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The Use of Chromium and Chromium (III) Oxide PVD Coatings to Resist the Corrosion Driven Coating Delamination of Organically Coated Packaging Steel

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This paper describes a systematic study into the role of chromium and chromium (III) oxide thickness in preventing corrosion driven coating disbondment of organically coated packaging steel. A graded wedge of chromium and chromium (III) oxide is applied to steel using physical vapour deposition (PVD). A polyvinyl butyral (PVB) overcoat is applied and corrosion is initiated from an artificial defect using NaCl. Scanning Kelvin probe (SKP) potentiometry is used to monitor coating delamination. Wedge thickness variation allows for high throughput investigations into the effect of both metallic chromium and chromium (III) oxide thickness, on coating disbondment rate. A linear reciprocal relationship is observed between chromium metal thickness and disbondment rate. Increasing chromium (III) oxide thickness (applied over chromium metal) results in a decrease in disbondment rate. This work highlights the ability of PVD to produce chromium/chromium (III) oxide corrosion resistant coatings to use as alternatives to hexavalent chromium-based systems.

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Packaging materials such as electro chromium coated steel (ECCS) or tin free steel (TFS) are commonly used in food applications to produce can ends and 2 piece cans. They consist of a low carbon, low gauge (~0.13–0.49 mm) steel substrate covered in a chromium metal and hydrated chromium oxide layers and are traditionally produced using hexavalent chromium based chromic acid electrolyte baths.

The replacement of the hexavalent chromium used in such baths is an area of much current research due to health and environmental concerns.1–5 Trivalent chromium-based coatings are one proposed alternative, both for packaging and decorative applications.5–9 Investigation into the use of trivalent chromium conversion coatings (TCC) for aluminium alloys began in the 1990s10–15 and trivalent chromium chemistries have been commercialized for use with aluminium alloys,16 and by coating suppliers such as Henkel (Alodine T 5900 RTU) and Socomore (Socosurf TCS).17,18

Chromium based coatings are typically applied to provide corrosion resistance to packaging steel substrates, which have been shown to corrode in the case that they are exposed during the can making deformation process.19 An organic topcoat is therefore commonly added to enhance protection. In the case that the organic overcoat is damaged, creating a defect, the metal substrate can become exposed and atmospheric corrosion of the external surface of the packaging may occur. Organic coating delamination is subsequently of significant interest when considering novel packaging materials.

During the corrosion driven cathodic delamination, the rate at which the organic coating becomes detached from the metal substrate is limited by the cathodic reaction, commonly the cathodic oxygen reduction reaction (ORR), given by Eq. 1. Anodic metal dissolution at an organic coating defect is coupled to the ORR, which occurs at the delamination front, by a thin (~<5 μm) electrolyte.20 The susceptibility of ECCS replacements to the ORR is therefore of importance.

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]  

The electrolyte bath chemistry has been found to have a significant effect on final coating composition.3–9,21–25 For example, the conductivity of chromium (III)-based coatings, applied using electroplating, has been found to fall in the case that chromium hydr(oxide) forms.22 Furthermore, a decreased rate of ORR has been reported in the presence of both Cr (OH)323 and Cr2O3,24 this being attributed to the reduced rate of electron transfer through thin oxide films,25 which has been found to decrease exponentially with increasing coating layer thickness.26 The corrosion driven cathodic disbondment of a PVB coating from production line chromium (III) metal-oxide-carbide coated steel has been shown to decrease with increased chromium (III) oxide content in previous work.27 However, in that work, the total chromium (III) metal-oxide-carbide coating thickness was also varied, and the effect of chromium (III) oxide thickness was not investigated in isolation.27 The role that chromium hydr(oxide), present within chromium-based coatings, plays in determining the rate of the ORR, and thus corrosion driven coating disbondment, is therefore of interest when considering design of alternatives to traditional coatings.

Small variations in the chemistry of the electroplating bath can result in changes in the properties of electroplated packaging materials and reduced corrosion performance. Alternatives to electroplating, such as physical vapour deposition (PVD) can offer greater control over coating properties and should be considered as an application process which can be used in cases that coating composition is critical. PVD has been considered as a “clean” alternative by which to apply protective and decorative coatings and offers savings with respect to both energy and waste.28–30 Previous work has compared the performance of thin chromium films that have been applied via PVD and electroplating.31 PVD is subsequently considered a suitable method by which to apply chromium metal and chromium (III) oxide coatings of controlled thicknesses, with the aim of systematically studying the independent role that each coating component plays in the prevention of cathodic delamination. The ability to sputter multilayer Cr/C2O3 films23 and corrosion resistant Cr2O3 plasma coatings34 has been demonstrated elsewhere.

