



The corrosion of chromium based coatings for packaging steel



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ABSTRACT

Chromium/chromium oxide based coatings, cathodically electrodeposited from either Cr (VI) or Cr (III) containing electrolytes are compared with respect to their ability to resist the corrosion driven delamination of an adherent polymer overcoat. Cathodic disbondment rates are determined using an in-situ scanning Kelvin probe technique. Anodic disbondment (filiform corrosion, FFC) rates are determined optically. The Cr (VI) derived coatings were fully resistant to corrosion driven disbondment. The Cr (III) derived coatings exhibited measurable rates of both FFC and cathodic disbondment. Disbondment kinetics are explained in relation to coating morphology, porosity and chemical composition determined using a combination of scanning electron microscopy (SEM), transmission electron microscopy (TEM) and xray photoelectron spectroscopy (XPS).

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1. Introduction

Hexavalent chromium based electrolyte baths are traditionally used during the production of coatings for packaging steel, primarily electro chromium coated steel (ECCS), or tin free steel (TFS). The material consists of a thin gauge (0.13–0.49 mm) low carbon steel substrate with a thin coating, comprising of a base layer of chromium metal and a top layer of chromium oxide, produced using chromic acid.

There is significant current interest in the development of chromium free coatings due to the international concern regarding environmental health [1–5]. Alternatives should be equivalent or better than existing treatments, non-toxic, acceptable to the food industry, and capable of application under similar tinning line conditions [6]. One approach to doing this has been the application of the chromium/chromium oxide coating from a trivalent (III) chromium salt based electrolyte [5,7].

The principal purpose of the coating on packaging materials is to provide corrosion resistance. In the case of ECCS iron, exposed during can forming, has previously been found to act as an initiation site for corrosion [8]. The material is therefore used in conjunction with an organic (lacquer or laminate) overcoat. Two mechanisms of corrosion are of primary concern; firstly, wet corrosion where the internal packaging surface is in contact with the contents [9] and secondly, atmospheric corrosion of the external surface.

The aim of the current paper is to present a detailed study of the role of technologically important chromium based coatings in resisting corrosion driven coating delamination that occurs at penetrative defects in these organic coatings. Firstly, the well understood cathodic disbondment mechanism, during which the delamination of the organic coating from the metal substrate is driven by the cathodic reaction (usually oxygen reduction), is studied. Within the localised corrosion cell, anodic metal dissolution located in the vicinity of the defect is coupled to the cathodic delamination front by a thin (<5 μm) gel like electrolyte, which ingresses beneath the coating [10]. Secondly anodic delamination, or filiform corrosion (FFC), which produces ‘threadlike’ corrosion product deposits, whereby failure is often linked to an anodic reaction [10]. It is widely accepted that filament advance involves anodic undercutting at the ‘active head’, driven by differential aeration arising from facile O₂ diffusion in the filament tail, which consists of dry corrosion products [10–15].

Although passivation systems based on titanium [9] and zirconium [16] have previously been investigated on tinplate, they were found to be poor in terms of performance and often require different application technologies. Trivalent chromium based coatings have been found to perform effectively on both aluminium and zinc [17,18]. When directly comparing trivalent and hexavalent chromium based conversion coatings using polarisation data, Zhang et. al found that Cr(III) based baths inhibited the corrosion of zinc to a significant degree, but less effectively than the coating produced using a Cr(VI) bath. The difference was attributed to the thinner layer produced in the case of Cr(III) based coatings [19].

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During the work described here steel, used in conjunction with both trivalent and hexavalent chromium based systems (ECCS), are organically coated using a model polyvinyl butyral organic lacquer, and their resistance to corrosion driven organic coating delamination, by both anodic and cathodic mechanisms, are investigated. Corrosion driven cathodic delamination is investigated by employing a 'Stratmann' type cell, and a 0.86 mol dm⁻³ aqueous sodium chloride (NaCl) electrolyte is used to reflect standard accelerated corrosion test conditions [20,21]. The time dependent extent of cathodic disbondment is determined by repeated in situ scanning using a scanning Kelvin probe (SKP) apparatus. The capability of the SKP to visualise the spatial distribution of localised free corrosion potential variation with time has been demonstrated previously [20,21]. Anodic disbondment (FFC) is initiated using FeCl₂ and the time dependent extent of corrosion is determined optically. Results are explained in relation to coating morphology, porosity and chemical composition determined using a combination of scanning electron microscopy (SEM), transmission electron microscopy (TEM) and x-ray photoelectron spectroscopy (XPS). In doing this we hope to determine the viability of using trivalent chromium based coating systems, which make use of the same application technology as for current sodium dichromate passivation systems, as alternatives to those produced using hexavalent chromium.

2. Experimental

2.1. Materials

Iron foil of 0.15 mm thickness and 99.5% purity was obtained from Goodfellow Cambridge Ltd. Low alloy mild strip steel of 0.2 mm gauge, with two different types of coatings applied, were obtained from Tata Steel Packaging. In the case of the first material the chromium-chromium oxide layer was applied to the cathodic steel strip from a hexavalent chromium based chromic acid electrolyte. This product is referred to as ECCS. In the case of the second material the coating was applied from a trivalent chromium salt based electrolyte using a process described elsewhere [7].

