



Effects of organic and inorganic treatment agents on the formation of conversion layer on hot-dip galvanized steel: An X-ray photoelectron spectroscopy study

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ABSTRACT

The formation of a Cr-free conversion layer on hot-dip galvanized (HDG) steel involves various interfacial processes which radically influence the composition of the coating and thus its performance. Here, we investigate the role of the main constituents contained in the treatment bath, the polymeric compounds and manganese phosphate species, by using derivative versions from the standard solution. A detailed X-ray photoelectron spectroscopy (XPS) analysis allowed distinction between oxygen originating from polymeric compounds and oxygen of inorganic nature in oxides/hydroxides or phosphate species. Our results revealed that manganese phosphate present in the treatment bath promotes the polymer adsorption on HDG substrate. Angle-resolved XPS and depth profile showed the presence of TiO₂ layer on the outer part of the conversion layer, when polymeric compounds are not detected.

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1. Introduction

In the coil-coating industry, conversion layers are of primary importance to improve adhesion of the organic coating to the metallic substrate and to enhance corrosion resistance [1–7]. Despite their excellent performance, the use of Cr(VI)-containing treatments was restricted for environmental and health reasons [8,9]. Cr-free environmentally friendly treatments based on fluorotitanic acid are reported to be promising alternatives. These treatments generally contain other dissolved inorganic species and organic compounds. Their performances in terms of corrosion protection and adhesion were thoroughly investigated when applied on aluminum alloys [10–16]. However, little information is available regarding their efficiency on hot-dip galvanized (HDG) steel [17,18]. In a previous study, the behavior of a Cr-free treatment applied on HDG by dip-coating was investigated [19]. The treatment bath consists of fluorotitanic (H₂TiF₆) and phosphoric acids (H₃PO₄), manganese phosphate Mn₃(PO₄)₂ and organic compounds [19–21]. From the electrochemical point of view, the conversion layer acts as a physical barrier, leading to a significant decrease in the cathodic current density, particularly in the vicinity of the corrosion potential [19]. Furthermore, in addition to the performances related to corrosion resistance, one main advantage of such treatment is the fact that it does not require any rinsing step (i.e. alkaline oxidation) which is time-saving for industrial applications and eliminates polluting effluents [22].

Regarding the mechanism of the conversion layer formation, it is commonly considered to be induced by zinc oxide/hydroxide dissolution (pickling reaction) that occurs at low pH values. This initial step leads to a local pH increase in the liquid phase followed by precipitation of dissolved zinc and ions contained in the treatment bath. The conversion layer composition was determined in previous studies by means of various techniques [10,11,13,18,19]. However, due to the multiplicity of interfacial processes, its chemical nature has not been accurately elucidated so far. Many assumptions regarding oxides/hydroxides, fluoride and phosphate-based compounds were indeed reported without direct analytical evidences. Such system complexity may be explained by the large range of parameters influencing the conversion layer formation. This includes parameters related to the efficiency of the degreasing step before the conversion coating application, intrinsic properties of the treatment bath (pH, organic and inorganic constituents) and interfacial processes (adsorption, oxidation, dissolution...).

The aim of this work is to point out the role of the main constituents of the treatment bath on the conversion layer composition based on full surface characterizations. To this end, derivative versions from the standard Cr-free treatment solution (without either manganese phosphate or organic species) were studied with a view to understanding the role of each compound on the conversion layer composition. Depth profiles and angle-resolved X-ray photoelectron spectroscopy (XPS) analyses were carried out as a function of the treatment bath. Results were correlated to electrochemical tests and inductive coupled plasma (ICP) measurements performed in a 3.5 wt.% NaCl solution at room temperature.

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2. Materials and methods

2.1. Sample preparation

The substrates used in this study were 500 μm thick HDG steel supplied by ArcelorMittal (Montataire, France) in the skin-passed state with a zinc layer of 10 μm . HDG samples were submitted to alkaline treatment to remove oils and the thin aluminum oxide layer resulting from the galvanizing process. Samples were then treated by dip-coating during 10 s. For this purpose, three solutions were investigated: (i) the commercial one, (ii) a solution without the organic species and (iii) a solution without manganese phosphate (Table 1). Details regarding the organic species present in the bath are depicted in Fig. 1. A curing step was then performed in a drying oven during 4 min at 80 °C. The amount of titanium applied on each treated sample (traditionally referred as coating weight) was measured by X-ray fluorescence. All specimens exhibited comparable amount, between 7 and 9 $\text{mg}\cdot\text{m}^{-2}$ of Ti (data not shown), in accordance with values obtained on industrial lines. For electrochemical tests, a non-treated HDG sample was also investigated and referred as “Ref” sample.

