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## Novel insight to aluminum compounds in the outermost layers of hot dip galvanized steel and how they affect the reactivity of the zinc surface

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## ABSTRACT

Hot dip galvanized zinc coatings (containing about 0.2% of aluminum) were studied with surface analytical techniques. A few nanometer thick aluminum oxide ( $\text{Al}_2\text{O}_3$ ) layer dominated the very outermost surface of such zinc coatings. The inert  $\text{Al}_2\text{O}_3$  layer formed a continuous impermeable barrier on zinc, providing short term humidity resistance. However, this barrier effect was largely lost during temper rolling. Residues of  $\text{Al}_2\text{O}_3$  were shown to prevent titanium hexafluoride pretreatment chemical from reacting with the zinc surface. Segregated aluminum/iron (Al/Fe) intermetallic compounds were also detected at the surface of the zinc coating. The Al/Fe compounds populated the surface immediately beneath the  $\text{Al}_2\text{O}_3$  layer. The Al/Fe precipitates were found predominantly in the dendritic valleys. Repulsion between the Al/Fe precipitates and the pretreatment chemical was observed.

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### 1. Introduction

Color coated hot dip galvanized (HDG) steel is widely used for example in construction industry and household appliances. Zinc coatings inhibit corrosion of steel by barrier and galvanic protection [1]. HDG steel for color coating is typically manufactured by immersion of the steel strip in a molten bath of zinc in a continuous process. Hot dip galvanizing is initiated by the formation of a Fe–Al layer on the steel strip, followed by zinc nucleation on top of the Fe–Al layer. The nucleated zinc grain growth continues until the entire interface is covered with dendritic zinc grains. The final surface appearance and the grain shape are readily determined even though the outer zinc surface still is in a liquid phase. Finally, the segments of individual grains emerge [2]. The quality of a zinc coating is affected by the chemical composition of the bath, the bath time and temperature, the cooling time and the substrate steel [3,4]. The zinc quality has been proposed to affect the paint adhesion [5,6]. Aluminum is one of the commonly used additives in zinc baths. Small amounts of aluminum (0.1–0.3%) are typically added in hot dip galvanizing baths in order to improve the mechanical surface properties of zinc coated steel. Aluminum has been reported to reduce the rate of oxidation of molten zinc, to reduce the spangle size and to improve the uniformity of coating. Aluminum suppresses the growth of a brittle Fe–Zn intermetallic layer and reduces iron loss into the bath via the formation of  $\text{Fe}_2\text{Al}_5$  and  $\text{FeAl}_3$  intermetallic layers [7–11].

Al has been observed to exist in two forms in the bath; dissolved in the liquid and as intermetallic particles entrapped in the bath. The dissolved Al is the effective form in order to avoid the formation of the brittle Fe–Zn phases. A galvanized zinc bath with 0.1–0.3% Al may further contain dross particles in the form of Zn and Al oxides, as well as Zn–Fe and Fe–Al intermetallic compounds. These segregated particles originate in Al addition to the bath, solution of iron from the steel strip and in potential insufficient temperature uniformity and chemical homogeneity of the bath. In a solidified zinc coating, Al has been reported to exist in three main forms: (i) in Al–Fe intermetallic compounds at the interface of steel and zinc, (ii) in segregated Al-containing moieties, and (iii) in a thin continuous film of aluminum and oxygen that covers the entire zinc surface [12]. The  $\text{Al}_2\text{O}_3$  layer on the outermost surface is generated by diffusion of Al from the bulk because of its affinity to oxygen. Negligible amounts of Al have been detected in the bulk of the zinc coating, since the solid solubility of aluminum is very limited and it is not thermodynamically favorable for Al to be dissolved in Zn as the temperature decreases during solidification [13]. The submicroscopic distribution of Al at the steel/Zn interface has been intensively studied lately due to the development of new steel grades and improving the properties of zinc coatings on high strength steel [8,14].

