
A study of chromate film formed on zinc-iron alloy

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The chromate films on pure zinc-iron alloy deposits obtained from sulphate-chloride solutions were studied by X-ray photoelectron spectroscopy. It has been established that iron present in the alloy deposits has no effect on the thickness of chromate film. The chromium compounds formed on zinc-iron alloy deposits are of the same composition as those on pure zinc deposits. Iron does not interact with the constituents of chromating solution and does not form any compound with them. However, iron present in the alloy affects the chromating process. The chromate film formed was found to be more uniform and to offer a better anticorrosive protection.

Key words: zinc-iron alloy, chromate film, XPS

INTRODUCTION

Zinc-iron alloy electrodeposits have been known for application in steel plating [1–3]. To attain a high corrosion resistance of zinc-iron coating, the content of iron in an alloy should be about 20% [4]. A non-passivated Zn-Fe deposit with a low iron content will not provide an increased corrosion resistance as compared to zinc. Only application of chromate film allows to achieve an improved corrosion resistance [3, 5, 6]. The corrosion rate of chromated zinc-iron coating is approximately 24–28 $\mu\text{A}/\text{cm}^2$, *i.e.* about three times lower than that of chromated pure zinc [5]. Chromated Zn-Fe samples withstand an attack by 1800–3000 hours longer than chromated zinc coatings do in neutral salt spray tests before red rust appears [6]. A chromate film on zinc-iron alloy has different physical properties and stability to dissolution, as well as different adherence to metal in comparison with the chromating layers on ordinary zinc. This is due to the mechanism of chromate film formation on zinc-iron being different from that on zinc. According to Loar et al. [3], iron in a deposit migrates into the chromate film and interacts there with its components to provide a corrosion-resistant film.

To summarize, the reasons for a better corrosion resistance of chromated zinc-iron coatings in comparison with chromated zinc alone may be as follows:

- the chromate layer formed on zinc-iron alloy is thicker than that on pure zinc;
- the composition of the chromate layer developed on zinc-iron is different from that on pure zinc: iron is involved into the composition of the chroma-

te film, and chromium compounds with oxygen are of different composition.

The aim of the present work was to study the composition of chromate films formed on electrodeposited zinc-iron alloy, to compare it with the film on pure zinc, and to establish the possible reasons for a better protective efficiency of the film on zinc-iron.

EXPERIMENTAL

Zinc-iron coatings were electrodeposited from chloride-sulphate electrolytes. The plating bath composition, the operating parameters and the iron content in these coatings are listed in Table 1. Zinc coatings were deposited from the same electrolyte without FeSO_4 . All coatings obtained were smooth and bright. The iridescent chromating solution Likonda – 2 (Vilnius, Lithuania) [7] was used to prepare a chromate conversion film on zinc and zinc-iron coatings. The total salt concentration in the chromating bath was 66 g/l. The pH of the solution was 1.8.

The elemental composition of the film was calculated from the X-ray photoelectron spectra (XPS) recorded using an ESCALAB MK11 spectrometer (X-radiation of MgK_α with the energy of 1253.6 eV). The analyzer pass energy was of 20 eV. The vacuum in an analytical chamber was of 10^{-6} Pa. To analyze a deeper film layer, sputtering by ionized argon with a beam current of 100 μA was used. This beam corresponded to a sputtering rate of 10 nm/min [8, 9]. Data on the factors of element sensitivity and their binding energy values were taken from [8].

Table 1. Composition of plating baths and obtained coatings, and operating parameters

Electrolyte and coating components Operating parameters	Electrolyte	
	No. 1	No. 2
ZnCl ₂	0.5 M/l	0.5 M/l
NH ₄ Cl	3.5 M/l	3.5 M/l
FeSO ₄ · 7H ₂ O	0.15 M/l	0.2 M/l
Stabilizer Limeda* SNZ**	20 g/l	20 g/l
Brightening agent Likonda ZnSR [7]	15 g/l	15 g/l
Electrolyte pH	4.0	4.0
Temperature	Room	Room
Cathodic current density	2 A/dm ²	2 A/dm ²
Iron content in obtained coating	2.5–3.5 at %.	3.7–5.6 at %.