2.2. Electrochemical measurements

The electrochemical behavior of the conversion layer-coated samples was investigated during immersion of the treated samples in a 3.5 wt.% NaCl solution at room temperature, using a Gamry Potentiostat FAS2/Femostat (Gamry Instruments, USA). This set-up was connected to a three-electrode flat cell, composed of a platinum grid (counter electrode), a saturated calomel electrode (SCE – reference electrode), the treated sample being the working electrode. Polarization curves were recorded using a linear scan voltammetry with a scan rate of 5 $\text{mV}\cdot\text{s}^{-1}$ between -150 and $+150$ mV with respect to the open circuit potential (OCP).

2.3. Inductive coupled plasma-atomic emission spectroscopy measurements

In situ analyses of immersion baths were performed by inductive coupled plasma-atomic emission spectroscopy (ICP-AES) using a set-up described in recent studies [17,23–25]. The apparatus was composed of a cell containing 0.2 mL of 3.5 wt.% NaCl solution. Once the treated

HDG sample set inside the cell, the electrolyte passed through with a 3 $\text{mL}\cdot\text{min}^{-1}$ flow rate. Chemical composition of the electrolyte was evaluated via the ICP as a function of sample immersion time. Zn^{2+} , Mn^{2+} , Ti^{4+} and PO_4^{2-} concentrations were calculated on the basis of comparisons with reference solutions containing known amount of these elements (from 1 to 5 ppm).

2.4. X-ray photoelectron spectroscopy

XPS analyses were performed using a SIA 100 spectrometer (Cameca-Riber) equipped with a monochromatized aluminum X-ray source (powered at 20 mA and 10 kV) and an eight channeltron detector. Samples were fixed on the support using a double-sided adhesive conducting tape. No charge stabilization device was used on these conductive samples. The resulting analyzed area was about $200\times 200\ \mu\text{m}^2$. A 20 eV pass energy was used for narrow scans. The pressure in the analysis chamber was around 10^{-7} Pa. Depth profile experiments were performed using an Ar^+ ion gun (operating at 500 eV, sputtered area about $2\times 2\ \text{mm}^2$). Angle-resolved XPS was performed at photoelectron collection angles (defined with respect to the perpendicular of the sample surface) $\theta = 45, 60$ and 80° . The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, N 1s, P 2s, Zn 2p, Mn 2p, Ti 2p, and F 1s. The binding energy scale was set by fixing the C 1s component due to carbon only bound to carbon and hydrogen at 284.8 eV. Data treatment was performed by means of Casa XPS software (Casa Software Ltd., UK). Peaks were decomposed using a linear baseline and a component shape defined by the product of a Gauss and Lorentz function, in the 70:30 ratio, respectively. Molar concentration ratios were calculated using peak areas normalized according to acquisition parameters, relative sensitivity factors and the transmission function provided by the manufacturer.

3. Results and discussion

3.1. Conversion layer behavior in chloride-containing medium

With a view to evaluating performances of the conversion layers (formed in the different treatment baths) in an aggressive medium, treated samples were immersed in a 3.5 wt.% NaCl solution at room temperature. Open circuit potential (OCP) evolution reveals significant

Table 1

Details about sample's designations and the composition of the corresponding treatment bath. “Ref” designates the non-treated HDG sample.

Sample	Treatment bath pH	Treatment agents		
		Acids H_2TiF_6 and H_3PO_4	Organic phase	$\text{Mn}_3(\text{PO}_4)_2$
Ref	–	–	–	–
A	3.3	●	●	●
B	2.9	●	–	●
C	2.4	●	●	–

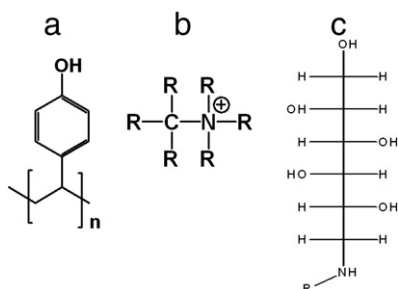


Fig. 1. Structure of (a) poly-(4-vinylphenol), (b) quaternary ammonium and (c) N-methyl glucamine groups included in the organic species of the standard treatment bath.

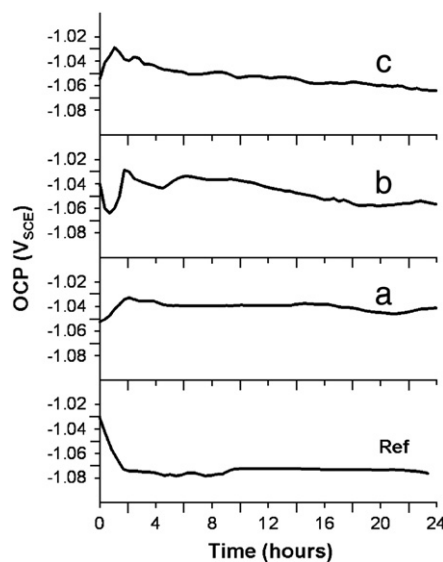


Fig. 2. Evolution of the open circuit potential (OCP) as a function of immersion time in 3.5% NaCl at room temperature for the reference sample (Ref), the same treated with the standard solution (a), without the organic species (b) and without manganese phosphate (c).

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