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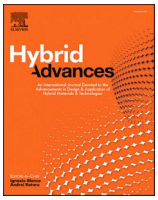

Scanning and transmission electron microscopy examinations of composite hybrid chromate and chromate phosphate conversion coatings exposed in hot 100% relative humidity environments

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ABSTRACT

Conversion coatings are sine qua non in the finishing of aluminium alloys. They may be put into service without coating of paints. However, for aesthetics in architectural applications, paint overcoat is common. Chromate phosphate coatings are relatively less toxic than chromate which gained the pride of place until recently. Thus, aluminium specimens coated with hybrid chromate/phosphate conversion coatings have been subjected to 100% relative humidity for 480 h at 313K in comparison to chromate coatings and bare aluminium. Scanning electron microscopy examination revealed that initial dried river bed morphologies on coated specimens were obliterated. The friable outer coatings collapsed into the cracks/environment leaving a relatively smooth surface after exposure. Additionally, transmission electron microscopy of sections before and after exposure revealed similar texture and morphological striations nearly parallel to each other throughout the length of the coatings to the metal/coating interface. These were not disrupted as well as the metal/coating interface which remained relatively smooth with no visible corrosion products after exposure. Thus, the coatings formed effective barrier between the substrate and the relatively harsh environment. From EDS, elemental compositions were the same albeit, spectral intensities remained relatively constant after humidity exposure regimes. The coatings are made up of either Cr, O and Al for chromate and Cr, P, O and Al for chromate/phosphate. At deliberately breached regions, the coatings prevented spread of corrosion and paint delamination over the substrates. On the other hand, bare aluminium was decorated with mounds of hydrated aluminium oxide/hydroxide after exposure as revealed in the SEM/TEM.

1. Introduction

Conversion coated aluminium can be put into service in a mild corrosive environment with or without a top coating of lacquer or paint. In both cases, the corrosion of the underlying aluminium substrate may occur, albeit, at scratches and/or defects in the bare or composite coatings [1–5]. Conversion coatings on aluminium usually exposed to atmospheric environment are those based on the so-called chromate--phosphate and chromate baths. The former imparts a greenish tone on aluminium while the later gives aluminium a golden yellow tint. The golden yellow tint may be washed off to a lighter shade of yellow by immersion of the coated aluminium in hot water. This may reduce the adhesion properties [6] and corrosion protection performance [7] of the coating while in service. The non-chromium types are, however, employed in situations where there is zero tolerance to the use of chromium such as in the canning industries. Chromium compounds have been implicated as carcinogens; hence, various authors are searching widely for partial or full chromate replacements in conversion coating baths. Replacements, such as cerium [9] and other non-toxic and/or less-toxic salts based on transition element compounds have received attention from various researchers [10–15]. The corrosion performances of these alternatives were adjudged to be inferior to those

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of chromate coatings. Also, wherever the use of some of these substitutes may be permitted, the extensive pre-treatment time to obtain a high-quality coating on aluminium proved to be a major disadvantage. Another solution being canvassed for the elimination of chromium (VI) as contaminants in the environment is the use of microbes to reduce chromates in the presence of constituents present in such chromate coating baths [16]. However, this may not gain traction nor prominence among researchers and the industries for obvious costs implications. It is common in practice to encounter breached regions of metallic structures carrying composite conversion coating/paint which may constitute vulnerable areas where corrosion of underlying substrates may commence. Also, it has been found in practice that chromates are good inhibitors while present in conversion coatings, the mechanism of corrosion inhibition has not been fully elucidated. For chromate conversion coatings, it is believed that chromates present in the conversion coatings are reduced at corroding sites to form a plug of Cr III oxide/-hydroxides which stifle corrosion reactions in such regions [17]. Whereas current interests are to fully elucidate the mechanisms of conversion coatings' mode(s) of protection. In addition, to help in the search for alternatives to chromate containing coatings [7–14], the current investigation seeks to compare the performances of bare aluminium with chromate-phosphate conversion coatings and generic chromate coatings, which compositions have received attention [2,3, 17–21] in recent times. The former contains Cr^{6+} species while the latter, within the resolution limits of XPS, have little or no Cr^{6+} species [22,23] and hence the current interest. Thus, if the concentration of phosphates were increased beyond those referred to in Refs. [22,23], it is more likely to completely eliminate Cr^{6+} from the coating. Hence, the best litmus test for this notion is to perform simple corrosion test on the new formulation with enhanced phosphate concentration.