* Limeda is the trademark of Institute of Chemistry, Vilnius, Lithuania
 ** Stabilizer Limeda SNZ is manufactured at the Institute of Chemistry, Vilnius

RESULTS AND DISCUSSION

The distribution of elements comprising a chromate film formed on zinc and zinc-iron alloy are shown in Figs. 1–4. The thickness of the film could be estimated by taking into account both the sputtering time needed to obtain a zinc-rich surface and the used sputtering rate of 10 nm/min. The results for the specimens obtained by chromating the coating for a different time show that the thickness of the chromate film on the Zn-Fe coating (Figs. 1 and 2) increases with an increase in the duration of chromating in the same manner as for the zinc coating (Figs. 3 and 4). Meanwhile, a comparison of the data on the Zn and Zn-Fe coatings (cf. Fig. 1 with Fig. 3, and Fig. 2 with Fig. 4) leads to the conclusion that the iron present in the zinc coating does

not change the chromate film thickness. Hence, the hypothesis that the greater thickness of the film as the reason for the improved protective efficiency of the chromate layer formed on the zinc-iron coating should be rejected.

In order to identify the state of chromium in the chromate film, the Cr 2p_{3/2} spectra from the chromated zinc and zinc-iron coatings were recorded (Figs. 5 and 6). The peak corresponding to the Cr(III) compound (for Cr₂O₃ E_b = 576.6 eV; for Cr(OH)₃ E_b = 577.2 eV) was found to be obviously non-symmetric in the spectra from the film formed on both zinc and zinc-iron. A change in the peak shape may be

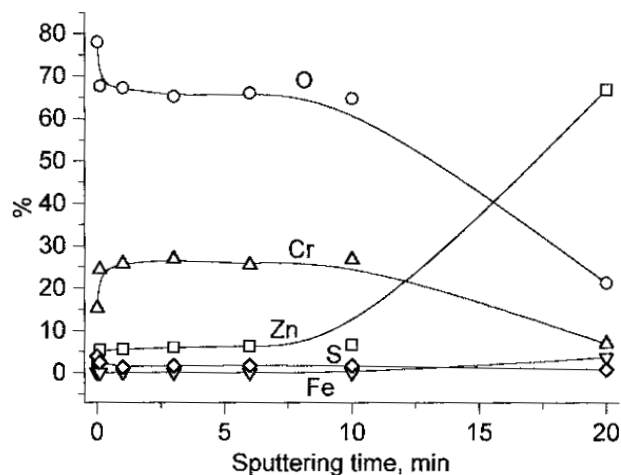


Fig. 1. Distribution of elements comprising the chromate film on zinc-iron alloy, obtained from electrolyte No 1. Duration of chromation 30 s. Sputtering rate 10 nm/min

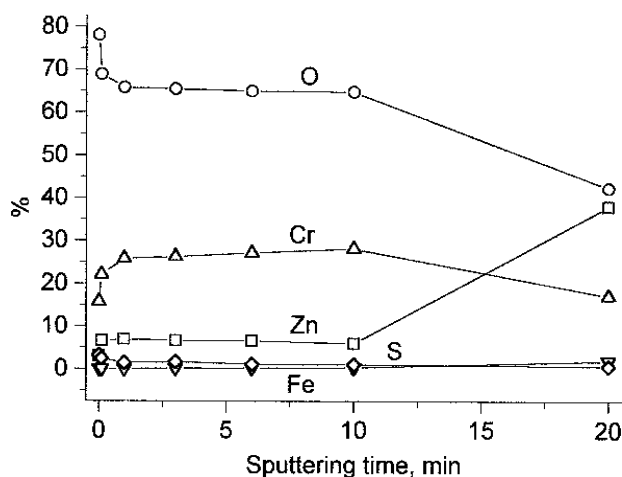


Fig. 2. Distribution of elements comprising the chromate film on zinc-iron alloy, obtained from electrolyte No 1. Duration of chromation 60 s. Sputtering rate 10 nm/min

