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Evaluation of the growth mechanism of Ti-containing conversion coatings using XPS

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Abstract. Ti-containing coatings as chromate replacement were prepared on electrogalvanized steel. Zinc coatings were deposited from a weak acid chloride bath. Cr-free conversion coatings were deposited from bath composed of: $TiCl_3$, H_2SiF_6, H_2O_2 and oxalic acid. XPS was used to evaluate chemical composition of the coatings as a function of deposition time. Deposited coatings were of conversion type. Regardless of the achieved conversion coating thickness, Zn from the substrate was always present. In the coatings were identified: Zn_2SiO_4 / $Zn_4Si_2O_7(OH)_2$, $ZnTiO_3$, ZnO, $Zn(OH)_2$, Zn^0, SiOx and Ti-O-Si in varying proportions. The chemical composition of the outer surface of the coating depended on deposition time, e.g. in a time interval 0-300 s 30 fold increase of the Si:Ti ratio and 20 fold of the Si:Zn ratio were observed. Estimated thickness of conversion coating was 3, 14, 35, and 100 nm for the time deposition of 1, 40, 80 and 300 s respectively. It is the proposed model for distinguishing Zn(0) phase from Zn(2+) quantitatively, based on the Zn $L_3M_{45}M_{45}$ spectrum. The composition of the ZnTiSi conversion coating determined its mechanical properties and corrosion resistance. Standard tests carried out showed that the coatings obtained at the time of 20-40 s had the best corrosion performance and mechanical resistance

Introduction

Zinc coatings are commonly applied to protect unalloyed steel against corrosion. The protective properties of zinc stem from its anodic behaviour towards steel. Due to the relatively high corrosion rate of zinc, a post-treatment is necessary in order to increase the lifetime of electrogalvanized steel. For many years the chromate treatment was the most popular method. Today less harmful baths based on Cr(III)-compounds are mostly used. Nevertheless, because of the toxicity and harmfulness of chromium compounds, many centres pursue research on the development of Cr-free surface treatments. In the literature on the subject one can find descriptions of Cr-free coatings, among them Ti-containing conversion coatings seem to be highly promising substitutes for chromate coatings. Exploratory studies have shown the duration of depositing conversion coatings from a bath containing $TiCl_3$ has a significant effect on their morphology, chemical composition and protective properties [1].

Experimental

Samples of conversion coatings deposited from a bath containing Ti(III), on a substrate in the form of a ca. 7 μm thick zinc coating electrodeposited on carbon steel, were subjected to XPS analyses. Prior to conversion coating deposition the zinc coating surface had been activated in 0.5% by vol. HNO_3 and washed with distilled water. The conversion coating was obtained in a bath containing: $TiCl_3$, H_2SiF_6, H_2O_2 and oxalic acid with fixed pH=2.5 [4]. Since the aim of the studies was to identify conversion coating formation dynamics, coating composition versus deposition time was analyzed and additionally, shallow depth profiles of each of the coating were determined. The deposition time was in a range of 0-300 s. The chemical composition of the coating surface layer determined by XPS is shown in table 1. The (high-resolution) XPS analyses were performed using

a 250 W Al Kα (1486.6 eV, 12 kV) photon source with a constant pass energy (CAE) of 5 eV. 8x8 mm surface areas were examined. Depth profiling was conducted at moderately low Ar^+ ion energy (2.5 keV, 4 μA/cm^2) corresponding to the experimental etch rate of 0.34 nm/min (relative to SiO_2). In order to avoid the crater effect the entire surface of the samples was etched.

Table 1. Chemical composition versus deposition time for ZnTiSi coatings on zinc substrate after 1 min of etching with Ar^+ (4μA/cm^2).