The mechanism for the formation of conversion coatings generally follows the activation of the metal, with release of electrons thus (Eq. 1):

$$2Al \rightarrow 2Al^{3+} + 6e^{-} \quad (1)$$

This reaction (1) will be possible through the complex formation actions of activating ions, such as fluorides, CN^{-}, Nitrites, etc, such as (Eq. 2):

$$Al_2O_3 + 2xF- + 6H+ \rightarrow 2AlFx^{(3x)} + 3H_2O \quad (2)$$

Giving overall oxidation of Al as (Eq. 1):

$$2Al(s) \rightarrow 2Al^{3+} + 6e^{-} \ (1)$$

Reaction (1) is rapidly followed by cathodic reaction of the reduction of species with multiple oxidation states in solution such as vanadate, molybdate, chromate etc. In case of chromate and chromate phosphate, the reactions (Eqs. (3) and (4)) are:

$$2Cr^{3+} + 3H_2O \rightarrow Cr_2O_3 + 3H_2 \quad (3)$$

and

$$2Cr^{3+} + 3H_2O \rightarrow 2Cr\ (OH)_3 \quad (4)$$

In the presence of large concentration of phosphates reaction 5 (Eq. (5)) takes place predominantly.

$$Cr^{3+} + PO_4^{\ 3-} \rightarrow CrPO_4 \quad (5)$$

For chromate formulation, it was established that chromate was occluded within the coating and as well migrated through crow-feet like pathways within the sections of the coating causing their enrichment in the outer regions of the formed coating. On the other hand, phosphate enrichment in the presence of huge concentrations of phosphate ions [23] was also established.

The formation and development of conversion coatings through electrochemical routes have long been established as reported by Hagans et al. [24] in their Auger studies on chromate conversion coatings. From earlier studies in which coating formation was monitored through high impedance potentiometer from OCP and beyond, it was recognized that upon immersion of electrodes in the bath, there was a sharp drop in voltage indicating activation of the electrode. Shuai Huang et al. [25] in their studies on phosphate coatings made similar observations. A rapid increase in voltage within 30 s of immersion followed, which indicated deposition of coating materials to partially passivate the electrode surfaces [24]. The morphology and microstructure of the 30 s coating was described as mapping the grain boundaries of the substrate. While within the coating materials, there were dark and light features depicting thick and thinner sections [26]. Other researchers have reported similar findings which are thought to be related to the anode/-cathode regions of the substrate [4]. The micro-roughness produced by conversion processes constitute anchors for improved paint adhesion through mechanical interlocking [27]. Although in the opinions of the authors and Kinloch [6], chemical bonding between the conversion layers and paint moieties may play some part as well.

2. Materials and methods

2.1. Materials

All chemicals employed were laboratory grade reagents from British Drugs House Chemicals, Poole, UK and distilled water was employed throughout this investigation. Spade-like electrodes were made from aluminium with nominal impurities of 0.002% Cu; 0.004% Fe; 0.003% Si. These were electropolished at 20–22 V in a perchloric acid/ethanol mixture for 5 min. After electropolishing, specimens were washed with water and dried at ambient laboratory temperature.

2.2. Methods

2.2.1. Specimens preparation

For chromate conversion coatings formation by immersion procedures on spade electrodes, two coating baths were made up with 1 L of water using 3.5 g chromium trioxide as chromate and 1.5 g chromium trioxide plus 150 g of phosphoric acid as chromate-phosphate bath. Both solutions incorporated 0.5 g of NaF and pH adjustments to between 3 and 5 was by addition of either HNO_3 or NaOH. These bath compositions were achieved after several trials using a standard ratio of 1:3 of activator to coating-forming species. Conversion coating formation was by fully immersing aluminium electrodes, supporting air-formed film in the respective baths for 3 min at room temperature. After immersion treatment in the respective coating baths, the specimens were rinsed in distilled water and dried in a cool air stream. The final top coating was performed with a nitrocellulose lacquer by immersing the spade-like end of the pretreated specimens as near vertical as possible in 50 ml of the lacquer for 60 s and withdrawn as immersed, allowed to dry for 24 h before further examinations. The thickness of the lacquer as obtained from Permascope, EC8, Fischer's instrument was of the order of 6000 ± 2000 nm.