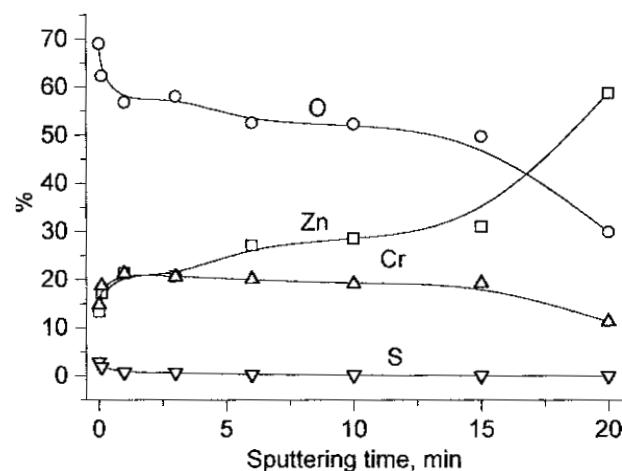


Fig. 3. Distribution of elements comprising the chromate film developed on pure zinc. Duration of chromation 30 s. Sputtering rate 10 nm/min

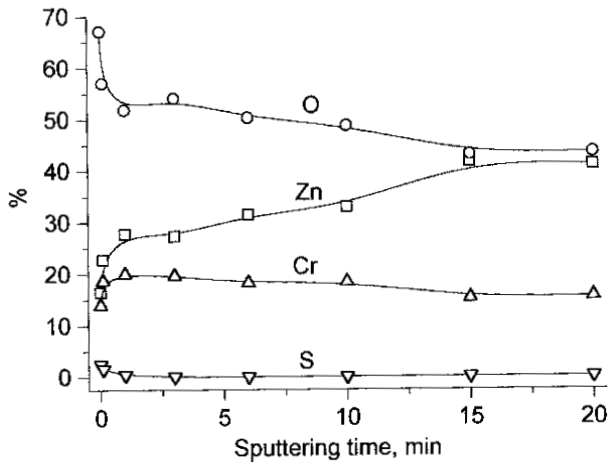


Fig. 4. Distribution of elements comprising the chromate film on pure zinc. Duration of chromation – 60 s. Sputtering rate 10 nm/min

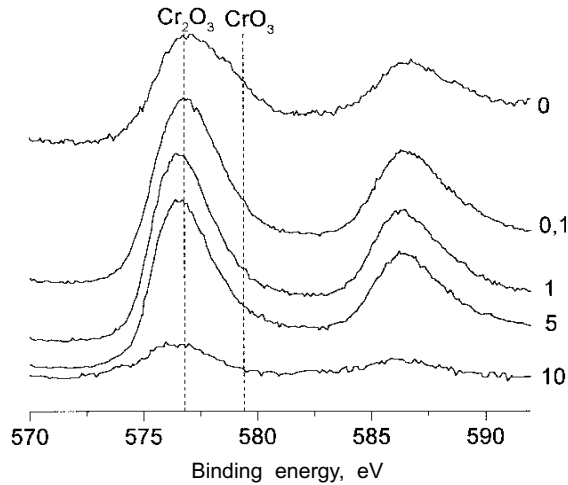


Fig. 5. X-ray photoelectron Cr_{2p_{3/2}} spectra from the chromate film formed on Zn-Fe coating obtained from electrolyte No 1 after various sputtering time. Chromation duration 60 s. Sputtering duration (min) is displayed on the chart by the corresponding curves.