Unprotected zinc coated steel undergoes rapidly surface deterioration in humid conditions [15,16]. Typical corrosion products for zinc coatings are zinc hydroxide, oxide, hydroxycarbonates and different salts [17,18]. In the absence of air pollutants other than carbon dioxide, the zinc corrosion products are mainly oxides, hydroxides and carbonates. Spherical zinc oxide and hydroxide particles are typically formed

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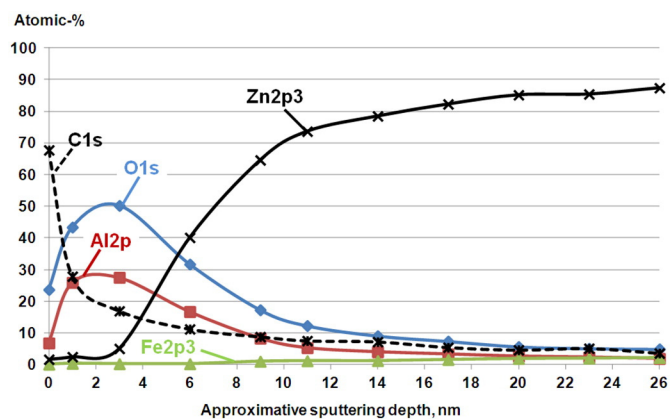


Fig. 1. XPS depth profiles of the prominent elements in the outermost surface layers of nontemper rolled hot dip galvanized steel.

at the early stages of aging, while the formation of zinc carbonate ( $Zn_5(CO_3)_2(OH)_6$ ) requires longer exposition times [15,19–21]. ZnO and  $Zn(OH)_2$  do not contribute to paint adhesion, but  $Zn_5(CO_3)_2(OH)_6$  improves adhesion [19]. Zinc oxide has been proposed to have surface protecting effect [21]. Due to the change that these compounds impart to the visual appearance of zinc coated steel, this type of zinc corrosion is also termed white rust formation. It is not yet fully understood how aluminum compounds affect the reactivity of zinc in different environments.

The surface  $Al_2O_3$  layer is typically to a large extent removed by alkaline cleaners prior to color coating [22–25]. However, Al-containing dross particles have been detected on the HDG surface even after the alkaline cleaning [25]. It has not been thoroughly investigated how the presence of segregated Al-containing dross particles affects the reactivity of the surface.

From a color coating perspective it is of great importance to understand the chemistry between the substrate and the pretreatment, since the long-term performance of a coated steel depends on their compatibility [26]. In this work, the distribution of aluminum in the outermost layers of a zinc coating was studied. The effects of the aluminum compounds on surface reactivity of HDG were investigated.

## 2. Materials and methods

Hot dip galvanized material (~0.2% Al in the zinc bath) with a total coating mass of 275 g/m<sup>2</sup> was obtained from SSAB Europe Oy, as well as the pretreated samples. Both nontemper rolled and temper rolled samples were studied. The mildly acidic pretreatment chemical (Bonderite M-NT 1455T, Henkel) contained titanium hexafluoride, manganese phosphate and organic polymer.

Scanning electron microscopy (SEM) characterization was performed using a JEOL JSM-6335F equipped with an X-ray energy

dispersive spectrometer (EDS) and a Merlin™ field emission scanning electron microscope (Zeiss GmbH).

Preparation of the cross section sample was carried out with an Ilion + Advantage Precision Cross-Section System (Model 693, Gatan Inc., USA).

Depth profiling was performed using X-ray photoelectron spectroscopy (XPS) (PHI Quantum 2000). The spectra were obtained using a monochromated Al K $\alpha$  beam with 100  $\mu$ m spot size. The sputtering was done with Ar<sup>+</sup> ions, and the approximative sputtering depth was calculated using a SiO<sub>2</sub> calibration standard.

Element mapping was performed using time of flight secondary ion mass spectrometry (ToF-SIMS, PHI Trift II). The ToF-SIMS measurements were carried out at 25 kV and with a 200  $\mu$ m raster size. Element mapping was also carried out using an electron probe microanalyzer (EPMA) with wavelength-dispersive X-ray spectrometers (WDS) (JEOL JXA-8600).

