CHARACTERISATION OF SELF-HEALING BEHAVIOUR IN CHROMATE-BASED AEROSPACE PAINT SYSTEMS

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Chromate-based paint systems exhibit self-healing behaviour, providing excellent corrosion protection to aluminium aerospace alloys. In this paper, an overview is provided of extensive characterisation studies on chromate-based paint systems on aluminium alloy 2024-T3. A wide range of experimental techniques have been utilised to investigate the properties governing paint system performance, such as the distribution of chromate before and after exposure to corrosive environments, the uptake of water by the paint system, the leaching of chromate and subsequent reaction at defect sites in the paint system. These characterisation studies, in combination with investigations on chromate leaching kinetics and computational modelling, have provided significant insights into how these paint systems respond to defects and hence exhibit self-healing behaviour. In addition, given the hazardous nature of chromate, this work supports the drive to find new chromate-free paint systems, by highlighting the physical and chemical parameters that may be important in their design.

1 Introduction

Chromate-based self-healing paint systems have been used to provide corrosion protection to aluminium alloys, particularly in the aerospace industry, for many decades. However, due to their Cr(VI) content these coatings pose a substantial hazard to the environment and to human health. As a consequence, there is currently a significant research effort directed at finding effective, chromate-free alternatives. A detailed understanding of the mechanisms by which chromate-based paints inhibit corrosion is therefore essential to the development of these new paint systems.

In general, chromate-based paint systems consist of three distinct layers: (i) a conversion or anodised coating, (ii) an inhibited primer and (iii) a topcoat [1-3]. The conversion coating is usually a chromate conversion coating (CCC), while the primer most commonly consists of a chromate pigment (such as SrCrO₄) in an epoxy polyamide matrix together with other compounds such as fillers, UV absorbers and colouring agents [4-7]. Finally, the topcoat is usually composed of a robust polymer layer such as a polyurethane [8].

This three-layer paint system provides both passive and active forms of protection to the underlying metal surface. Passive protection is afforded by the barrier properties of the paint layers, which prevent contact between moisture, corrosive species and the metal surface.
Active protection is imparted by the primer layer, which contains a reservoir of corrosion inhibitor (in the form of chromate pigment) that is available for healing defects in the coating system.

Chromate inhibits corrosion by leaching from the primer, migrating through condensed moisture on the surface and reacting with actively corroding sites, thereby resulting in passivation. In order to fully understand the fundamental processes, several key questions need to be answered. For example, how does moisture penetrate the paint system? What are the key parameters controlling the amount and rate at which chromate leaches out? How does chromate react with the metal surface to inhibit corrosion and thereby heal the defect site?

Here, we present an overview of our extensive characterisation studies, which we have undertaken in order to address these key questions [9-13]. A wide range of characterisation techniques have been utilised to investigate the structure-property relationships governing the performance of this coating system. Raman microscopy, electron microprobe analysis (EMPA), X-ray diffraction (XRD) and proton induced X-ray emission (PIXE) have been used to determine changes in the distributions of various phases (such as the chromate corrosion inhibitor) both before and after exposure to corrosive environments [9,13]. Positron annihilation lifetime spectroscopy (PALS) and Doppler broadening energy spectroscopy (DBES) have enabled an understanding of the uptake of water by the polymer matrix and changes in void space resulting from subsequent dissolution and leaching of chromate [11]. Raman microscopy and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX) have also been used to examine the migration and reaction of chromate inhibitor at corroding sites in defects present in the paint system [13].

These characterisation studies, in combination with investigations on inhibitor leaching kinetics [10] and computational modelling [14-18], have provided significant insights into how chromate-based paint systems respond to defects and hence exhibit self-healing behaviour. The aim of this paper is to provide an overview of this work and to highlight its relevance to the development of new, chromate-free systems.

2 Experimental

2.1 Sample preparation

The metal substrate investigated was aluminium alloy 2024-T3, containing 4.31 wt% Cu, 1.5 wt% Mg, 0.6 wt% Mn, 0.08 wt% Si and 0.17 wt% Fe. Panels of the alloy were wiped with acetone and processed through alkaline cleaning, deoxidising and conversion coating steps as detailed in [9]. The panels were then primed with either PRC Desoto PR143 chromate-inhibited primer (BAE Systems, Salisbury, Australia) or an Anzol chromate-inhibited primer (DSTO Aeronautical and Maritime Research Laboratories, Maribynong, Australia), both of which are qualified under Mil-P-23377 specification. Primer thicknesses were determined to be 24.2 ± 3.3 µm for the PR143 primer and 43.9 ± 0.5 µm for the Anzol primer. A subset of panels was then coated with FE103 PRC Desoto black topcoat (BAE Systems, Salisbury, Australia).
2.2 Leaching experiments

Leaching experiments were undertaken in order to generate specimens exposed under simple, controlled conditions for both characterisation purposes and to provide data for kinetic modelling [10]. These experiments have been described in detail elsewhere [9]. In brief, primed panels prepared with no topcoat were immersed in 5% w/v NaCl solutions adjusted to four different pH values (1, 3, 5 or 7) using HCl and/or NaOH. The panels were immersed for a duration of 73 days and small aliquots of the solution were removed at various intervals. These solutions were then analysed for Cr in order to determine inhibitor leaching rates from which a quantitative model for leaching was deduced [10]. Prior to and after immersion, the primers were characterised by Raman microscopy, EMPA, and XRD [9], as well as by PALS and DBES [9,11].