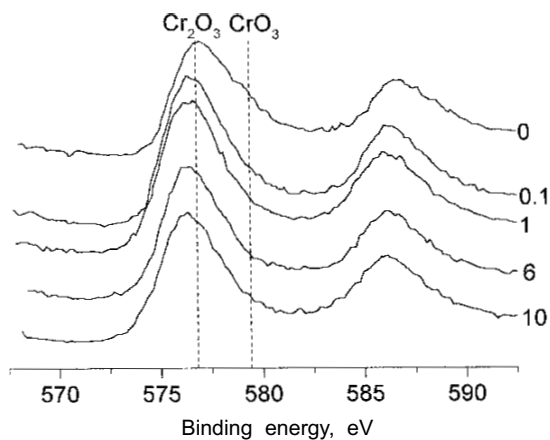


Fig. 6. X-ray photoelectron Cr_{2p_{3/2}} spectra from the chromate film formed on Zn coating after various sputtering time. Chromation duration 60 s. Sputtering duration (min) is displayed on the chart by the corresponding curves

caused by the presence of Cr(VI) compound (for CrO₃ E_b = 578.6) in the chromate layer. The signal belonging to Cr(VI) is particularly pronounced in the spectrum obtained from the uppermost layer of the chromate film. In deeper layers, it is feeble or quite absent. That finding means chromium to exist in 3- and 6-valence forms in a chromate film formed on both zinc and zinc-iron coatings.

The content of oxygen in the uppermost layer of the chromate films formed on both zinc and zinc-iron coating was higher than in deeper layers, and no relation between the oxygen quantity and the coating composition was detected (Figs. 1–4). An increased oxygen content was explained by the fact that oxygen was adsorbed from the air on the film surface. The data on the elemental composition of the deeper layers of the chromate film showed that the content of oxygen as well as the content of chromium were higher in the chromate film on Zn-Fe than those on the pure zinc coating. However, the ratios between the amounts of oxygen and chromium in the chromate film formed on the zinc and zinc-iron coatings were similar and averaged between 2.4 and 2.7 (Table 2). It means that the same chromium compounds are formed on the coatings of both types. Of the chromium compounds that may cons-

Table 2. Ratios between amounts (%) of chromium and oxygen, and between chromium and zinc at different depth of chromate layer formed on zinc and zinc-iron coatings

Coating	Depth, nm	Chromating duration, s			
		30		60	
		O/Cr	Cr/Zn	O/Cr	Cr/Zn
Zn	At surface	4.69	1.10	4.80	0.84
	0.1	3.34	1.08	3.06	0.82
	1	2.67	0.99	2.59	0.72
	3	2.81	0.99	2.70	0.72
	6	2.61	0.74	2.75	0.58
	10	2.74	0.67	2.65	0.55
	15	2.58	0.68	2.83	0.36
	20	2.66	0.19	2.81	0.37
Zn-Fe obtained from electrolyte No 1	At surface	4.76	9.45	5.71	4.36
	0.1	2.71	7.68	2.70	6.87
	1	2.20	8.74	2.16	6.69
	5	2.23	3.01	2.19	2.52
	10	2.49	0.05	1.71	0.21
	At surface	4.97	5.25	5.13	5.45
Zn-Fe obtained from electrolyte No 2	0.1	3.13	3.37	2.78	4.53
	1	2.56	3.69	2.61	4.66
	3	2.49	4.01	2.43	4.46
	6	2.39	4.12	2.59	3.98
	10	2.31	4.77	2.42	4.07
	20	2.47	0.45	3.04	0.10

Table 3. Chromium compounds as possible constituents of chromate film and the ratio of oxygen with chromium in the film	
Compound	O/Cr ratio in compound
Cr_2O_3	1.5
$\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3 \cdot x\text{H}_2\text{O}$: $x=1$	2.33
$x=2$	2.67
$x=3$	3.0
$\text{Cr}(\text{OH})_3$	3
$\text{Cr}(\text{OH})_3 \cdot \text{Cr}(\text{OH})\text{CrO}_4$	2.67
$\text{ZnO} \cdot \text{Cr}_2\text{O}_3$	2
$3\text{ZnO} \cdot \text{Cr}_2\text{O}_3$	3
ZnCrO_4	4
$2\text{ZnCrO}_4 \cdot \text{Cr}_2\text{O}_3$	2.75
$\text{ZnCrO}_4 \cdot 4\text{Zn}(\text{OH})_2$	12
$\text{ZnCrO}_4 \cdot \text{ZnX} \cdot \text{Zn}(\text{OH})_2$	6

titate a chromate film formed on zinc (Table 3) [10], $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{Cr}(\text{OH})_3 \cdot \text{Cr}(\text{OH})\text{CrO}_4$ have a ratio O/Cr (2.67) close to that of the chromate film determined by XPS. It can be assumed that these compounds constitute the chromate film formed on zinc-iron alloy.