Time of deposition [s]	Chemical composition (% at.)								
	C	O	Si	Ti	Zn	Si/Ti	Si/Zn	Ti/Zn	O/ (Si+Ti+Zn)
substrate	7.77	52.16			40.07				1.30
1	4.91	48.43	4.21	10.96	31.49	0.38	0.13	0.35	1.04
5	4.62	54.60	3.76	11.61	25.40	0.32	0.15	0.46	1.34
20	5.40	57.92	6.71	10.45	19.51	0.64	0.34	0.54	1.58
60	7.65	58.25	12.93	7.43	13.74	1.74	0.94	0.54	1.71
300	3.58	65.84	20.62	2.26	7.69	9.12	2.68	0.29	2.15

The results reveal that deposition time mainly affects the selective increase in the amount of silicon incorporated into the conversion coating. Silicates (Zn_2SiO_4, $Zn_4Si_2O_7(OH)_2$) and non-stoichiometric oxides SiO_x and SiO_2 have been identified among the chemical forms of the silicon [1].

The depth profiles have shed light on conversion coating formation. Table 2 shows the composition of a conversion coating obtained in 1 s, versus time of etching with Ar^+ ions (2.5keV, 4μA/cm^2).

Table 2. Chemical composition of ZnTiSi coating deposited for 1 s, versus time of etching with Ar^+ ions (2.5keV, 4μA/cm^2).

Etching time, [min]	Etching depth, [nm]]	Chemical composition [% at.]							
		C	O	Si	Zn*	Ti	Si/Ti	Ti/Zn	Zn^0/Zn
0	0	21,1	47,3	1.7	23.1	6.8	0.25	0.29	0
1	0.34	5.0	48.1	4.0	35.0*	8.9	0.57	0.19	0.26
2	0.68	4.9	47.5	3.7	37.2	6.7	0.55	0.18	0.39
7	2.38	5.5	39.1	2.6	47.7	5.2	0.50	0.11	0.55
17	5.78	6.0	27.1	1.5	63.0	2.5	0.60	0.04	0.81
27	9.18	5.3	11.6	0.4	81.9	0.8	0.5	0.01	0.89

* - the values were calculated for the Zn LMM peak

The Zn $2p_{3/2}$ spectra for the conversion coating obtained in 1 s are shown in fig. 1. Generally, two components have been distinguished on the surface cleaned of neutral carbon. One with the assigned energy of 1021.17 eV covers phases: Zn^0, ZnO and $Zn(OH)_2$, which, as a rule, are not separated because of the small chemical shifts between them. The higher energy peak proves that a bond has formed between the Zn substrate and Ti and Si. When investigating $ZnTiO_3/TiO_2$, Krylova et al. [2] assigned the energy of 1022.1 eV to the Zn-O-Ti and OH-Zn-O-Ti-O bonds, and on a TiO_2 substrate admixed with SiO_2 in the amount of 5% and having the suggested bond structure: O-Ti-O-Si-OH, would observe a further shift of the Zn $2p_{3/2}$ bond energy to 1022.4 eV. The values are consistent with the current results for the ZnTiSi conversion coating on the Zn substrate. The presence of silicate forms was postulated previously on the basis of Si 2p spectra and literature data [1,3,4]. In the NIST/XPS database the Zn $2p_{3/2}$ bond energy of 1022.6 eV is assigned to, among other things, Zn_2SiO_4 [5]. The formation of this silicate was deemed highly probable, the more so that there are grounds for it in the quantitative calculations (table 2) and in the assumed stoichiometry of the compounds.

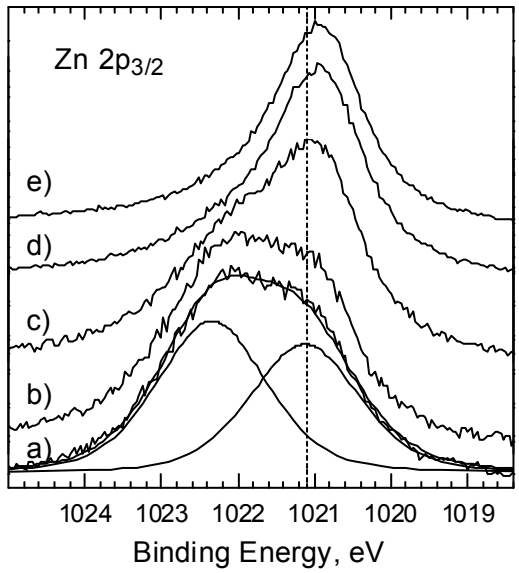


Fig. 1. Zn $2p_{3/2}$ spectrum of ZnTiSi coating deposited for 1s and etched with Ar^+: a) 1, b) 2, c) 7, d)17 and e) 27 min.