The specimens, prepared in triplicates were made as follows: (i) electropolished aluminium, (ii) electropolished and chromate treated, (iii) electropolished and chromate-phosphate treated, (iv) electropolished Al and over-coated with lacquer, (v) chromate coated Al and over-coated with lacquer, (vi) chromate phosphate coated Al and over-coated with lacquer. These specimens were exposed vertically in the 100% humidity cabinet set at 313K.

2.2.2. Electron microscopic examination

Prior to exposure regimes and at the end of 480hrs, various specimens were examined in scanning electron microscope (SEM) Phenom proX SEM, model MVE0224651193, operated at 15 KeV with attached EDS facility. Further, some specimens were sectioned using an LKB ultratome III 8800 ultramicrotome. The sections obtained on copper grids were examined in a Philips EM 301 transmission electron

microscope (TEM). Using the EDX facility attached to Philips EM400T transmission electron microscope and a probe size of 10 nm, elemental compositions of the coatings were obtained at different regions from the coating/solution interface to the metal/coating interface Both SEM and TEM examinations were carried out to study any morphological changes on the surface and in-section respectively of the conversion coatings during prolonged exposure at 100% humidity and a relatively high-temperature environment.

3. Results and discussions

3.1. Morphology and composition of as formed conversion coatings

The initial electropolished surface is usually characterized by orange peel effects [28] and occasional pits developed by the removal of intermetallic constituents on the substrate during the electro polishing procedure [7,8].

The surface morphologies of both chromate and chromate phosphate conversion coatings were similar. The surfaces were characterized by cracks that developed as a result of shrinkage stresses consequences of the drying out of precursor gel-like coating materials. A typical example is displayed in Fig. 1. The crack morphologies decorated the grains and sub-grain boundaries as discussed elsewhere [8] and corroborated by other researchers [2–4]. From EDS analyses, the coatings were either mainly composed of Al, Cr, P and O (Table 1a) or Cr, Al, and O (Table 1b) for chromate/phosphate and chromate coatings, respectively. Table 1 (a and b) showed the quantitative analysis of all elements detected.

The transmission electron micrograph portrayed in Fig. 2 presents the sectional morphology of a typical coating developed on aluminium from a generic chromate coating bath. The striations which run nearly parallel to each other from the coating/solution interface at the top of the micrograph to the metal/coating interface towards the bottom of the micrograph are unique features that are thought to transport coating solution species to the metal. Here, conversion coating formation occurred beyond the initial coating deposition on the microscopic metal surfaces through electron tunneling [28,29]. The coating developed in a manner that suggested discontinuities in the pathways as some were blocked by coating materials depositions before other routes were opened up in less resistant adjacent regions.

Running parallel to the metal/coating interface is a disaggregated coating material which has been described as features due to electron tunneling by Brown et al. [29] and observed by Oki and Charles [8] during similar examinations of chromate coatings on an Al/Fe alloy.

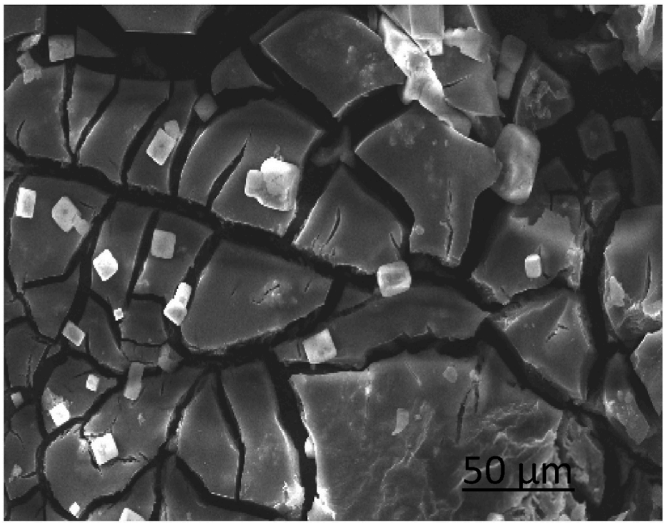

Fig. 1. SEM micrograph of a typical chromate conversion coating on aluminium.

Table 1a
EDS Quantitative analysis for Chromate conversion coating on aluminium.

