[1-7], however, the restrictions to their use is mostly in the packaging industries. In other applications chromate formulations in one form or the other, such as either dry in place or non-rinse pre-treatment operations are still in use. Currently, while chromate replacement has occurred in some applications, matching the characteristics and high performance of chromate coatings using non-chromate in some other applications such as in the aerospace industry has not been successful for the most part. Thus further advances in chromium –free coating processing and performance are desirable [8-10]. Aluminium and its alloys are susceptible to pitting and stress corrosion cracking when exposed to chloride and other environments. Studies [11] have shown that pitting corrosion of aluminium usually commence from the flaws inherent in the oxide skin which it normally presents to the atmosphere. Such flaws may arise from

imperfection in the oxide layer or as a result of second phase material in the substrate. In either case, such flaws represent vulnerable areas where the substrate may be transiently exposed to chloride attack and such pits may be the sites where stress corrosion cracking commences [12]. The precise mechanism of the inhibition of pitting corrosion by Cr^{6+} is not very clear [13-17]. However, it is believed that Cr^{6+} present [18-23] in chromate conversion coatings can be released [22, 24-25] to repair defects and damaged regions of the coating. Also, since $\text{Cr}(\text{OH})_3$ and /or hydrated Cr_2O_3 , the main coating materials in the chromate conversion coating offers good barrier on aluminium and other light alloys[26], the introduction of Cr^{6+} leached from the coating to corroding sites provides for a very good corrosion resistant coating.

Thus, in order to formulate environment friendly non-chromium pre-treatment chemicals for aluminium and its alloys, there is a need to understand fully the mode of protection afforded by chromate conversion coatings on aluminium especially in chloride environments. In view of this, the present investigation seeks to further study the effect of chlorides on the morphology of chromate coatings using electron-optical techniques. Thus, formulators of non-chromium coatings will benefit from a better understanding of the mode(s) of protection afforded on substrates by chromium species.

2. MATERIAL AND METHODS

Aluminium with nominal impurities of 0.004wt% Fe, 0.002wt%Cu and 0.003 wt % Si was made into spade-like electrodes. The electrodes were electropolished in perchloric acid/ethanol mixture, rinsed in water and dried over a stream of air. Some of the electrodes were treated for 2 minutes in chromate solution containing 3.5g/l of $\text{Na}_2\text{Cr}_2\text{O}_7$, 4g/l of CrO_3 and 1g/l NaF. Another set of electrodes was treated for 3 minutes in chromate-phosphate solution made up of 100g/l H_3PO_4 , 4g/l CrO_3 and 1g/l NaF. All chemicals employed are of analytical grade from BDH Chemicals, UK.

A set of pre-treated specimens which included electropolished aluminium was coated with a vinyl aerosol clear lacquer in 20 ml beaker by dipping as near vertical as possible for 90 seconds. A calibrated Permascope (ECS, Fischer's Instrument) was used to determine the thickness of the dried lacquer to be $6 \pm 2\mu\text{m}$. Individual specimen was immersed in 150 ml of stagnant, near neutral 1M KCl solution for times ranging for 24 Hrs to 30 days. From the start of immersion, the potential of each specimen was measured relative to saturated Calomel electrode and monitored by means of a high impedance voltmeter and a potentiometric chart recorder. A set of similarly treated specimens was exposed at right angle to the base of a salt spray cabinet set at 18°C for 255Hrs. At the end of each exposure, the specimens were rinsed with running distilled water, dried and examined in ISI DS 130 scanning electron microscope(SEM) and analysed using the EDX attachment in the SEM. Selected specimens were ultramicrotomed by the method adopted by Oki [27] and examined in a Philips EM301 transmission electron microscope (TEM). Also, the EDX attachment in the microscope using nominal electron probe size of 10nm was employed to analyse different areas of the ultramicrotomed sections with the aluminium substrate attached.