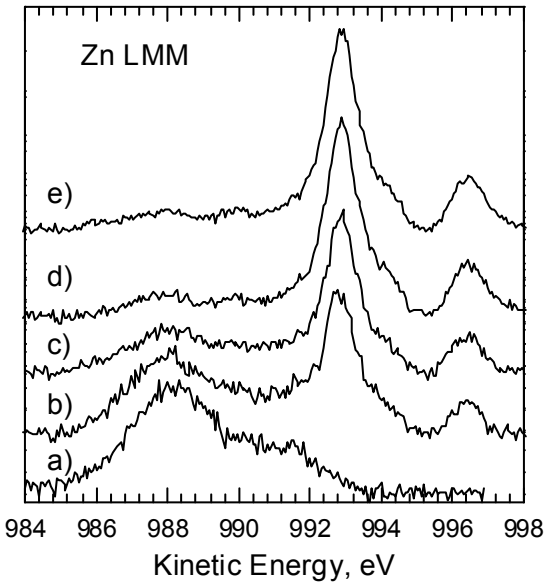
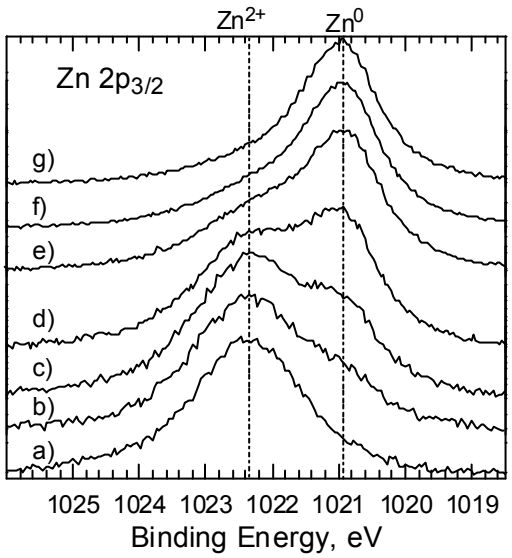


Fig. 2. Zn LMM spectrum of ZnTiSi coating deposited for 1s and etched in UHV Ar^+: a) 'as received', b) 2, c) 7, d)17 and e) 27 min.

Because of the similar bond energy values in $ZnTiO_3/Zn_2SiO_4$ (peak 1022.4 eV) and ZnO/Zn^0 (peak 1021.17 eV), the presented deconvolution of the Zn $2p_{3/2}$ spectrum (Fig. 1a) has only an approximate character. The next etchings with Ar^+ (+1', +5', +10') show the fast decay of the component at about 1022.4 eV, accompanied by a decrease in the Ti and Si content, which further corroborates the assumptions. After 17 min of etching, 81% of the zinc present on the surface is Zn^0, as evidenced by the value of modified Auger parameter α'=2013,86 eV. Zn^{2+} amounted to about 12% of the surface composition, 5.5% of which is bound with $ZnTiO_3+Zn_2SiO_4$. If oxygen is balanced in the same way, it is found that 13% of its total surface content of 27% is bound with $ZnTiO_3+Zn_2SiO_4$.