Element	Atom Number	Norm C wt.%	Atom C wt%	Error
O	8	43.48	49.10	3.34
Al	13	29.06	19.46	0.88
C	6	16.35	24.60	1.71
Cr	24	6.85	3.49	0.71
S	16	4.26	3.35	0.20

Table 1b
EDS Quantitative analysis for Chromate phosphate conversion coating on aluminium.

Element	Atom Number	Norm C wt.%	Atom C wt%	Error
O	8	45.55	53.90	3.43
Al	13	27.32	19.17	0.81
Cr	24	0.60	0.50	0.05
P	15	14.12	7.54	0.31
C	6	11.71	18.47	1.37
S	16	0.7	0.41	0.05

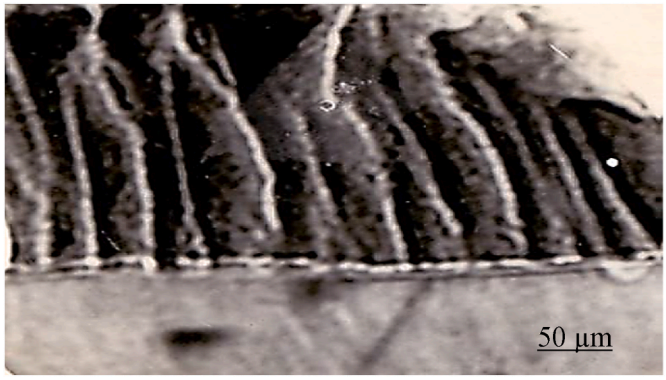

Fig. 2. Transmission electron micrograph of the sectional morphology of a typical chromate Conversion coating on aluminium.

Furthermore, spot analyses of the coating materials along the length and breadth of the coating revealed that the intensities of aluminium increased while those of chromium and phosphorous decreased towards the metal/coating interface. Thus, chromium and phosphorous compounds, as well as fluoride species in conversion coating baths, migrated in one manner or the other through the pathways described earlier to the metal/coating interface. Here, further growth of the conversion coatings occurred.

3.2. Morphology of specimens after exposure to high humidity regimes

Scanning electron microscopy revealed that after 480 h of exposure in the humidity cabinet, the cracks on the surfaces of bare chromate specimens became less defined as the friable outer regions of the coatings had collapsed and removed into the cracks/environment in the cabinet. Also, transmission electron microscopy (TEM) examination of ultra-microtome sections of similarly exposed specimens revealed similar features as in the as-formed coatings. This suggests that the coatings formed an inert barrier between the substrate and the outside relatively hostile environment [3–7]. However, for bare aluminium specimens after the exposure regimes, mounds of aluminium oxide/-hydroxide were revealed on the specimens. These occurred as a result of the transformation of the initial thin electropolishing film in the warm, humid environment to bulky hydrated corrosion products [7] with cracked morphology. The cracks occurred drying out of gel-like precursor, hydrated, aluminium oxide/hydroxide, Fig. 3. Further examination of the bare specimen after exposure in the humidity cabinet

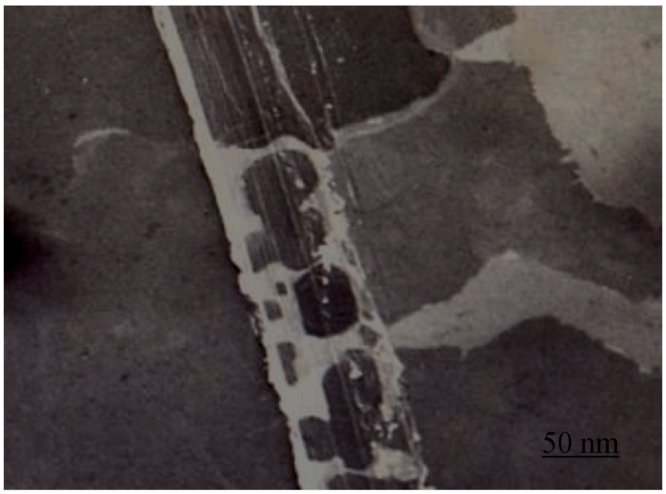

Fig. 3. Scanning electron micrograph of bare aluminium specimen exposed to 100% relative humidity at 313 K for 480 h.

revealed some incipient pits which decorated the surface feature as dark spots ranging in sizes from about less than 1 μm to about 5 μm. Curiously, the corrosion products within the middle of the pre-inscribed scratch developed more than at the edges of the scratch. This implied that moisture must have been retained for longer periods in such regions.