2.3 Artificial defect experiments

Artificial defect experiments were carried out in order to study the leaching, migration and reaction of corrosion inhibitor from well-defined, simulated defects in the paint system. These experiments have been described in detail elsewhere [12]. In summary, artificial defects (slots) were produced in primed, topcoated panels by milling through the paint system to expose the underlying alloy surface. Slots were generated with various widths ranging from 0.2 to 4.0 mm. These panels were then exposed to accelerated weathering conditions in a neutral salt spray (NSS) chamber for up to 16 days. Runoff from the panels was collected and analysed for Cr. Prior to and after exposure, the panels were characterised by Raman microscopy, SEM/EDX and PIXE [12,13].

3 Results and discussion

3.1 Characterisation of unexposed chromate primer

The unexposed primer was characterised by a variety of techniques in order to provide a baseline for the chemical and physical structure of the paint system prior to self-healing behaviour. Figure 1 shows a secondary electron image of a cross-section through the unexposed PR143 paint system. The primer layer and topcoat are adjacent to an artificial defect (slot). It can be seen that the primer is a heterogeneous material comprising a number of different phases that vary in both size and shape.

Figure 1: Secondary electron image of a cross-section through the unexposed PR143 paint system showing topcoat (top left), primer layer (middle left) and artificial defect (right)
The crystalline and non-crystalline phases present in the primer were identified by XRD and Raman spectroscopy. A Raman spectrum averaged over a $96 \times 34 \, \mu m$ area of the primer is shown in Figure 2, together with Raman spectra of reference compounds of SrCrO$_4$, BaSO$_4$ and TiO$_2$ (anatase).

![Figure 2: Raman spectra from (a) the unexposed PR143 primer, together with reference compounds of (b) SrCrO$_4$, (c) TiO$_2$ (anatase) and (d) BaSO$_4$](image)

Peaks corresponding to the active corrosion inhibitor SrCrO$_4$ (866, 893, 915 and 929 cm$^{-1}$), together with the fillers BaSO$_4$ (987 cm$^{-1}$) and TiO$_2$ (anatase: 638, 615 and 397 cm$^{-1}$), can clearly be identified in the Raman spectrum of the primer. Additional weak peaks can be seen at 1112, 1186 and 1609 cm$^{-1}$, which can be assigned to vibrational modes associated with the epoxy polyamide matrix [19].

In order to determine the spatial distribution of the different phases in the primer, Raman maps of SrCrO$_4$, BaSO$_4$ and TiO$_2$ (anatase) were obtained by mapping the intensity of the corresponding spectral peaks. These Raman maps are shown in Figure 3. It can be seen that the TiO$_2$ is dispersed relatively evenly throughout the primer, whereas SrCrO$_4$ and BaSO$_4$ have locally high concentrations consistent with the large particle sizes observed by SEM in Figure 1. The distribution of SrCrO$_4$ can be further elucidated by examination of the Cr distribution obtained by EMPA, as shown in Figure 4. Clearly, SrCrO$_4$ is present in the primer as platelets with a range of sizes. The Cr map also confirms the presence of a thin CCC between the primer layer and the alloy surface.
Figure 3: Raman maps showing the distribution of (a) TiO$_2$ (anatase), (b) SrCrO$_4$ and (c) BaSO$_4$ in a cross-section of unexposed PR143 primer. An optical micrograph of the collection area is shown in (d) with crosses marking the points at which spectra were collected. The spacing between crosses is 2 $\mu$m. The metal is the bright band at the top of the image, while the dark band at the bottom of the image is the embedding resin.

Figure 4: Cr distribution in the unexposed PR143 primer as determined by EMPA.
3.2 Characterisation of water uptake

Following exposure to moisture, chromate release from the primer should occur via a number of steps including (i) uptake of water into the primer, (ii) dissolution of SrCrO₄ and (iii) diffusion of dissolved SrCrO₄ through the primer and into solution. PALS was used to examine the uptake of water by the PR143 primer for different immersion times. In general, PALS probes the free volume or void space within a material via the decay of ortho-positronium ($o$-Ps), where the $o$-Ps lifetime (represented here by $\tau_3$) increases as the corresponding free volume cavity gets larger. A more detailed description of these experiments can be found in [9].

Figure 5 shows $\tau_3$ and its intensity ($I_3$) for immersion times of 0 to 48 hr for the PR143 primer. For immersion times up to 4 hr, an increase in $\tau_3$ together with a decrease in $I_3$ was observed. This can be attributed to water first filling free volume cavities in the primer (decreasing $I_3$) and subsequently swelling of the primer (increasing $\tau_3$). It is likely that swelling of the primer has a significant impact on the kinetics of chromate release, since this has also been recognised in drug deliver applications [20].