The intention of the current work is therefore to build upon the findings obtained that showed that corrosion driven cathodic disbondment of a PVB coating, from production line chromium (III) metal-oxide-carbide coated steel, decreased with increased chromium oxide thickness. It does so by following a methodology used previously for aluminium32 and magnesium based coatings,35 to apply a chromium and chromium (III) oxide wedge of graded thickness to a steel substrate using PVD. This allows one to
determine the specific role that either the metallic chromium layer thickness ($t_{Cr}$), or 2.) chromium (III) oxide thickness ($t_{ox}$) plays in determining the rate of corrosion-driven coating disbondment. In so doing, the disbondment of an electrochemically non-conducting polyvinylbutyral (PVB) overcoat will be investigated using scanning Kelvin probe (SKP) potentiometry. The ability of the SKP apparatus to study the corrosion driven cathodic delamination of coatings has been shown elsewhere.36-40 The results will allow determination of the optimum coating composition and thickness with the aim of identifying the lowest coating thickness necessary to provide resistance to coating delamination at minimal cost.

Experimental

Materials.—Sheets of low alloy T61 grade mild steel of 0.2 mm gauge, along with electrolytic chromium coated steel (ECCS) were obtained from Tata Steel UK. The ECCS sample consisted of the T61 grade steel with the addition of a ∼30 nm chromium/hydration chromium oxide coating. The chromium deposition sources used for PVD were acquired from Kurt J Lesker and were of at least 99.2% purity. Polyvinyl butyral-co-vinyl alcohol-co-vinylacetate (PVB), molecular weight 70,000-100,000 Da and all other chemicals were obtained from Sigma Aldrich Chemical Co. at analytical grade purity.

Methods.—Samples were cut from larger steel sheets and were polished using Buehler 5 μm abrasive alumina powder before being rinsed using distilled water and ethanol.

Thin metallic layers were sputtered on to the steel substrate using a Kurt J Lesker PVD75 Physical Vapour Deposition system following a procedure described previously to apply aluminium41 and magnesium42 PVD wedge coatings. Samples were attached to the sample holder using countersink head machine screws in order to keep them flat. Vacuum compatible polyimide tape (CHR K250 Saint-Gobain Performance Plastics) was used to expose an area on which to deposit the film. The sample holder was then placed in the vacuum chamber of the PVD system such that it could not obstruct the sliding shutter mechanism, that was used to apply films of variable thickness. A pressure was maintained at $3 \times 10^{-3}$ Torr during deposition (the base pressure of the vacuum pump was $5 \times 10^{-8}$ Torr). Prior to deposition the surface of the samples underwent a plasma etch for 20 min. An argon gas flow rate of 100 standard cubic centimeters (SCCM) per minutes and an applied power of 60 Watts were employed.

To avoid depositing surface oxide from the target the first 5 min of a deposition was carried out onto the shutter until the deposition rate stabilized. In the case of duplex chromium/chromium (III) oxide coatings, a 500 nm thick planar chromium metal layer was firstly applied to the steel substrate. The addition of oxygen to the PVD chamber has previously been found to result in the production of metal oxide coatings. As such, 3 SCCM of O₂ equivalent in the ratio 1:10 oxygen to argon during the sputtering of chromium41,42 to produce the overlying Cr (III) layer.