The electropolished specimen with a top coating of lacquer behaved similarly to its unpainted counterpart after 480 h of exposure with carpet-like corrosion products of aluminium decorating the surface of the specimen. On the other hand, the specimens carrying composite lacquer/chromate/phosphate conversion coatings did not show any sign of corrosion even within the deliberately scratched regions of the specimens. This corroborates the findings of others [3,4,7,17] that Cr^{6+} species inhibited corrosion processes around breached regions of the coatings. The mechanism regarded as electro-migration of chromate species breach regions where electrons are released by Al. These electrons release reduce chromates to hydrated chromium III oxides by stifling corrosion reactions in such regions. Such electro-migration can also occur for phosphate to form hydrated aluminium phosphate which stifled corrosion reactions. Paint delamination did not occur on the lacquer coated chromate phosphate specimens as well. The TEM examination of a scratched section of electropolished aluminium specimen similarly exposed in humidity cabinet is displayed in Fig. 4. It can be observed that the corrosion product, marked A, mapped the undulating surface features of the scratched region. Hence, the conversion coating formation fronts decorated the interface between coating and substrate as displayed in Fig. 2. The corrosion product at the top of the micrograph is lighter in shade than the parent metal. It is about 50 nm in thickness using the mean thickness of the corrosion products. Also, within the specimen, a grain boundary B was revealed. In this boundary, selective oxide/hydroxide growth had occurred during the warm and humid exposure regimes. Thus, there was preferential corrosion attack which suggested initial conversion coating development at the grain boundaries [5,7,23].

Thus, it is obvious from these examinations that with the conversion coatings, aluminium substrate was protected from corrosion activities in the warm humid environment. The corrosion protection by conversion coatings demonstrated here corroborated findings described by others in various environments [2,4,17]. The conversion coatings prevented paint delamination as well as corrosion of aluminium in the relatively hostile humidity cabinet. Thus, confirming the barrier function of conversion coatings in the protection of substrate on to which they are applied [28,29].

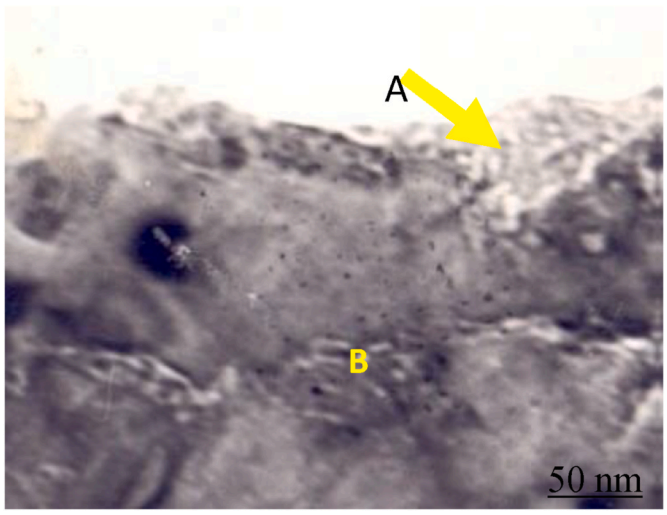

Fig. 4. Transmission electron micrograph of the scratched region of bare aluminium exposed to 100% relative humidity for 480 h.

4. Conclusions

The following conclusion are derived from this study.

1. Chromate phosphate compared favourably with chromate conversion coatings. Both conversion coatings improved the corrosion resistance and paint adhesion characteristics on 99.99% aluminium.
2. In case of a breach to expose underlying substrate, the composite lacquer/chromate/phosphate conversion coatings prevented hydroxyl-thermal transformation of aluminium and paint delamination in the cabinet.
3. There was evidence for preferential reactions along grain boundaries of the substrate. By extension, coating developments were initially more favoured at grain boundaries.
4. The chromate phosphate conversion coating exhibited corrosion and paint adhesion characteristics as much as the chromate for 480 h.
5. The phosphate enrichment in the outer regions of the chromate phosphate may have played similar roles as the chromate in the chromate conversion coating.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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