For longer immersion times, Figure 5 shows that $\tau_3$ remains constant while $I_3$ increases. This behaviour appears to be coincident with chromate release (also shown in Figure 5). It can therefore be ascribed to an increase in the number of free volume cavities arising from dissolution of SrCrO₄ in the primer.

![Figure 5](image-url)

Figure 5: (a) $o$-Ps lifetime $\tau_3$ (●) and (b) intensity $I_3$ (■) together with amount of Cr released into solution (□) as a function of immersion time for the PR143 primer.
3.3 Characterisation of chromate release

The depletion of chromate from the primer was investigated by a variety of techniques [9,13], of which only a selection will be shown here. Figure 6 shows the results of XRD analysis in which the reflections associated with SrCrO$_4$ in the PR143 primer can be seen to decrease significantly after 73 days immersion in solutions at different pH. Importantly, for all pH values there was no significant change in the TiO$_2$ and BaSO$_4$ content, indicating that these phases were not leached from the primer upon immersion, thereby maintaining the structural integrity of the paint system.

![XRD analysis results](image)

Figure 6: Results of XRD analysis on PR143 primer (a) unexposed, and after 73 days immersion in solutions at (b) pH 7, (c) pH 5, (d) pH 3 and (e) pH 1. Reflections corresponding to SrCrO$_4$ (•), TiO$_2$ (anatase) (■) and BaSO$_4$ (●) are highlighted.

PIXE studies were undertaken to obtain the Cr distribution across an artificial defect in the primer following exposure to NSS. Since PIXE measurements can be made through the topcoat to the underlying primer, they are non-destructive to the paint system. Results are shown in Figure 7 and indicate that the Cr depletion zone increases with exposure time. It can also be seen that the depletion front is very uneven, which probably reflects the dissolution of large, individual SrCrO$_4$ platelets in the primer. Importantly, the Cr level in the depletion zone does not decrease to zero even after 5 days NSS exposure [13].
Therefore, it appears that a small amount of SrCrO$_4$ remains within the depletion zone after this time and is available for ongoing release at low levels.

![Figure 7: PIXE maps of the Cr distribution at the edge of a 0.6 mm slot as a function of exposure time to NSS. The maps are shown in inverse thermal intensity, with orange representing depletion and blue the highest concentration. Chromate particles can be seen in the primer as blue particles.](image)

### 3.4 Characterisation of chromate reactions (healing)

The self-healing action of these paint systems is afforded by the release of chromate from the primer and its subsequent reaction at defects in the paint system. The reaction of SrCrO$_4$ with exposed metal surface in artificial defects following release from the primer was therefore examined in detail [12,13]. The Cu, Cr and Al maps obtained by EMPA in Figure 8 clearly show a Cr layer on the surface adjacent to the leached primer. This layer extends some distance away from the edge of the primer on the exposed alloy surface, representing a significant penetration into the defect region.

![Figure 8: Cr, Al and Cu elemental maps obtained by EMPA from a polished section of a 4 mm artificial defect exposed to NSS for 3 days. The blue rectangle indicates the position of the topcoat, and the yellow triangle highlights a depletion zone of Cr.](image)
While these data demonstrate that SrCrO₄ leaches from the cut edge of the primer and onto the exposed metal in the defect, they do not provide direct evidence for reaction of SrCrO₄ at the alloy surface. The chemical speciation of Cr in the defect was therefore investigated by Raman microscopy [13]. Figure 9 shows the distribution of a broad peak centred at 840 cm⁻¹ observed in a defect after 2 days exposure to NSS. Notably, this peak was not observed in the primer or on the bare, unexposed alloy surface. The position and width of this peak are consistent with the presence of a mixed Cr(VI)/Cr(III) oxide or Cr(VI)/Al(III) oxide [21], therefore suggesting that SrCrO₄ has indeed reacted with the surface. Moreover, the concentration of this species appears to be highest in the vicinity of surface features where corrosion rates would be expected to be high, such as along the vertical crevice at top left and in the black pit at bottom left (see optical image in Figure 9). Hence, SrCrO₄ appears to react where it is needed most, in regions of high corrosion activity.

![Figure 9: Surface in artificial defect after 2 days exposure to NSS. Optical image of surface with mapped area indicated by green crosses (top left). Raman map of 836 cm⁻¹ peak (bottom left) and corresponding single point Raman spectra (right)](image)

4 Conclusions and future work

Chromate-inhibited aerospace paint systems have been characterised by a wide range of techniques in order to improve our understanding of their self-healing behaviour. These paint systems have been examined as applied to aluminium alloy 2024-T3, prior to exposure as well as following exposure to various simulated corrosive environments. The results obtained have provided important information on the size, shape and spatial distribution of the various paint system constituents including the active corrosion inhibitor (in this case, SrCrO₄). Changes were observed following exposure, including swelling upon uptake of water, dissolution and leaching of SrCrO₄ from the primer, and subsequent reaction of SrCrO₄ with the exposed alloy surface.
These observations have provided physical insights into the various models proposed to explain the observed leaching kinetics [10,22]. Furthermore, this work has highlighted the numerous physical and chemical parameters that need to be considered when designing new, chromate-free paint systems [23].

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