For application of both the Cr and Cr(III) oxide wedge coatings, the shutter was positioned in such a way that it covered the entirety of the exposed area (Fig. 1) at the start of the deposition process. The rate at which the shutter was withdrawn, and thus the rate at which the film thickness varied was controlled using Eq. 2, where $v$ is the shutter speed, $w$ is the width of the area to be coated, $T$ is the maximum film thickness required, and $D$ is the deposition rate.

$$v = \frac{w}{T/D} \quad [2]$$

The shutter moved until all of the unmasked area was exposed and deposition was stopped. The argon gas flow rate used was 30 SCCM and the power was 250 W. The mass deposition rate was determined using a sigma instruments oscillating crystal microbalance. The microbalance was used to estimate a mass (per unit area) deposition rate. The coating weight is then given by the product of mass deposition rate and deposition time. The sliding shutter varies deposition time in a linear fashion, that allows the coating weight to be estimated at every point in the resulting film deposit “wedge.” Using density values tabulated for the relevant material, the thickness of the PVD film may then be calculated from the coating weight at any point. In the case of chromium metal coatings, the density was assumed to be that of bulk metal. The theoretical density value used for chromium oxide coatings assumes the deposition of a stoichiometric, perfectly crystalline layer. In reality, the chromium oxide PVD deposit is likely to be significantly defective and the calculated coating thickness is therefore likely to represent a minimum estimate. A rate of 2–3 Å.s⁻¹ was achieved throughout.

Corrosion driven coating disbondment was investigated using a “Stratmann” type cell, as shown in Fig. 2.36-40 Following application of the PVD coatings, a 15 mm × 50 mm strip of clear adhesive tape was applied across one end of the sample, parallel to the coating wedge profile. Two parallel strips of insulating tape were attached to the coupon, perpendicular to the clear adhesive tape. An anodic solution (15.5 wt.%) of PVB was bar cast on the area that remained, the insulating tape acting as a height guide. In all cases the PVB used was unpigmented. Although PVB does not fully represent industrial coating systems, it was used in the current work as it allows a measurable degree of delamination over a short time-scale. It is therefore considered to be a suitable alternative when the principal aim is the comparison of substrates with respect to their ability to resist corrosion driven coating disbondment of organic coatings. The dry film thickness was 30 μm as measured using a micrometer screw gauge. The clear tape was then partially peeled back to expose a 15 mm × 20 mm area of bare metal, that acted as an artificial PVB coating defect. A barrier between the intact coating and defect area was formed by the residual clear adhesive tape and PVB overcoating. The remaining sides of the defect were lined with non-corrosive silicone rubber and a 2 cm³ volume of 0.86 mol.dm⁻³ aqueous NaCl electrolyte was applied to initiate corrosion.

Calibration of the SKP, needed to convert Volta potential values recorded to corrosion potential ($E_{corr}$) has been described in detail previously.36-40 The Volta potential difference above metal (Ag, Cu, Fe and Zn) wells filled with 0.5 mol.dm⁻³ aqueous solution of the respective metal chloride salt (nitrate salt in the case of Ag) was measured by the SKP. The values obtained were compared to the metal electrode potential values that were simultaneously measured vs SCE using a Solartron 1280 potentiostat.

Reservoirs of 0.86 mol.dm⁻³ aqueous NaCl were used within the SKP chamber to ensure a constant humidity of ca. 93% RH and the temperature was maintained at 25 °C. The SKP gold wire (125 μm diameter) probe was scanned along a 12 mm line, perpendicular and contiguous to the defect/coating interface. The probe was positioned at a constant height of 100 μm above the sample. The sample was scanned immediately after application of the aliquot of electrolyte to the defect and subsequent scans took place at intervals of 1 h. $E_{corr}$ values were taken at regular intervals along individual lines (dotted lines in Fig. 2) in such a way that that each line represented a different coating thickness value. The number of scan lines was based on the lateral resolution L of the SKP (Eq. 3), where $d$ is probe-specimen distance and $D$ is the probe diameter. For this work, $d = 100 \mu m$ and $D = 125 \mu m$. The lateral resolution, according to Eq. 3, will be $\sim 140 \mu m$. The number of lines was therefore chosen to maximise the amount of chromium thickness values, whilst ensuring that the inter line spacing was greater than 140 μm, and therefore that the Volta potential values recorded for each scan line were not influenced by the adjacent scan line (for which Cr thickness would be substantially different).