3. RESULTS AND DISCUSSION

3.1 General Observation

Visual examination of the lacquer coated specimens showed that various blisters developed on the electropolished specimen after 30 days of exposure in 1M KCl solution. However over short immersion periods, the color of the lacquer appeared white, due to the absorption of

water and chloride into the matrix of the lacquer. This may as well be due to the color of corrosion products, hydrated aluminium oxide and/or hydroxides on the substrate. To the naked eye, the conversion coated specimens with a top coating of lacquer appeared similar after exposure to the chloride solution for 30 days having a lacquer with a white tint as a result of saline water uptake by the lacquer. The substrate was apparently protected after the exposure period. For the specimens without a top coating of lacquer exposed to 1M KCl for 30 days, the electropolished specimen was pitted and had a grey appearance. Similar appearance was observed for the specimen exposed for 255 hours in the salt spray cabinet which revealed a pitted surface with pit sizes greater than 1/10 mm. The golden color of the chromate coated specimen faded to a lighter shade after exposure to the chloride solution and salt spray cabinet. This showed that the Cr VI species in the coating was gradually removed into the environment and some are likely to have been reduced to hydrated Cr III oxide and/or hydroxide at corroding sites to stifle corrosion reactions. On the other hand, the chromate phosphate specimen retained its reflective greenish purple coloration after exposure to both 1M KCl solution and salt spray cabinet. However, some local whitish corrosion products were observed on the specimens but generally the coating appeared to have protected the aluminium substrate.

105

106 **3.2 Potential – Time Response in 1M KCl Solution**

107 The initial responses for the various specimens appeared similar. A potential surge in both
108 negative and positive directions was observed but the amplitude of surges was higher for the
109 lacquer coated specimens than for those without a top coating of lacquer. For the
110 electropolished specimens, the initial potential recorded was -0.85V (w.r.t. S.C.E), thereafter
111 surges in potential hovered between -0.78 and -0.8 V, giving an amplitude of about 0.02V.
112 Beyond the initial surges, the potential gradually shifted to a more negative value of about -
113 0.9V which was sustained over the time of exposure. The initial surges in potential are
114 related to the crack/heal events occurring at the bases of flaws in the electropolishing film
115 where transiently revealed bare aluminium is exposed to the chloride environment [11, 28].
116 The sustained shift in potential to more negative values is partly associated with increases in
117 sizes of flaws/pits and also as a result of flaws developing into pits. In addition, on the basis
118 of the generally accepted Evans theory [29], the cathodic and anodic reactions polarise
119 towards each other to give the free corrosion potentials measured in this study. Thus the
120 sustained shifts in potentials towards negative values further indicate that the overall
121 reaction is cathodically controlled. The revelation of anodic sites cause negative surge in
122 potential and as cathodic reaction establishes itself positive potential surge will occur.
123 However as the anodic area increases, the overall potential will decrease during which cycle
124 cathodic reaction products, which in this case, are likely to be hydroxyl ions, will increase the
125 pH at the electrode/electrolyte interphase and rendering further cathodic reduction of
126 dissolved oxygen sluggish. The initial relatively frequent, fluctuating potential recorded for
127 the lacquer coated electropolished aluminium in near-neutral KCl solution was between -
128 0.75 and -0.85V with amplitude of about 0.1V. The value of the potential also moved with
129 time to more negative values as further areas of the substrate was exposed to the chloride
130 environment with saline water intake of the lacquer; other flawed regions will become active.
131 The potential responses for the conversion coated followed the same pattern of surges, Fig.
132 1, however, for the chromate and lacquer coated chromate - phosphate specimens the surge
133 in potential was recorded till the end of exposure on the 30th day.

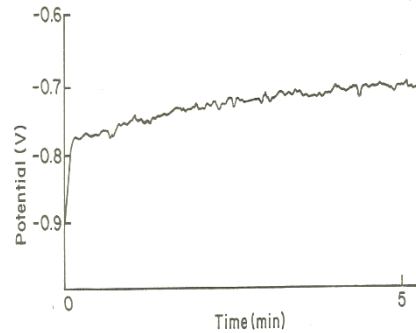


Fig.1 Potential time curve for chromate coated specimen in 1M KCl solution.

