

Characterization of chromate conversion coatings on zinc using XPS and SKPFM

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Abstract

Chromate conversion coatings (CCCs) on zinc have been studied using SEM, AES, XPS and scanning Kelvin probe force microscopy (SKPFM), aiming at understanding the protective mechanism of the CCCs. The SEM images show that the size of microcracks increases with the dipping times in chromate bath, and no crack has been observed when the dipping time is shorter than 5 s. The AES depth profiles show that the concentration of chromium decreases with the depth in the chromate layer, and zinc oxide exists mainly at the interface between the chromate layer and the zinc metal substrate for a coating with dipping time 60 s. The photoreduction of Cr(VI) caused by the X-ray radiation in a vacuum chamber has been investigated by sequentially acquiring the XPS spectra for a chromate coating. By limiting the acquisition time within 45 min, the Cr(VI) reduction by the X-ray radiation is less than 17%. For as-chromated samples, the percentage of Cr(VI) varies from 32% to 42% of the total Cr content in the outer layer of chromate coatings with dipping time from 1 to 60 s. After immersion in the 0.01 M NaCl solution for 24 h, the relative amount of chromium decreased due to mainly loss of Cr(VI) species and zinc oxide/hydroxide emerged on the surface. A lower Volta potential of a chromate layer than the bare zinc has been observed using SKPFM in air, which is in agreement with the open circuit potential measured in 0.01 M NaCl solution using a normal reference electrode. This suggests that the chromate in the coating has a cathodic inhibitive effect in the corrosion of zinc.

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1. Introduction

Despite the good corrosion resistance of chromate coatings, many researchers have explored the protective mechanism because of health hazards invoked by Cr(VI) species [1–4]. The aim is to find an alternative protective system. A chromate layer provides not only a protective barrier layer, but also a “self-healing” effect that is attributed to the soluble hexavalent chromium species, which may migrate to and passivate wherever the layer gets damaged [5–9]. Many investigations on chromate coatings have been

performed, and valuable results have been obtained, but the protective mechanism of the chromate coatings is still not fully understood. Thus, extensive fundamental investigations are needed to understand the protective mechanism of the CCCs and finally find alternatives.

The morphology and the composition of a conversion coating play an important role in corrosion protection. Corrosion in green and yellow chromate coatings starts and propagates along cracks within the coatings [10]. The cracks in the chromate coatings are attributable to the tensile stress in the coatings, and this stress increases with chromate thickness [11]. Although chromate coatings have cracks, excellent corrosion protection is still found, and this is probably attributable to the composition of the coatings [10,12]. Auger electron spectroscopy (AES) is a useful tool

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to study the composition and the elemental distribution in depth of a layer. X-ray photoelectron spectroscopy (XPS) is one of the powerful methods to study the chemical state of elements in a solid surface layer. Using XPS to analyse chromate coatings on aluminium alloys and zinc alloys has been reported by some researchers [13,14]. When using XPS to study a chromate layer, the photoreduction of hexavalent Cr under X-ray radiation has to be considered [15,16]. By controlling the analysis condition, it is still possible to use XPS to assess the Cr species in the chromate layers [17].

Scanning Kelvin probe force microscopy (SKPFM) is a relatively new technique which is a combination of the well-known Kelvin probe technique and the atomic force microscopy (AFM) [18–20]. It can measure the surface topography and potential distribution simultaneously on a line-by-line basis using metal-coated silicon tips that are electronically conducting. It was reported that the potential values measured in air for pure metals are linearly related to open circuit potentials measured in aqueous solution [20]. Although a passivated metal surface is different from a bare metal surface, the potential measured by this technique is strongly related to the Volta potential difference, and this potential does not vary for the distance between the tip and the measured surface from 100 nm to a few micrometers [19].

The present study attempts to enhance the understanding of the nature of the chromate conversion coatings (CCCs) on zinc. The morphology, the composition and the chemical state of elements in the CCCs on zinc are investigated by means of SEM, AES and XPS. The Volta potential distribution across the boundary between a chromate layer and the bare zinc is measured using SKPFM technique before and after exposure to 0.01 M NaCl solution.

2. Experimental

2.1. Sample preparation

In this work, pure zinc sheets, 0.5 mm thick, were used as substrates. Before applying a chromate coating, the specimens were cut into 2×1.6 cm specimens for surface analysis and 2×2 cm specimens for open circuit potential analysis. The surfaces to be analysed were polished using 1- μ m diamond grains in the final step. The specimens were ultrasonically cleaned in acetone and ethanol for 2 min, respectively. Before chromating, the surfaces of polished specimens were activated in 0.25% nitric acid for 10 s.

The chromate conversion coating was applied in a bath containing 200 g/L $\text{Na}_2\text{Cr}_2\text{O}_7 + 10$ g/L H_2SO_4 (pH 1.1–1.3) for 1, 5, 10, 30 or 60 s at room temperature. After this chromating, the samples were rinsed in deionized water. The wet chromated samples were first dried using a hair dryer and then heated in an oven at 60 °C for 30 min. A sample prepared for the SKPFM measurements was chromated in

half area of the surface with a dipping time of 5 s, without activating the surface before chromating and without rinsing the whole surface after chromating in order to keep the unchromated zinc area intact. The immersion tests were performed in a quiescent 0.01 M NaCl solution (pH 6) for 24 h.

2.2. AES analysis

AES measurements were performed on a PHI 4300 SAM with a LaB_6 cathode. A cylindrical mirror analyser (CMA) and a 5-keV ion gun (PHI 04-303) were used. The capture angle of the CMA was $42 \pm 6^\circ$. The spectrometer (CMA) was calibrated according to the method described in Ref. [21]. The base pressure in the analysis chamber was 3×10^{-10} Torr. A primary electron beam with energy of 5 keV and a current of 1 μ A was incident on the sample surface at 30° to the normal. All the Auger electron spectra were acquired with an energy analyser resolution of $\Delta E/E = 0.6\%$.

For the AES analysis, a 40-nm gold layer was deposited on the chromated zinc in order to increase the conductivity of the surface. Alternate sputtering and data acquisition were used to obtain the depth profile for two locations on the sample. The surface was rastered using a 3-keV Ar ion beam over an area of 2×2 mm² for the chromate coating. The emission current was 20 mA, and the Ar pressure was 10 mPa. The ion beam was used at intervals of 1 min and impinged on the sample surface at 50° to the normal. The Auger electron spectral regions recorded in the depth profiling are given in Table 1. Within each of these acquisition regions, data were recorded at 1.0-eV intervals except in the O1s region where a 0.5-eV interval was used.

The recorded spectra were analysed with Multipak 6.1A software (Physical Electronics). Firstly, the spectra were differentiated using a five-point Savitsky–Golay method [22]. The energy range for each element was redefined in order to isolate the peak for the transition of different elements (noted as analysis range in Table 1). For Zn, a linear least square fitting was performed to separate zinc metal from zinc oxide.

2.3. XPS analysis

XPS analysis was carried out with a PHI 5400 ESCA using 400-W Mg K_{α} radiation (1253.6 eV). This instrument

Table 1
The spectral line designations and acquisition details of the elements detected in the AES analysis

Element	Auger line	Sensitivity factor at 5 keV [21]	Acquisition region (eV)	Analysis region (eV)
Au	NNV	0.044	220–250	230–250
O	KLL	0.296	450–600	500–518
Cr	LMM	0.359	500–600	519–539
Zn	LMM	0.296	960–1030	980–1000

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