$$L = 0.884d + 0.4D \quad [3]$$

Results

Cathodic delamination of chromium coatings.—To establish baseline delamination kinetics, the cathodic disbondment of PVB
from a plain steel substrate was monitored using the SKP. Time-
dependent $E_{\text{corr}}(x)$ profiles (shown in Fig. 3) became established
within ca. 120 min of the electrolyte being introduced into the defect
region and are typical of those described previously. The potential value associated with the undelaminated, intact coating
remains constant at a value of ca. 0.1 V vs SHE. The potential
values measured are $\sim -0.4$ V vs SHE within the defect region are
consistent with those expected for freely corroding iron ($-0.44$ V vs
SHE), both these values being consistent with measurements made
previously. The anodic activity at the artificial coating defect is
coupled to the cathodic oxygen reduction reaction (ORR) at the
delamination front. The products of the ORR, OH$^-$ or reactive

**Figure 1.** Schematic representation of (a.) the process by which a graded wedge coating is formed using a sliding shutter mechanism and (b.) the finished wedge coating produced in the case of a chromium coating.

**Figure 2.** Schematic representation of (a.) the use of masking tape and PVB to produce a “Stratmann” cell and (b.) the sample configuration for study of corrosion driven coating disbondment using in situ SKP.
intermediates, are believed to attack the bond between the PVB coatings and metallic substrate, this resulting in loss of coating adhesion. The sharp increase in potential that occurs at the boundary between the delaminated and intact coating can be used as a semi-empirical means by which to locate the position of the delamination front.

Figure 3 also shows a false colour map of the \( E_{\text{corr}} \) obtained 12 h after the electrolyte was introduced into the defect. The defect is positioned at the left hand side of the map and the coating therefore delaminates from left to right, as indicated. The potential within the regions where the coating has delaminated (represented by the darker regions) is ca. \(-0.3\) V vs SHE. The areas in which the coatings are intact (lighter) are associated with higher potentials of ca. 0.2 V vs SHE. In the case of the thickest coatings (bottom of each colour map) the distance over which the coating has delaminated after 12 h is approximately 4.5 mm. In comparison, the distance of the delamination front from the defect in the case of the thinnest coatings is ca. 8 mm distance. After 17 h the thinnest part of the coating has delaminated across the entire scanned region, whilst the thickest part of the coating has delaminated \( \sim5.5\) mm, reaching \( \sim8\) mm after 22 h. The position of the delamination front changes across the width of the sample, and thus with coating thickness. This is in direct contrast to the uniform front observed in Fig. 3.

Figures 5a and 5b show time-dependent \( E_{\text{corr}}(x) \) profiles obtained by extracting the \( E_{\text{corr}} \) values measured along each scan line (where each scan line is associated with a different \( t_{cr} \) value) when \( t_{cr} = 100 \) nm (Fig. 5a) and 1000 nm (Fig. 5b). Comparison of Fig. 3 with Fig. 5 indicates that the presence of chromium does not significantly change the \( E_{\text{corr}} \) profiles from those observed in the case of a plain steel substrate. Whilst the time before initiation appears to increase from (120 ± 60) min in the case of plain steel, to (288 ± 60) min in the case of \( t_{cr} = 1000 \) nm chromium coatings, it should be remembered that the SKP is incapable of measuring Volta potential values immediately up to the defect. The initiation time (time at which first \( E_{\text{corr}} \) profile detected) is therefore associated with some error. The \( E_{\text{corr}} \) values associated with \( t_{cr} = 100 \) nm are similar to those obtained in the case of \( t_{cr} = 1000 \) nm. Parabolic kinetics, consistent with cation migration control are observed in both cases. By the end of the 24-hour experimental time period the 100 nm coating fully delaminated from the 12 mm region of interest. In
The delamination front has only reached a distance of ca. 9 mm from the coating defect region in the case of 1000 nm thick coatings.

The time-dependent distance of the delamination front from the artificial defect \(x_{\text{del}}\) can be acquired by detecting the point at which the highest potential gradient in the relevant \(E_{\text{corr}}\) profiles (shown in Fig. 5) occurs. Values of \(x_{\text{del}}\) can then be plotted as a function of the delamination time \(t_{\text{del}}\) with which it is associated (Fig. 6) and the delamination kinetics can be investigated. For unpigmented PVB coatings, migration of cations (here Na\(^{+}\)) within the underfilm electrolyte has been found to control the rate of coating disbondment.\(^{37-39}\) Delamination kinetics are parabolic follow Eq. 4, where \(k_d\) is the parabolic delamination rate constant and \(t_i\) is the delamination initiation time.

\[
x_{\text{del}} = k_d(t_{\text{del}} - t_i)^{1/2}
\]

The initial rate of coating delamination was used for purposes of comparison. Initial rates were estimated using a least squares regression method. The values obtained are shown in Table I. Values shown are based on the average of at least three readings and error intervals represent one standard deviation on the mean.