The content of iron in the chromate film is low and depends on the depth of the layer (Figs. 1 and 2). The peak corresponding to iron in the metallic state appeared in the $\text{Fe}2p_{3/2}$ spectrum after a sputtering time of 10 min only (Fig. 7). The peaks corresponding to iron in oxidized form were not found. This means that iron does not form compounds with chromates and does not enter into a chromate film. Consequently, iron is present in the metallic state under the chromate film.

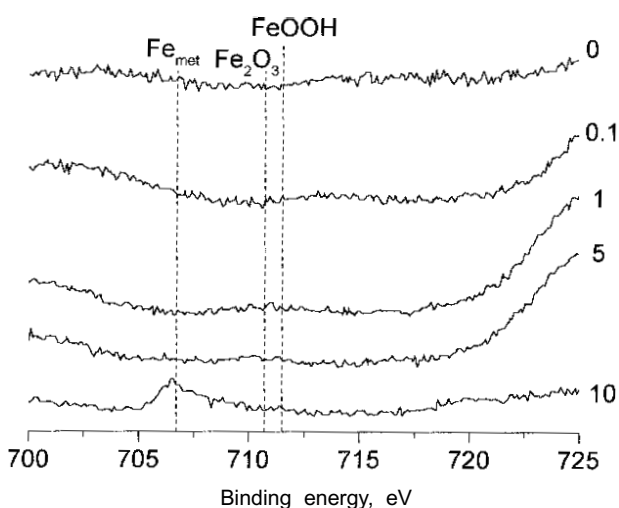


Fig. 7. X-ray photoelectron $\text{Fe}2p_{3/2}$ spectra from the chromate film formed on Zn-Fe coating obtained from electrolyte No 1 after various sputtering time. Chromation duration 60 s. Sputtering duration (min) is displayed on the chart by the corresponding curves

A small amount of sulphur was found in the chromate film formed on all types of coatings (Figs. 1–4). The amount of sulphur was low and decreased with a decrease in the chromium amount. Sulphur entered supposedly the film with the sulphate present in the chromating solution.

From the results it follows that the chromate film formed on zinc-iron alloy consists of the chromium-oxygen compounds of the same composition as the film formed on zinc. Iron does not change the composition of the chromate layer and does not enter into the chromate film.

Data on the elemental composition (Figs. 1–4) show that chromate films formed on zinc or zinc-iron coatings contain considerable amounts of zinc. Zinc was found to be in metallic and oxidized forms – two peaks, at 992.5 eV corresponding to metallic zinc and at 988.5 eV corresponding to ZnO, were observed on the Auger $\text{Zn L}_3\text{M}_{45}\text{M}_{45}$ spectra (Fig. 8). Due to the charge of the chromate film, the latter peak in the spectra obtained from the film surface is shifted towards the lower kinetic energy values.

As can be seen from the data on the elemental composition (Figs. 1–4), the zinc content in a chromate film formed on zinc-iron is obviously lower than on pure zinc. The difference is more evident when the ratio between the content of Cr and Zn is used (Table 2). The ratio of Cr/Zn for the chromate film on pure zinc is 0.8–1.0, whereas for the film on Zn-Fe this ratio is 3.4–5.5, and it reaches 9.5 for the chromate film on the Zn-Fe coating obtained from electrolyte No. 1. It may be suggested that the iron present in the coating operates as an active center which catalyzes the chromating pro-