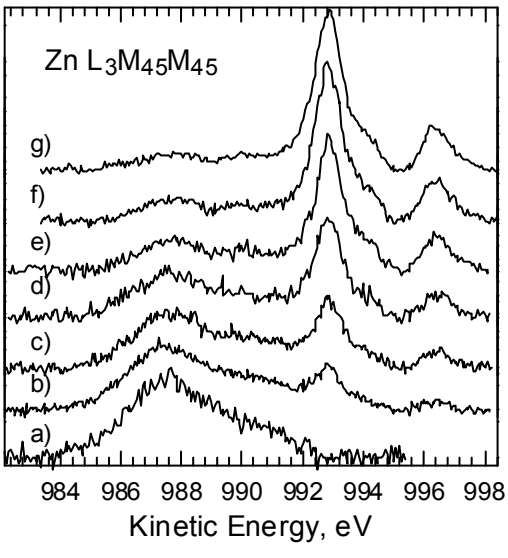


Fig. 3. Zp 2p3/2 and Zn LMM spectra of ZnSiTi coating versus time of etching with Ar^+ (2.5 keV, 4 $\mu m/cm^2$): a) 1, b) 4, c) 9, d) 19, e) 30, f) 40 and g) 50 min.

The thickness of a deposited coating, particularly of a multicomponent coating, cannot be explicitly determined. The time after which a 50% reduction in the content of a selected component in the deposited coating was achieved as a result of etching with Ar^+ was adopted as the thickness criterion. This time amounted to 9 minutes and 11 minutes for respectively Ti 2p and silicon (Si 2p). This corresponds to a thickness of 3.4 nm. By extending the bath time to 40 (fig. 3), 80 and

100s, thicker coatings, i.e. respectively 14, 35 and 100 nm thick, were obtained. This means that the increments were not a linear function of deposition time.

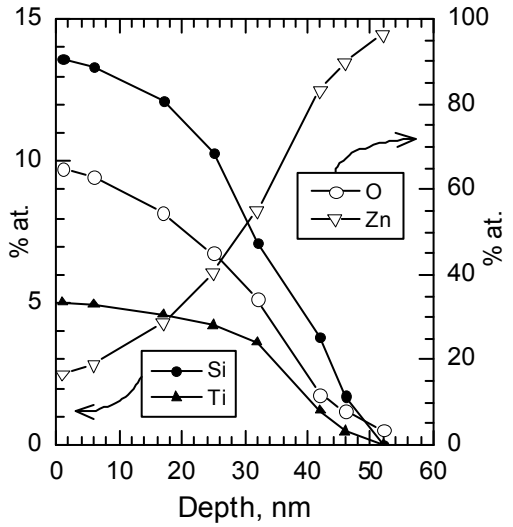


Fig.4. Depth profile of ZnTiSi conversion coating deposited for 80 s.

The inexplicitness of conversion coating thickness estimation, due to the blending of Zn substrate and bath components, is well illustrated by the depth profile of the coating deposited for 80 s, shown in fig. 4. The coating was estimated to be 35 nm thick, whereas Si and Ti, wholly originating from the bath, were visible to a depth of 55 nm.

On the other hand, moving deeper into the layer the gradual transition of Zn^{2+} to Zn^0 is observed (at the depth of 17 nm Zn^0 constituted 8% at. and wholly originated from the solution) since the exemplary inelastic mean free paths of Zn LMM electrons in Zn_2SiO_4 or in metallic zinc amount to merely 2.4 and 1.7 nm, respectively [6]. This means that maximum sampling depth $d_{max} = 3\lambda$ in the coating is below 7 nm, whereas the deposited coating calculated from this place has still a thickness of at least 18 nm.

Summary

- The coatings deposited on the zinc substrate have a conversion character since regardless of coating thickness, zinc was always present in the coating.
- The chemical composition of the outer surface of the conversion coating depends on the duration of its deposition; in a bath time range of 0-300 s a 30-fold increase in the Si-Ti ratio and a 20-fold increase of the Si:Zn ratio in the composition of the outer surface of the coating were observed for the given bath composition and deposition conditions [6].
- The thickness of the coatings and their depth profile are a function of bath time; the estimated coating thicknesses amounted to 3, 14, 35 and 100 nm for baths lasting for respectively 1, 40, 80 and 300 s.
- Zn_2SiO_4/ $Zn_4Si_2O_7(OH)_2$, $ZnTiO_3$, ZnO, $Zn(OH)_2$, Zn^0 and Ti-O-Si and SiO_x bonds of different proportions were identified in the coatings.

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