On the other hand the potential surge of the bare chromate- phosphate specimen ended on the 15th to 16th day when it stabilised at about -0.9V (w.r.t. S.C.E). As discussed earlier, the surges are related to crack and heal events occurring at the bases of flaws/pits. In addition, the chromate species leached into the environment played roles, where they are reduced to Cr III compounds to stifle corrosion reactions at the bases of flaws/pits hence the prolonged continuous surges recorded. In order to confirm the role of leachable Cr VI species, the potential of an electropolished aluminium specimen, Fig. 2, was monitored in 1M KCl solution containing Cr VI species. It is obvious that the surges in potential are similar which corroborates the idea of leachable chromates playing critical roles in passivating the aluminium substrate at vulnerable sites.

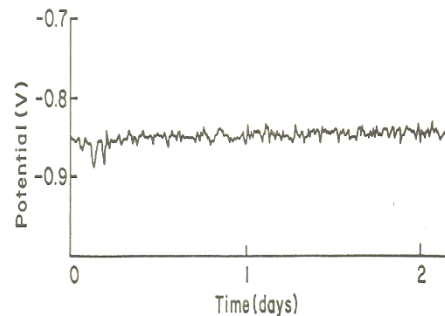


Fig.2. Potential time curve for aluminium specimen in 1M KCl solution with Cr⁶⁺ species

3.3 Scanning and Transmission Electron Microscopy Examination

After 24 hours of immersion in 1M KCl solution, SEM examination revealed incipient pits on 'bare' aluminium specimen whereas microscopy examination of the other specimens did not reveal any notable feature different from the initial features they carried at inception of the experiments. On the 30th day, the bare aluminium had been severely pitted and displayed in Fig. 3 is a typical pit revealed through electron microscopy examination. The pit is about 100 μm wide with other smaller pits at its perimeter suggesting that the bigger pit is a coalescent of smaller pits. As noted by Pereira et al [30], the pit is hemispherical suggesting that its growth after initiation was lateral rather than vertical. Other pits revealed on other specimens followed this pattern of geometric transition which may be associated with increased immersion time.

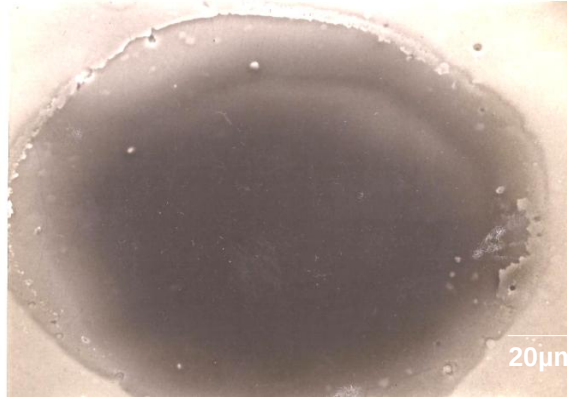


Fig. 3 SEM micrograph displaying a pit on lacquer coated aluminium specimen immersed in chloride solution for 10days.

The micrograph in Fig 4 displays the surface morphology of aluminium specimen exposed to salt spray cabinet for 255 hours. The micrograph depicts pitted portion of the specimen with a pit of about 1µm in diameter undermining the film in the adjacent regions of the metal surface.

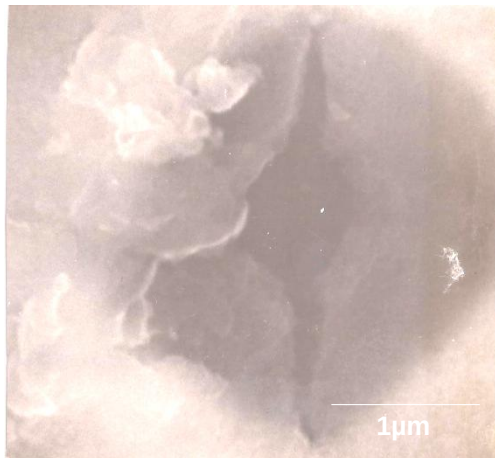


Fig. 4 SEM micrograph of Aluminium specimen exposed in Salt spray cabinet for 255 hours.

However, displayed in Fig. 5 is the micrograph of the chromate specimen immersed in KCl solution after 24 hours, where examination revealed disaggregated coating materials within a generally cracked surface appearance on a chromate conversion coated aluminium substrate.