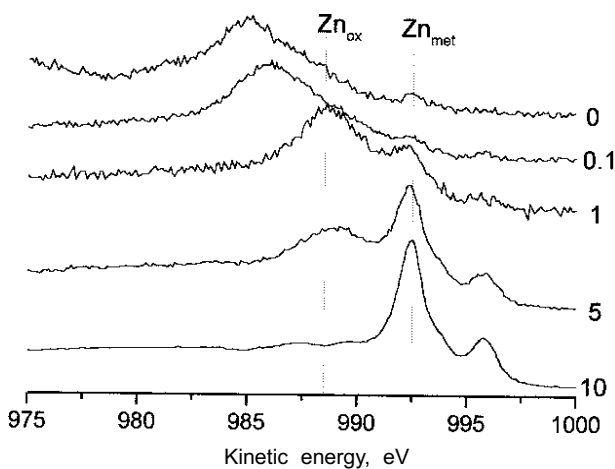


Fig. 8. Auger $\text{Zn L}_3\text{M}_{45}\text{M}_{45}$ spectra from the chromate film formed on Zn-Fe coating obtained from electrolyte No 1 after various sputtering time. Chromation duration 60 s. Sputtering duration (min) is displayed on the chart by the corresponding curves

cess. As a consequence, the chromating process proceeds more completely.

An additional point to emphasize is that the composition of the chromate film on zinc-iron remains invariant with changing the depth (Figs. 1 and 2), whereas the contents of Zn, Cr and O in the chromate layer on zinc vary with increasing the sputtering time (Figs. 3 and 4). That finding means that the chromate film formed on zinc-iron alloy is more uniform in the composition and has enhanced mechanical and corrosion-resistant properties.

CONCLUSIONS

1. The iron present in the Zn-Fe coating does not influence the thickness of the chromate film.

2. Chromium compounds formed on Zn-Fe alloy during chromation are of the same composition as those on the pure zinc coatings. Iron does not interact with the constituents of the chromating solution and does not form compounds with them.

3. The iron present in the coating affects the chromating process and causes a more complete chromating of zinc. The chromate film formed on the Zn-Fe coating contains a low zinc amount and is more uniform. Such a film offers a better anti-corrosive protection.

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CHROMATINĖS PLĖVELĖS ANT CINKO-GELEŽIES LYDINIO TYRIMAS

S a n t r a u k a

Rentgeno fotoelektroninės spektroskopijos būdu buvo tirtos chromatinės plėvelės ant cinko ir cinko-geležies lydinio elektrolitinių dangų, nusodintų iš sulfatinių-chloridinių elektrolitų. Nustatyta, kad geležis, esanti lydinyje, neturi įtakos chromatinės plėvelės storiui. Chromo junginiai, susidarę ant Zn-Fe lydinio dangų, yra tokios pačios sudėties, kaip ir ant gryno Zn dangų. Geležis nesąveikauja su chromatavimo tirpalo komponentėmis ir nesudaro junginių su jomis. Tačiau geležis, esanti lydinyje, veikia patį chromatavimo procesą. Susidariusi chromatinė plėvelė yra vienodesnė ir geriau apsaugo paviršius nuo korozijos.

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ИССЛЕДОВАНИЕ ХРОМАТНОЙ ПЛЕНКИ, ОБРАЗОВАВШЕЙСЯ НА СПЛАВЕ ЦИНК-ЖЕЛЕЗО

Р е з ю м е

С использованием рентгенофотоэлектронной спектроскопии исследовали хроматные пленки на гальванопокрытиях цинка и сплава цинк-железо, осажденных из сульфатно-хлоридных растворов. Установлено, что железо, находящееся в составе сплава, не оказывает влияния на толщину хроматной пленки. Соединения хрома, образовавшиеся на цинк-железо сплавах, имеют тот же состав как и в случае покрытий из чистого цинка. Железо, находящееся в сплаве, не взаимодействует с компонентами раствора хроматирования и не образует соединения с ними. Однако железо оказывает действие на сам процесс хроматирования. Образовавшаяся пленка является более однородной и лучше защищает поверхность от коррозии.