The \(k_d\) values obtained using Fig. 6 were plotted as a function of \(t_e\), and are shown in Fig. 7. An almost linear reciprocal relationship exists between \(k_d\) and \(t\). Despite the improvement in cathodic delamination resistance offered by chromium coatings at higher \(t_e\) values, mass transport remains rate determining and coating failure is not limited by a significant amount.

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**Figure 4.** A false colour map of SKP derived \(E_{\text{corr}}\) values obtained during the delamination of a model PVB coating from a PVD chromium wedge coated steel substrate. \(t_{CR}\) varies from 0 nm (top) to 1000 nm (bottom). Measurements were taken 12 h, 17 and 22 h after initiation using a 0.86 mol.dm\(^{-3}\) NaCl electrolyte.

**Figure 5.** SKP derived \(E_{\text{corr}}\) as a function of distance from defect \((x)\) profiles for the delamination of a PVB model coating from PVD chromium wedge coated steel substrate after initiation using a 0.86 mol.dm\(^{-3}\) NaCl electrolyte where \(t_{CR}\) is (a.) 100 nm and (b.) 1000 nm. Key: (a.) (*) 192 min and (b.) 288 after initiation. Profiles are shown at intervals of 96 min thereafter.

**Figure 6.** Plots of delamination distance \(x_{\text{del}}\) vs \((t_{\text{del}}-t_i)^{1/2}\) for the disbondment of a model PVB coating from a PVD chromium wedge coated steel substrate.
Cathodic delamination of chromium oxide coatings.—As previously mentioned, ECCS is commonly used throughout the packaging industry, and consists of a steel substrate covered in a chromium and hydrated chromium oxide layer. A PVB coating did not delaminate from an ECCS substrate over the 96 h time period for three repeat experiments. The absence of coating disbondment is made evident in Fig. 8 that shows profiles of $E_{\text{corr}}$ vs distance from the penetrative defect, obtained at various times. It may be seen from Fig. 8 that potential values recorded using the SKP show a time-dependent evolution but tend to stabilize as time increases. Thus, initially, values of $E_{\text{corr}}$ measured over the intact (un-corroded) surface ($E_{\text{intact}}$) increase progressively with time but tend toward an approximately constant value of $0.06 \pm 0.02 \text{ V vs SHE}$. The physicochemical processes influencing $E_{\text{intact}}$ have been described at length elsewhere. The value of $t_{\text{CR}}$ was kept constant at 500 nm. A chromium (III) oxide overlayer was then applied. Figure 9 shows an optical image of the sample surface following application of a chromium (III) oxide wedge. Colourful thin-film interference patterns are clearly visible, this providing evidence that the oxide thickness is comparable to the wavelength of visible light.

The variation in coating delamination rate with $t_{\text{OX}}$ can be seen clearly in Fig. 10 which shows three false colour maps of the $E_{\text{corr}}$ measured at various times after initiation of coating delamination. The defect is positioned at the left hand side of each map and the coating therefore delaminates from left to right, as indicated. As with Fig. 4, the potential within the regions where the coating has delaminated (represented by the darker regions) is ca. $-0.3 \text{ V vs SHE}$. The areas in which the coatings are intact (lighter) are associated with higher potentials of ca. $0.2 \text{ V vs SHE}$. In the case of the thickest coatings (200 nm) at the top of each image (note this is in contrast to Fig. 4 when the thickest coatings are at the bottom of the image), the coating remains intact over the entire length of the scan line at each of the three time points. In comparison the distance of the delamination front from the defect in the case of the thinnest coatings is ca. 4 mm after 48 h.

| PVD Cr layer thickness (nm) $t_{\text{CR}}$ | $k_d$ (μm.min$^{-1/2}$) |
|------------------------------------------|-------------------------|
| 1000                                     | 171 ± 6                 |
| 900                                      | 255 ± 10                |
| 800                                      | 302 ± 16                |
| 700                                      | 357 ± 12                |
| 600                                      | 359 ± 12                |
| 400                                      | 414 ± 50                |
| 200                                      | 570 ± 64                |
| 100                                      | 614 ± 28                |
| 1                                        | 681 ± 18                |