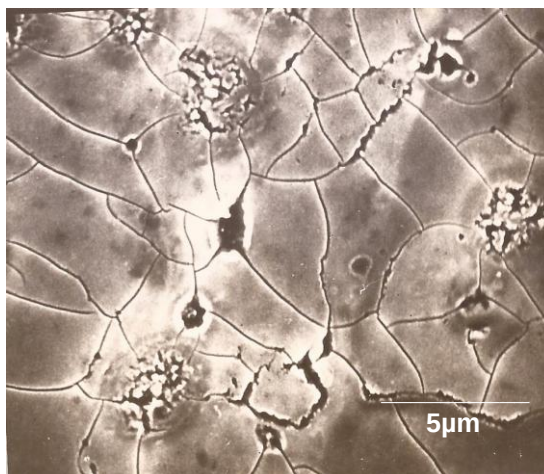


Fig. 5 SEM micrograph of chromate coating immersed in chloride solution for 24 hours.

Similar surface feature was observed after 8 days of immersion and on the specimen exposed in salt spray chamber for 255 hours. The local regions of disaggregated coating materials are related to flawed/cracked areas which penetrated to the metal surface where film free aluminium is exposed to the chloride environments. The repassivation of anodic dissolution of aluminium will occur due to the deposition of hydrated alumina aided by the reduction of Cr VI to Cr III hydrated oxides. The eventual stifling of the corrosion reactions in such regions of the specimen will be achieved by the deposition of mixed aluminium and Cr III hydrated oxides/ hydroxides.

The chromate phosphate specimen without a top coating of lacquer did not show this capability, however it retained its reflective greenish purple appearance after immersion in KCl solution for several days. This was observed on similar specimens exposed for 255 hours in a salt spray cabinet; although the specimens revealed local greyish corrosion products.

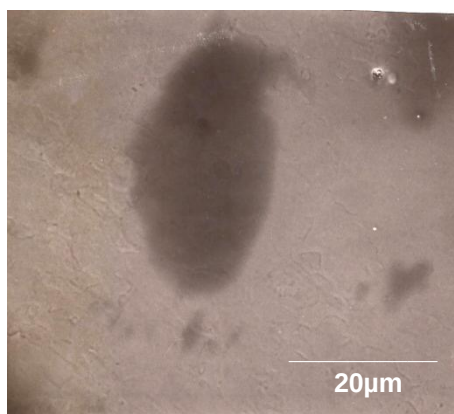
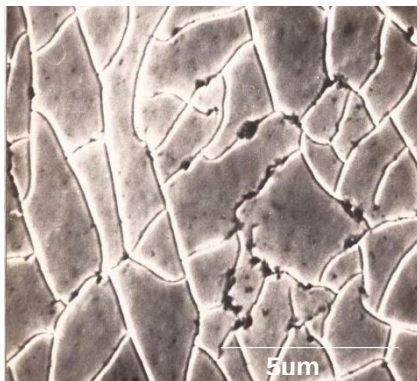


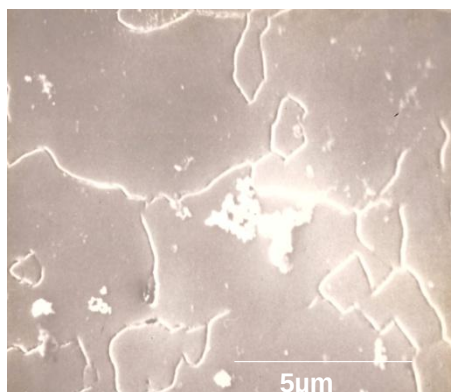
Fig. 6 SEM micrograph of chromate-phosphate coating showing undermined regions of the surface after 8 days of exposure in chloride solution.