Polyvinyl butyral (PVB) and all other chemicals were obtained from Aldrich Chemical Co. and of analytical grade purity.

2.2. Methods

2.2.1. Materials Characterisation

X-ray Photoelectron Spectroscopy (XPS) spectra and depth profiles were recorded on a Kratos Axis Ultra using Mg K α x-rays of 1253.6 eV. The measured spot size was 700 μ m \times 300 μ m. The depth profiles were recorded using 4 keV Ar⁺ ions creating a sputter crater of 3 mm \times 3 mm. The composition was determined by fitting the XPS spectra of the Cr2p, O1s and C1s peak. The latter two were used to refine the quantification of the oxide and carbide content [5]. Determination of the individual Cr-species from the XPS spectra, Fig. 1, was performed using the following procedure. Peaks from metallic chromium and chromium carbides overlap. The carbide part of the C1s peak was well separated from other species within the peak and can therefore be quantified reliably. The amount of chromium carbide present was thus calculated, assuming it existed in the form Cr₃C₂.

The overall Cr weight, determined by integrating over the entire depth, was ca. 60 mg m⁻² (25.1 mg m⁻² metallic chromium, 16.1 mg m⁻² chromium oxide and 18.8 mg m⁻² chromium carbide). In comparison, in the case of ECCS, the overall Cr weight was ca. 80 mg m⁻² (69 mg m⁻² metallic chromium, 8 mg m⁻² chromium oxide and 3 mg m⁻² chromium carbide).

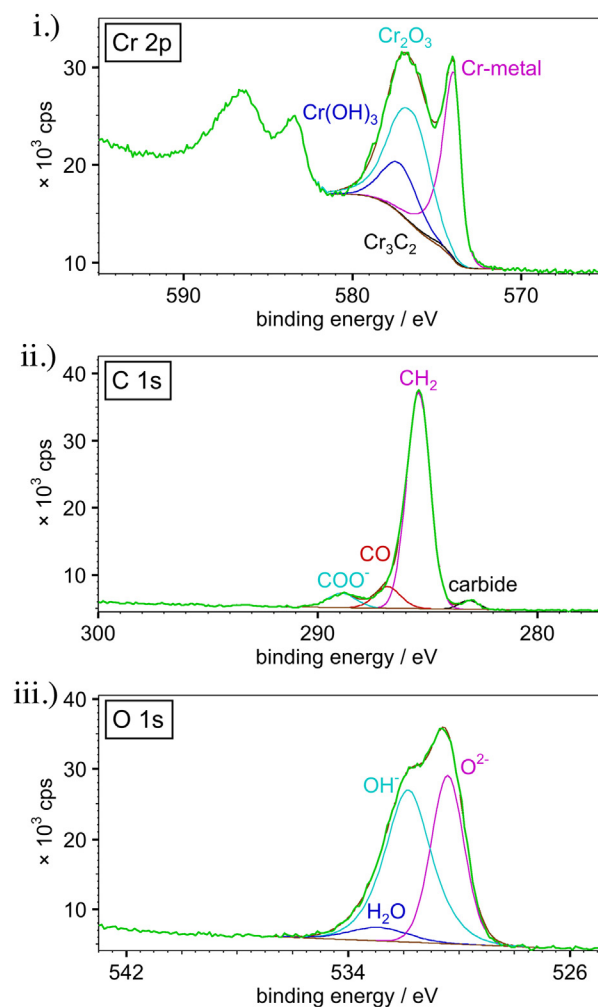


Fig. 1. Example of XPS spectra from the outermost surface of sample with fitted curves for i.) metallic Cr, ii.) Cr carbides and iii.) Cr oxides [5].

Scanning electron microscopy (SEM) images were collected using a Zeiss Ultra 55 with an InLens detector. Representative locations were found using light imaging microscopy (LIM) and SEM, and were selected for cross sectioning. Cross sections were prepared using a focused ion beam (FIB), before which they were ultrasonically cleaned in isopropanol for 10 minutes. The samples were coated with a thin (30 nm) pure metallic platinum (Pt) layer via sputter coating. A platinum layer was deposited by dissociation of a volatile organic Pt complex using an electron beam (which does not affect the sample). The organic Pt complex was dissociated using a Ga ion beam (where the sample is protected by the first two layers). The first Pt layer is easily recognised in the TEM and marks the original surface; subsequent layers contain more carbon and are thus less bright in the TEM images. The final thinning stage was performed on a Nova Nanolab200 Small Dual Beam.

Transmission electron microscopy (TEM) imaging and analysis was performed using a FEI Tecnai F30ST, operating at 300 kV, and equipped with a Field Emission Gun (FEG) and an energy dispersive x-ray spectrometer (EDX) spectrometer. The TEM was also equipped with a high angle annular dark field (HAADF) detector. The contrast in HAADF images is well resolved by atomic number (Z). Contrast in composition shown in images is thus similar to that obtained using the back scattered detector in an SEM.

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