The corrosion protection offered by Cr based coatings is attributed to the formation of passive chromium oxide, the nature of which differs to that of the chemically grown hydrated chromium oxide present in the case of ECCS. The resistance to cathodic delamination offered by a chromium oxide layer, when compared to that offered by ECCS is therefore of interest and the effect of $t_{\text{OX}}$ on the rate of PVB disbondment was therefore investigated. The value of $t_{\text{CR}}$ was kept constant at 500 nm. A chromium (III) oxide wedge overlayer was then applied. Figure 9 shows an optical image of the sample surface following application of a chromium (III) oxide wedge. Colourful thin-film interference patterns are clearly visible, this providing evidence that the oxide thickness is comparable to the wavelength of visible light.

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As with Fig. 3, the sharp increase in potential that occurs at the boundary between the delaminated coating and intact coating can be used as a semi-empirical means by which to locate the position of the delamination front. The potential within the regions where the coating has delaminated (represented by the darker regions) is ca. −0.3 V vs SHE. The areas in which the coatings are intact (lighter) are associated with higher potentials of ca. 0.2 V vs SHE. In the case of the thickest coatings (bottom of each colour map) the distance over which the coating has delaminated after 12 h is approximately 4.5 mm. In comparison, the distance of the delamination front from the defect in the case of the thinnest coatings is ca. 8 mm distance. After 17 h the thinnest part of the coating has delaminated across the entire scanned region, whilst the thickest part of the coating has delaminated ∼5.5 mm, reaching ∼8 mm after 22 h.

Figure 11 shows a plot of delamination distance ($x_{del}$) vs $t$ for the disbondment of a model PVB coating from Cr (III) oxide PVD wedge/chromium coating where $t_{CR}$ = 500 nm and $t_{OX}$ varies from 10 to 200 nm. A parabolic relationship, consistent with mass transport limited behaviour is observed in the case that $t_{OX}$ < 120 nm. When $t_{OX}$ = 180 nm, a linear relationship is observed, this being indicative of electron transfer control and suggests that the Cr (III) oxide layer is able to reduce the rate at which electrons travel to the cathode, thus stabilising the ORR. The $k_d$ values obtained from Fig. 11 are shown in Table II, and show that the $t_{cr}$ does not have a significant effect on the delamination rate. Values shown are based on the average of at least three readings and error intervals represent one standard deviation on the mean. Figure 11 also shows that the initiation time increases significantly from 100 min when $t_{OX}$ = 0 nm to 2100 min when $t_{OX}$ = 180 nm. At this point it should again be borne in mind that the SKP is unable to measure Volta potential values immediately up to the defect. Any difference in delaminated distance observed in Fig. 10 is therefore believed to be a consequence of the increase in initiation time with increasing $t_{OX}$, as opposed to a variation in delamination rate.

Figure 10. A false colour map of SKP derived $E_{corr}$ values obtained during the delamination of a model PVB coating from a PVD chromium (III) oxide wedge/chromium coated steel substrate. $t_{CR}$ = 500 nm and $t_{OX}$ varies from 0 nm (right) to 200 nm (left). Measurements were taken after 24, 36 and 48 h after initiation using a 0.86 mol dm$^{-3}$ NaCl electrolyte.
contain ca. 90 wt.% Cr and ca. 8 wt.% O. Although the amount of oxide present is less than that expected in the case of stoichiometric Cr₂O₃ (∼30–35 wt.%) the results indicate that chromium oxide is present in the outermost parts of the coating.

To mitigate the effects of crosstalk, a non-combinatorial approach was taken when investigating the role of Cr(III) oxide thickness in preventing cathodic delamination. As such, two different types of planar bi-layer coatings were produced. For both samples \( t_{cr} = 500 \text{ nm} \). In the case of the first sample, this chromium layer was overcoated with a uniform 10 nm chromium (III) oxide layer, and in the case of the second, the chromium (III) oxide layer was 200 nm thick. Figures 13a and 13b show the time-dependent \( E_{corr}(x) \) profiles obtained for each sample. The \( E_{corr} \) values within the defect and intact region, shown in Fig. 13a, are similar to those obtained in Fig. 5 for chromium coatings.