The SEM micrograph in Fig.6 displays the surface features of a chromium phosphate specimen after exposure in 1M HCl solution for 8 days on which transparent adhesive tape was firmly applied before it was subsequently pulled against itself. The surface revealed variously shaped dark pit-like features which undermined the conversion coating. The diameter of the dark features ranged from 5.5 to 35 µm. This provides evidence of the inert

208 role played by the conversion coating during pitting of the substrate and a circumstantial
209 evidence for the presence of flaws in the conversion coating.
210



211 Fig. 7: SEM micrograph of lacquer coated chromate conversion coating on
212 aluminium substrate after immersion in KCl solution for 30 days.
213 The lacquer coated chromate and chromate-phosphate specimens appeared unaffected by
214 the chloride solution as shown in Figs.7 and 8 which display the SEM micrographs of the
215 surfaces after 30 days exposure in the chloride solution.
216
217



218 Fig.8: SEM micrograph of lacquer coated chromate-phosphate conversion
219 coating after immersion for 30 days in KCl solution.
220 The lacquer was removed in acetone prior to examination in the SEM. In general, mud
221 cracking morphology, characteristics of chromate conversion coatings [31] is evident
222 although dark cavity – like regions are associated with some of the cracked areas of the
223 chromate specimen. However, evidence for corrosion products is displayed as whitish
224 features at the middle of the micrograph in Fig. 8 and other similar features in the
225 micrograph.
226 In general the TEM micrograph of both chromate and chromate-phosphate specimens
227 without a top coating of lacquer, after exposure in KCl solution appeared similar which is
228 expected, as the ultramicrotomed sections will have passed through a small fraction of the
229 coatings. A typical section for the chromate phosphate coating is in Fig 9.
230



Fig.9: TEM micrograph of chromate-phosphate conversion coating without a top coating of lacquer after immersion in KCl solution for 30 days.

The usual features described by Oki et al [32] as micro and macro linear features which represent cracks sandwiched among open textured coating materials that run through the section from the coating/solution interface to the metal/coating interface are still evident. The aluminium substrate is at the bottom of the micrograph and the coating at the top which is about 130 nm in thickness with striations described as 'crows' feet by Furneaux et al [31]. However, from this study, although the conversion coatings are inert inorganic materials, thinning of the coatings occurred at the rate of about 2 nm/day. The thickness of the chromate-phosphate coating before immersion was about 190 nm as against 130 nm after exposure for 30 days. Similar value for the thinning rate was observed for the chromate coating after immersion for 30 days in KCl solution; although thickness measurements prior to immersion and after were approximately 180 nm and 120 nm respectively. The metal/coating and coating/solution interfaces appeared relatively smooth; this is in agreement with the observation in the SEM that corrosion occurred only at discrete flawed regions in the conversion coatings which may have been excluded during ultramicrotomy. In addition, analyses of the coatings with energy dispersive analysis of X-rays, using a nominal probe size of 10 nm, at various spots on the coating, from the metal/coating interface to the coating/solution interface, Chlorine was not detected within the limits of the resolution of the EDX for both chromate phosphate and chromate specimens.

CONCLUSIONS

Lacquer coated chromate and chromate-phosphate conversion coatings fully protected aluminium substrate for 30 days in chloride environments. However the coating without a top coating of lacquer protected the aluminium substrate to a large extent although undermining of the inert conversion coating by chloride ions occurred at flaws in the coating leading to development of disaggregated coating materials on the chromate coating. These coating materials are hydrated compounds of aluminium and chromium. Within the detection limit of the EDX attachment in the TEM, chlorine was not detected within the intact coating which provided further circumstantial evidence for the theory that chloride attacks leading to pit formation occurred only at flawed regions of the coating where bare substrate was exposed to the environment. The bare aluminium specimens were severely corroded in similar chloride environments.

ACKNOWLEDGMENT

The author acknowledges the Head, Corrosion and Protection Centre, The University of Manchester, UK, for the use of laboratory facilities and Dave Moore for his assistance on the Scanning Electron Microscope.

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365 **COMPETING INTEREST**

366 Author declares that no competing interests exist.

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368 **AUTHORS' CONTRIBUTIONS**

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370

371

372 The author performed the experiments, interpreted the results and wrote the paper.

373 **CONSENT (WHERE EVER APPLICABLE)**

374

375 The manuscript is not meant for a medical journal.

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379 **ETHICAL APPROVAL (WHERE EVER APPLICABLE)**

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382 THIS SECTION IS NOT REQUIRED FOR THE CURRENT MANUSCRIPT.

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