## 3. Results and discussion

XPS depth profiles of the detected elements on a nontemper rolled HDG sample surface are illustrated in Fig. 1, and the measurement data is shown in Table 1. The high carbon content on the sample surface originates from adsorbed hydrocarbons on the surface, indicated by the rapid decrease of carbon intensity. The outermost surface of the sample was mostly composed of aluminum oxide with only traces of zinc (Table 1). Aluminum oxide zones of about 30–100 Å thickness have been reported to appear on the surface of hot dip galvanized steel [1,12,13,22,27]. Furthermore, the thickness of the surface  $Al_2O_3$  film has been suggested to be independent on the Al concentration in the galvanizing bath and the coating thickness [12,28].

The aluminum was present in its oxide form, which is in accordance with earlier findings [29]. Oxidized zinc was also detected on the surface (Table 1). However, the amount of metallic zinc increased rapidly with decreasing aluminum oxide. Similar observations have been made in other studies [13,28]. Small but significant amounts of iron were detected immediately beneath the aluminum oxide layer. Some investigators have proposed that sub-micron Al segregations populate the surface under the native oxide film, since they have detected small amounts of Al and O even after the sputtering of a film equivalent to the nominal thickness of the native  $Al_2O_3$  film [28]. However, sputtering can also be attributed to create micro-roughness and to push the elements enriched at the surface deeper into the sample matrix, probably explaining some of the tailing that is seen in the XPS depth profiles (Fig. 1) [7,13]. The tailing could also be due to the unevenness of the sample surface.

According to the ToF-SIMS positive ion measurements, the outermost surface of a temper rolled HDG sample was composed mostly of aluminum with minor contributions from zinc and iron (Fig. 2). The measured intensities, expressed as counts per element and rounded to nearest thousand, were: 2,212,000 (Al), 56,000 (Zn) and Fe 18,000 (Fe). The Al intensity was especially strong at the smooth areas of the

Table 1  
Measurement data of XPS depth profiling. The atomic-% values are averages of eight parallel measurements from different sites of the same sample.

Sputtering		C1s		O1s		Al2p		Fe2p3		Zn2p3		Zn <sup>2+</sup>	Zn	Al/Zn ratio
Time, min	Depth, nm	Atomic-%	Stdev	Atomic-%	Stdev	Atomic-%	Stdev	Atomic-%	St dev	Atomic-%	Stdev	Atomic-%	Atomic-%	Atomic-%
0	0	67.7	15.6	23.7	9	6.8	5.7	0.1	0.2	1.7	1.3	0.4	1.3	4.1
0.2	1	27.9	27.6	43.4	17.7	25.9	10.4	0.4	0.3	2.5	0.7	0.3	2.1	10.5
0.5	3	16.9	22.6	50.2	14.3	27.5	6.4	0.3	0.2	5.1	2.6	0.3	4.7	5.4
1	6	11.2	15.3	31.7	11.2	16.7	4.6	0.2	0.3	40.1	26.1	0.8	39.4	0.4
1.5	9	8.8	10	17.3	12.6	8.3	6.4	1	0.5	64.6	26.9	0.5	64.1	0.1
2	11	7.5	9.5	12.3	8.2	5.3	5.4	1.2	0.4	73.6	21	0	73.6	0.1
2.5	14	7.2	6.3	9.1	8.4	4	3.8	1.2	0.3	78.5	17.3	0	78.5	0.1
3	17	5.4	5.7	7.4	7.5	3.4	3.3	1.6	0.8	82.2	14.3	0	82.2	0
3.5	20	4.6	6.3	5.7	5.2	2.7	2.9	1.9	0.7	85.1	12.7	0	85.1	0
4	23	5.1	5.2	5.1	4.3	2.4	2.4	2	0.5	85.4	10.9	0	85.4	0
4.5	26	3.6	5.1	4.9	5.2	1.9	2.2	2.2	0.9	87.4	10.5	0	87.4	0

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