Figure 13b strongly resembles Fig. 8 and a similar \( E_{corr} \) plateau value of 0.1 V vs SHE is recorded. It is therefore clear that the \( t_{ox} = 200 \text{ nm} \) is sufficient to prevent cathodic delamination of the PVB coating over at least the 48 h experimental time period and it therefore seems plausible that it is the chromium (III) oxide, the presence of which is confirmed in Fig. 12, which is responsible for the decrease in cathodic delamination rate. The change from mass transport control to electron transfer control when \( t_{ox} \leq 120 \text{ nm} \) (Fig. 11) is indicative that the chromium (III) oxide is able to offer resistance to coating delamination as a result of its poor electronic conductivity. The resistivity of 140 nm thick Cr₂O₃ films applied using thermal evaporation onto a glass substrate have previously been reported as \( 4 \times 10^7 \Omega \text{ cm} \).

Conclusions

This work has shown that it is possible to produce a chromium and chromium/chromium (III) oxide coating combinatorial library on a single substrate through physical vapour deposition (PVD) of a “wedge” onto a steel substrate. This allows for a rapid, parallel investigation into the role of coating thickness in preventing the corrosion driven coating disbondment of organic coatings from packaging steel, using SKP.

- An almost linear, inverse relationship was observed between chromium coating thickness and parabolic rate constant of cathodic disbondment. The delamination process was controlled by mass transport of cations in the underfilm electrolyte in all cases.
- A 200 nm chromium (III) oxide wedge was applied over a 500 nm thick chromium coating. GDOES was used to confirm the presence of Cr (III) oxide. An increase in chromium (III) oxide coating thickness resulted in a dramatic decrease in cathodic delamination rate. At thickness values \( \geq 120 \text{ nm} \) kinetics became controlled by electron transfer.
- The delamination rate constants obtained for each Cr (III) oxide thickness were similar. This was believed to be a result of the lateral diffusion of electrolyte ions that can occur once the PVB coating has started to delaminate. Lateral OH⁻ diffusion would result in increased coating delamination rates. A non-combinatorial approach, whereby bi-layer (500 nm chromium metal overlayed with chromium oxide) planar samples were produced, was subsequently adopted.
- For the case that chromium (III) oxide thickness was 200 nm, cathodic delamination was not observed for the 48 h experimental time period. This also was also the case for traditional electroplated

Table II. SKP derived delamination rate constant \( k_d \) obtained for the delamination of a PVB coating from steel coated with 500 nm of PVD chromium metal and varying thicknesses of a chromium oxide PVD layer.

| PVD Cr layer thickness (nm) \( t_{cr} \) | \( k_d (\text{m} \cdot \text{min}^{-1}) \) |
|-----------------------------------------|-----------------------------------------------|
| 180                                     | 2.21 ± 0.02                                    |
| 120                                     | 3.81 ± 0.16                                    |
| 60                                      | 2.74 ± 0.09                                    |
| 10                                      | 3.03 ± 0.08                                    |
| 0 (500 nm PVD Cr)                       | 5.10 ± 0.26                                    |

Figure 12. GDOES analysis of a bilayer chromium (III) oxide/chromium metal coating for which \( t_{cr} = 500 \text{ nm} \) and \( t_{ox} = 200 \text{ nm} \).

Figure 13. SKP derived \( E_{corr} \) as a function of distance from defect \( x \) profiles recorded for 48 h for the delamination of a PVB model coating from PVD chromium (III) oxide wedge/chromium coated steel substrate after initiation using a 0.86 mol.dm⁻³ NaCl electrolyte where \( t_{cr} = 500 \text{ nm} \) and \( t_{ox} \) (a.) 10 nm and (b.) 200 nm. Key: (a.) (*) 900 min after initiation with 0.86 M NaCl and 120 min intervals thereafter and (b.) for a total experimental time period of 48 h.
chromium/hydrated chromium oxide coatings produced using hexavalent chromium.

- The ability of chromium (III) oxide to resist coating failure at a thickness of 200 nm is believed to be a result of the low electronic conductivity, and therefore the low rate of electron transfer, associated with Cr₂O₃.
- This work highlights the benefits of using chromium (III) oxide when developing delamination resistant alternatives to hexavalent chromium based coating systems for packaging steel.

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